Journal of Nanomaterials

Micro/Nanostructured Arrays: Fabrication, Applications, and Devices

Guest Editors: Yue Li, Bingqiang Cao, Fengqiang Sun, and Sung Oh Cho

Micro/Nanostructured Arrays: Fabrication, Applications, and Devices

Journal of Nanomaterials

Micro/Nanostructured Arrays: Fabrication, Applications, and Devices

Guest Editors: Yue Li, Bingqiang Cao, Fengqiang Sun, and Sung Oh Cho

Copyright © 2013 Hindawi Publishing Corporation. All rights reserved.

This is a special issue published in "Journal of Nanomaterials." All articles are open access articles distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Editorial Board

Katerina E. Aifantis, Greece
Nageh K. Allam, USA
Margarida Amaral, Portugal
Xuedong Bai, China
Lavinia Balan, France
Enrico Bergamaschi, Italy
Theodorian Borca-Tasciuc, USA
C. Jeffrey Brinker, USA
Christian Brosseau, France
Xuebo Cao, China
Shafiul Chowdhury, USA
Kwang-Leong Choy, UK
Cui ChunXiang, China
Miguel A. Correa-Duarte, Spain
Shadi A. Dayeh, USA
Claude Estourns, France
Alan Fuchs, USA
Lian Gao, China
Russell E. Gorga, USA
Hongchen Chen Gu, China
Mustafa O. Guler, Turkey
John Zhanhu Guo, USA
Smrati Gupta, Germany
Michael Harris, USA
Zhongkui Hong, China
Michael Z. Hu, USA
David Hui, USA
Y.-K. Jeong, Republic of Korea
Sheng-Rui Jian, Taiwan
Wanqin Jin, China
Rakesh K. Joshi, UK
Zhenhui Kang, China
Fathallah Karimzadeh, Iran
Alireza Khataee, Iran
Do Kyung Kim, Korea
Alan K. T. Lau, Hong Kong
Burtrand Lee, USA
Jun Li, Singapore
Benxia Li, China
Xing-Jie Liang, China
Shijun Liao, China
Gong Ru Lin, Taiwan
J.-Y. Liu, USA
Tianxi Liu, China
Jue Lu, USA
Songwei Lu, USA
Daniel Lu, China
Ed Ma, USA
Gaurav Mago, USA
Santanu K. Maiti, India
Sanjay R. Mathur, Germany
Vikas Mittal, UAE
Weihai Ni, Germany
Sherine Obare, USA
Atsuto Okamoto, Japan
Abdelwahab Omri, Canada
Edward Andrew Payzant, USA
Kui-Qing Peng, China
Anukorn Phuruangrat, Thailand
Suprakas Sinha Ray, South Africa
Ugur Serincan, Turkey
Huaiyu Shao, Japan
Donglu Shi, USA
Vladimir Sivakov, Germany
Marinella Striccoli, Italy
Bohua Sun, South Africa
Saikat Talapatra, USA
Nairong Tao, China
Titipun Thongtem, Thailand
Somchai Thongtem, Thailand
Alexander Tolmachev, Ukraine
Valeri P. Tolstoy, Russia
Tsung-Yen Tsai, Taiwan
Takuya Tsuzuki, Australia
Raquel Verdejo, Spain
Mat U. Wahit, Malaysia
Zhenbo Wang, China
Ruibing Wang, Canada
Shiren Wang, USA
Cheng Wang, China
Yong Wang, USA
Jinquan Wei, China
Ching-Ping Wong, Hong Kong
Xingcai Wu, China
Guodong Xia, Hong Kong
Zhi Li Xiao, USA
Ping Xiao, UK
Yangchuan Xing, USA
Shuangxi Xing, China
N. Xu, China
Doron Yadlovker, Israel
Yingkui Yang, China
Khaled Youssef, USA
Kui Yu, Canada
William W. Yu, USA
Haibo Zeng, China
Tianyou Zhai, Japan
Renyun Zhang, Sweden
Bin Zhang, China
Yanbao Zhao, China
Lianxi Zheng, Singapore
Chunyi Zhi, Hong Kong

Contents

Micro/Nanostructured Arrays: Fabrication, Applications, and Devices, Yue Li, Bingqiang Cao, Fengqiang Sun, and Sung Oh Cho
Volume 2013, Article ID 306479, 1 page

Surface Plasmon Resonance in Periodic Hexagonal Lattice Arrays of Silver Nanodisks, Jinlian Hu, Cong Wang, Shikuan Yang, Fei Zhou, Zhigang Li, and Caixia Kan
Volume 2013, Article ID 838191, 6 pages

Multifunctional Logic Gate by Means of Nanodot Array with Different Arrangements, Yasuo Takahashi, Shinichiro Ueno, and Masashi Arita
Volume 2013, Article ID 702094, 7 pages

Advances in Optical and Magnetooptical Scatterometry of Periodically Ordered Nanostructured Arrays, Martin Veis and Roman Antos
Volume 2013, Article ID 621531, 10 pages

Effect of Liquid Ga on Metal Surfaces: Characterization of Morphology and Chemical Composition of Metals Heated in Liquid Ga, Eun Je Lee, Min Goo Hur, Jeong Mun Son, Jeong Hoon Park, and Seung Dae Yang
Volume 2013, Article ID 619682, 8 pages

Fabrication of Self-Standing Silver Nanoplate Arrays by Seed-Decorated Electrochemical Route and Their Structure-Induced Properties, Guangqiang Liu, Guotao Duan, Lichao Jia, Jingjing Wang, Hongzhi Wang, Weiping Cai, and Yue Li
Volume 2013, Article ID 365947, 7 pages

Visible Light Irradiation-Mediated Drug Elution Activity of Nitrogen-Doped TiO_2 Nanotubes, Seunghan Oh, Kyung-Suk Moon, Joo-Hee Moon, Ji-Myung Bae, and Sungho Jin
Volume 2013, Article ID 802318, 7 pages

Effect of Annealing on the Structure and Photoluminescence of Eu-Doped ZnO Nanorod Ordered Array Thin Films, Wen-Wu Zhong, Da-Wei Guan, Yue-Lin Liu, Li Zhang, Yan-Ping Liu, Zhi-Gang Li, and Wei-Ping Chen
Volume 2012, Article ID 263679, 6 pages

Small-Sized Flat-Tip CNT Emitters for Miniaturized X-Ray Tubes, Hyun Jin Kim, Jun Mok Ha, Sung Hwan Heo, and Sung Oh Cho
Volume 2012, Article ID 854602, 6 pages

Effects of EDTA and Boric Acid on the Morphology of $CaCO_3$ Particles, Xingbo Shi, Julin Wang, and Xiaoping Cai
Volume 2012, Article ID 532847, 5 pages

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 306479, 1 page
http://dx.doi.org/10.1155/2013/306479

Editorial

Micro/Nanostructured Arrays: Fabrication, Applications, and Devices

Yue Li,[1] Bingqiang Cao,[2] Fengqiang Sun,[3] and Sung Oh Cho[4]

[1] *Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, China*
[2] *School of Materials Science and Engineering, University of Jinan, Jinan, Shandong 250022, China*
[3] *Department of Material Science and Engineering, South China Normal University, Guangzhou, Guangdong 510631, China*
[4] *Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea*

Correspondence should be addressed to Yue Li; yueli@issp.ac.cn

Received 2 July 2013; Accepted 2 July 2013

Copyright © 2013 Yue Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Recently, ordered micro/nanostructured arrays have attracted much interest due to their important applications in field emitters, nanogenerators, sensors, microfluidic devices, optoelectronic devices, and so forth. The traditional methods to fabricate micro/nanostructured arrays are generally based on lithographic techniques, for example, photolithography, electron beam lithography, ion beam lithography, and X-ray lithography, to name a few. However, these technologies are usually high costs and time consumption.

Therefore, scientists also endeavored to find other alternative strategies by facile routes with low costs. In this issue, S. Oh et al. and W.-W. Zhong et al. reported the self-assembly growth of one-dimensional oxide semiconductor nanostructures like TiO_2 nanotube and ZnO nanorods. The influence of visible light irradiation and annealing on the photoluminescence and drug elution activity properties was investigated. G. Liu et al. reported the fabrication of self-standing silver nanoplate arrays by seed-decorated electrochemical route using colloidal crystal as template. M. Veis and R. Antos review the advances in optical and magnetooptical scatterometry of periodically ordered nanostructured arrays. J. Hu et al. reported the metal surface plasmon resonance in periodic hexagonal lattice arrays of silver nanodisks, while E. J. Lee et al. reported the effect of liquid gallium on metal surfaces and characterized the morphology and chemical composition of metals heated in liquid gallium. As for device applications, Y. Takahashi et al. reported the multifunctional logic gate by means of nanodot array with different arrangements, and H. J. Kim et al. reported small-sized flat-tip CNT emitters for miniaturized X-ray tubes.

We believe that this specially organized issue could help readers to get more information on the fabrication of micro/nanostructured arrays and their device applications.

Yue Li
Bingqiang Cao
Fengqiang Sun
Sung Oh Cho

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 838191, 6 pages
http://dx.doi.org/10.1155/2013/838191

Research Article

Surface Plasmon Resonance in Periodic Hexagonal Lattice Arrays of Silver Nanodisks

Jinlian Hu,[1] Cong Wang,[1] Shikuan Yang,[2] Fei Zhou,[2] Zhigang Li,[2] and Caixia Kan[3]

[1] *School of Materials Science and Engineering, and Anhui Key Laboratory of Metal Materials and Processing, Anhui University of Technology, Ma-An-Shan, Anhui 243002, China*
[2] *Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, China*
[3] *College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China*

Correspondence should be addressed to Jinlian Hu; jlhu72@163.com and Shikuan Yang; skyang@issp.ac.cn

Received 30 November 2012; Accepted 18 January 2013

Academic Editor: Yue Li

Copyright © 2013 Jinlian Hu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The surface plasmon resonance (SPR) of periodic hexagonal lattice arrays of silver nano-disks positioned on glass slides is studied using finite-difference time domain (FDTD) simulations. We investigate numerically the influence of diameter of nano-disks and the gap between nano-disks on SPR transmission spectra and electric field enhancement. We find a strong dependence of resonance wavelength on diameter of the nanodisks. With increasing the gap, electric field enhancement factor could significantly increase and reach a maximum value, which indicates that a special long-range interaction plays an important role. This study is useful for optical modulation applied in near or far field optics, sensing and data storage, and solar cell.

1. Introduction

Surface plasmon resonance (SPR) can be generated in metal nanostructures such as gold, silver, and copper, which are promising materials in the fields of optoelectronics and plasmonics [1–5]. The SPR in periodic arrays has aroused great interest because of its uniform optical properties which can be applied in integrated optoelectronics device [6–10]. Previously, a silver nanostructure in periodic square lattice for label free nano-biosensors was proposed in [6] and SPR in periodic square lattice of gold nanodisks for broadband light harvesting was investigated in [7]. Recently, Yang et al. [11] developed surface pattern fabrications via a dewetting process on the surface of a bowl template derived from a monolayer colloidal crystal template composed of polystyrene (PS) spheres in periodic hexagonal lattice arrays, and each bowl in the template can be treated as a separate reactor, resulting in uniformly structured surface patterns, and then the periodic hexagonal lattice arrays of metal nanodisks can be easily formed. However, the theoretical simulation about the SPR properties of periodic hexagonal lattice arrays of silver nanodisks has scarcely been reported.

In this study, we show how by tuning the diameter and the gap to control the transmission and E-field enhancement properties of periodic hexagonal lattice arrays of silver nanodisks through the interactions of nanodisks. The long-range interaction of nano-particles is observed when E-field enhancement reaches a maximum value at the critical gap. The optical properties (transmission spectra and field enhancement) of silver nanodisk arrays are systematically studied numerically using Finite Difference Time Domain method.

2. Sample and Methods

Figure 1 shows the schematic representation of periodic hexagonal lattice arrays of Ag nanodisks on SiO_2 glass substrate. The height of nanodisk is held constant at 20 nm.

Figure 1: The schematic representation of periodic hexagonal lattice arrays of silver nanodisks positioned on glass slides.

The transmission spectra and E-field enhancement for the hexagonal array was calculated using a finite-difference time domain method (FDTD Solutions, from Lumerical). The calculations are set up as a three-dimensional system with a 2-nm resolution grid, for 500 fs. A plane wave source is chosen at a working wavelength range of 300–700 nm. The arrays are illuminated by a x-polarized plane wave source shining from the glass side towards the positive z-direction, which is perpendicular to the plane of the platform. Perfectly matched layers (PMLs) are used on the z-axis boundaries, while periodic boundaries conditions (PBCs) are placed on the x- and y-axis ones. The transmitted power is collected at positive z-direction at ends of the domain. The dielectric constant of the glass (silicon dioxide) and silver are described by the Palik values [12], which were provided in the material database from the software. The calculation of electric field enhancement factor, the relative total electric field intensity, and its image plot are obtained from $|E|^2/|E_0|^2$, and they are calculated on the top surface of nanodisks.

3. Results and Discussion

For comparison, Figures 2(a), 2(b), and 2(c) show relative field intensities $|E|^2/|E_0|^2$ distribution on the top surface of nanodisks along xy plane at respective resonance wavelength for three different patterns (i.e., single nanodisk, seven nanodisks system, and periodic hexagonal arrays). The transmission spectra of the above three patterns are presented in Figure 2(d). In the Figure 2, the diameter and the gap are 100 nm and 70 nm, respectively. It can been seen that the periodic hexagonal array has a strong SPR transmission peak at 555 nm, which is slightly different from the peak of seven nanodisks system at 564 nm, and much more different from the one of the single nanodisk at 600 nm. As for the E-field enhancement factor at respective resonance wavelength, the maximum value $|E_{\max}|^2/|E_0|^2$ of periodic hexagonal array is about 180, which is also slightly different from the maximum value of seven nanodisks system of 350, and much more different from the single nanodisk of 700. These results indicate that the interaction between nanodisks cannot be ignored. In the following, we present the influence of nanodisks diameter and gap on SPR transmission spectra and E-field enhancement considering electromagnetic interaction.

3.1. The Influence of Diameter of Nanodisks on Transmission Spectra and E-Field Enhancement. The SPR transmission spectra of the periodic structures have been calculated for diameter between 20 and 300 nm with fixed gap of 70 nm, as shown in Figure 3(a). As we can see, the SPR peak significantly red shifts from 414 nm to 633 nm with great change about 221 nm when the particle diameter increases from 20 nm to 150 nm. The full width at half maximum (FWHM) and intensity of the SPR peak also greatly increase with increasing diameter.

In Mie theory, extinction is directly proportional with the density of the nanostructures [1]. Obviously, the increase in diameter keeping the gap constant is expected to increase a real density of Ag in the periodic hexagonal arrays, which leads to the increase in the amplitude of resonance intensity. With increasing the size of each particle, the electromagnetic wave incident on the particles should no longer be considered to have a negligible phase difference across the single particle dimension, and the dipole resonance peak starts to shift towards longer wavelengths and

Figure 2: The relative field intensities ($|E|^2/|E_0|^2$) distribution on the top surface of nanodisks along xy plane at respective resonance wavelength for three different patterns: (a) single nanodisk, (b) seven nanodisks system, and (c) periodic hexagonal arrays. (d) The transmission spectra of the above three patterns. The diameter and the gap are 100 nm and 70 nm, respectively.

SPR peak gets wider due to phase retardation [1, 2]. Here, phase retardation plays a dominant role in leading to the significant change in peak position and FWHM When the diameter of each nanodisk changes. In addition to phase retardation, maybe the near field coupling between nanodisks gets stronger, which leads to broader peak when the diameter increase.

Figure 3(b) shows E-field enhancement factor of periodic arrays with fixed gap of 70 nm and different diameters illuminated at three laser wavelengths (488 nm, 532 nm, 632.8 nm). It can be seen that irradiation by the laser light with a wavelength of 532 nm or 632.8 has better E-field enhancement effect than by the laser light with a wavelength of 488 nm when the diameter increases up to 100 nm because

Figure 3: (a) The transmission spectra of periodic arrays with different diameters D between 20 nm and 150 nm. (b) E-field enhancement factor of periodic arrays with different diameters illuminated at three laser light wavelengths (488 nm, 532 nm, 632.8 nm). The gap between the nanodisks is fixed at 70 nm.

the resonance wavelength red shifts with the increase in diameter.

3.2. The Influence of the Gap between Nanodisks on Transmission Spectra and E-Field Enhancement. The SPR transmission spectra of the periodic structures have been calculated for different gaps with fixed diameter of 100 nm, as shown in Figure 4(a). With increasing gap, the intensity of the SPR extinction peak decreases as the density of silver nanodisks decreases and the SPR peak position has slight change. However, the FWHM of the peak gets much narrower with the increase in the gap, which could indicate the near-field coupling becomes weak. The strength of near-field coupling could be estimated from the FWHM of SPR peak.

In principle, two types of interaction can be distinguished: near-field coupling and far-field (dipolar) interaction. Near-field coupling is relevant for nearly touching particles due to the short range of the electromagnetic near fields in the order of some tens of nm. On the other hand, far-field interaction is mediated by the nanostructures' scattered light fields [13]. The near-field coupling of silver nanoparticles pairs is efficient at few tens nanometers distance and gradually vanishes when the $(D + \text{gap})/D > 2.5$ and long range dipole-dipole interaction is stronger as the gap increases in the periodic pattern [14].

Figure 4(b) shows E-field enhancement factor on the top of nanodisks along xy plane for periodic hexagonal arrays with fixed diameter of 100 nm and different gaps illuminated at three laser wavelengths (488 nm, 532 nm, 632.8 nm), which suggests the irradiation by the laser light with a wavelength of 532 nm or 632.8 nm has better E-field enhancement effect than by laser light with a wavelength of 488 nm under such condition.

Figure 4(c) presents E-field enhancement factor on the top surface of nanodisks along xy plane for periodic hexagonal arrays with different gaps and fixed diameter of 100 nm illuminated at their own resonance wavelength. It is interesting that with increasing the gap the electric field enhancement factor significantly increases and reaches a maximum value of about 2650 at a particular gap of 300 nm. Previously, such strong enhancements were only obtained with nano-gap structures (via short-range dipole-dipole interaction) but not easily seen in patterns with large intra-particle distance. Here, the interesting result suggests that a special long-range interaction plays an important role, which is very complicated and needs detailed research in near future.

4. Conclusion

In this study, we have presented the influence of diameter and the gap between nanodisks on SPR spectra and electric field enhancement factor for periodic hexagonal lattice arrays of silver nanodisks. An increase of extinction spectra, significant peak red-shift, and a broader plasmon resonance occur with increasing the diameter due to phase retardation of single large nanodisk and the near field coupling between nanodisks. FDTD calculations also show that with increasing the gap, electric field enhancement factor could significantly increase and reach a maximum value due to special long-range interaction. This study is useful for optical modulation applied in sensing and data storage, and solar cell, and is also important to the understanding plasmon

FIGURE 4: (a) The transmission spectra of periodic arrays with different gaps. (b) E-field enhancement factor on the top surface of nanodisks along xy plane for periodic hexagonal arrays with different gaps illuminated at three laser wavelengths (488 nm, 532 nm, 632.8 nm). (c) E-field enhancement factor at the top of nanodisks along xy plane for periodic hexagonal arrays with different gaps illuminated at their own resonance wavelengths. The diameter of the nanodisks is fixed at 100 nm.

about near field coupling and long range interaction between nanoparticles.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant no. 50701002, Grant no. 51001078, Grant no. 11204317, and Grant no. 11274173).

References

[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Springer, New York, NY, USA, 1995.

[2] J. Hu, L. Chen, Z. Lian et al., "Deep-ultraviolet-blue-light surface plasmon resonance of Al and Al_{core}/Al_2O_{3shell} in spherical and cylindrical nanostructures," *Journal of Physical Chemistry C*, vol. 116, no. 29, pp. 15584–15590, 2012.

[3] Y. Li, N. Koshizaki, H. Wang, and Y. Shimizu, "Untraditional approach to complex hierarchical periodic arrays with trinary stepwise architectures of micro-, submicro-, and nanosized structures based on binary colloidal crystals and their fine structure enhanced properties," *ACS Nano*, vol. 5, no. 12, pp. 9403–9412, 2011.

[4] J. Hu, L. Wang, W. Cai et al., "Smart and reversible surface plasmon resonance responses to various atmospheres for silver nanoparticles loaded in mesoporous SiO_2," *Journal of Physical Chemistry C*, vol. 113, no. 44, pp. 19039–19045, 2009.

[5] J. Hu, P. Liu, and L. Chen, "Comparison of surface plasmon resonance responses to dry/wet air for Ag, Cu, and Au/SiO_2," *Applied Optics*, vol. 51, no. 9, pp. 1357–1360, 2012.

[6] N. A. Cinel, S. Bütün, and E. Özbay, "Electron Beam Lithography designed silver nanodisks used as label free nanobiosensors based on Localized Surface Plasmon Resonance," *Optics Express*, vol. 20, no. 3, pp. 2587–2597, 2012.

[7] Y. Nishijima, L. Rosa, and S. Juodkazis, "Surface plasmon resonances in periodic and random patterns of gold nano-disks for broadband light harvesting," *Optics Express*, vol. 20, no. 10, pp. 11466–11477, 2012.

[8] G. Liu, Y. Li, G. Duan, J. Wang, C. Liang, and W. Cai, "Tunable surface plasmon resonance and strong SERS performances of Au opening-nanoshell ordered arrays," *ACS Applied Materials and Interfaces*, vol. 4, no. 1, pp. 1–5, 2012.

[9] G. Duan, F. Lv, W. Cai, Y. Luo, Y. Li, and G. Liu, "General synthesis of 2D ordered hollow sphere arrays based on nonshadow deposition dominated colloidal lithography," *Langmuir*, vol. 26, no. 9, pp. 6295–6302, 2010.

[10] Z. F. Dai, Y. Li, G.T. Duan, L.C. Jia, and W.P. Cai, "Phase diagram, design of monolayer binary colloidal crystals, and their fabrication based on ethanol-assisted self-assembly at the air/water interface," *ACS Nano*, vol. 6, no. 8, pp. 6706–6716, 2012.

[11] S. Yang, B. Cao, L. Kong, and Z. Wang, "Template-directed dewetting of a gold membrane to fabricate highly SERS-active substrates," *Journal of Materials Chemistry*, vol. 21, no. 36, pp. 14031–14035, 2011.

[12] E. D. Palik, *Handbook of Optical Constants of Solids*, Academic, New York, NY, USA, 1985.

[13] B. Lamprecht, G. Schider, R. T. Lechner et al., "Metal nanoparticle gratings: influence of dipolar particle interaction on the plasmon resonance," *Physical Review Letters*, vol. 84, no. 20, pp. 4721–4724, 2000.

[14] W. Khunsin, B. Brian, J. Dorfmüller et al., "Long-distance indirect excitation of nanoplasmonic resonances," *Nano Letters*, vol. 11, no. 7, pp. 2765–2769, 2012.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 702094, 7 pages
http://dx.doi.org/10.1155/2013/702094

Research Article

Multifunctional Logic Gate by Means of Nanodot Array with Different Arrangements

Yasuo Takahashi, Shinichiro Ueno, and Masashi Arita

Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan

Correspondence should be addressed to Yasuo Takahashi; y-taka@nano.ist.hokudai.ac.jp

Received 8 November 2012; Revised 11 February 2013; Accepted 12 February 2013

Academic Editor: Sung Oh Cho

Copyright © 2013 Yasuo Takahashi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Multifunctional logic gate devices consisting of a nanodot array are studied from the viewpoint of single electronics. In a nanodot array, the dots come in a random variety of sizes, which sometimes has a negative effect on the performance of electrical device applications. Here, this feature is used in a positive sense to achieve higher functionality in the form of flexible logic gates with low power consumption in which the variability of logic functions is guaranteed. Nanodot arrays with two input gates and one control gate in a variety of arrangements are considered, in which the two-input logic functions (such as NAND, NOR, or exclusive-OR (XOR) gates) are selected by changing the voltage applied to the control gate. To ensure the flexibility of the device, it is important to guarantee the performance with any one of the six important logic functions: NAND, AND, NOR, OR, XOR, and XNOR. We ran a selection simulation using a nanodot array consisting of six nanodots with different dot arrangements to clarify the relation between the variability of the logic functions and the dot arrangements.

1. Introduction

Single-electron devices (SEDs) are an attractive alternative for future large-scale integrated (LSI) circuits because of their small size and very low power consumption [1–6]. However, the dot sizes of room-temperature-operating SEDs are too small to control them accurately. To overcome this problem, we proposed the use of nanodot-array-type SEDs consisting of many nanodots connected via tunnel junctions [7]. The dot-size fluctuation is positively used to achieve a flexible logic gate in which the logic function of the device can be selected by setting the voltage applied to control gates. Our final objective is to achieve a reconfigurable logic device with very low power consumption.

Miniaturization is a problem that also affects metal-oxide-semiconductor (MOS) field-effect transistors (FETs) because it is difficult to suppress the fluctuation of their sizes, when the size is less than 10 nm [8, 9]. Although small MOSFETs in LSI circuits are capable of providing high-performance features such as high current drivability, the size fluctuation results in electrical characteristics that are fairly unpredictable. Even in CMOS LSIs, we have to introduce some tolerant operations. Another problem with highly integrated CMOS LSIs is their huge power dissipation [10]. SEDs enjoy a great advantage in this regard, even though their current drivability is quite low compared with the MOSFETs. However, nanodot arrays circumvent this disadvantage because the dots are directly connected to one another and do not have any wires to charge.

The simplest SED is a single-electron transistor (SET) that has only one dot. Its most unique characteristic is conductance oscillation as a function of the gate voltage, in which the oscillation period is determined by the capacitance between the dot and the gate. When many dots with different sizes are connected in one array, complicated characteristics seem to occur because many dots having a different oscillatory conductance with different periods and phases are connected in parallel and in series. Here, the fluctuation of the dot size can be used positively. Another important feature of SEDs is their multiple-gate capability, since the operation principle of SEDs enables them to inherently have many input gates [11]. When the nanodots and the gates are small and are arranged as shown in Figure 1, each gate couples with many nanodots capacitively. If we use one of the gates as a control gate,

Figure 1: (a) Schematic top view of a nanodot-array flexible-logic-gate device with many input gates and (b) cross section of the nanodot-array device.

the conductance oscillation of each dot shifts in accordance with each capacitance between the gate and each dot. This means that the total conductance of the array can be changed so as to select the function of the device by the voltages applied to the control gates. It thus works as a multifunctional device in which the functions can be selected by the control-gate voltage.

The biggest problem of this concept is that several sets of suitable control-gate voltage have to be found out corresponding to the expected logic functions because we cannot predict the actual characteristics of nanodot arrays. However, if the nanodots are fabricated with a size close to the designed size, current oscillations in which the periods and phases are slightly distributed are achieved as a function of the input- and control-gate voltages. Since the oscillation period and phase change in accordance with the input- and control-gate voltages, a control-gate voltage can be identified so as to produce a required logic function. After the specific control-gate voltage is identified, it should be stored into nonvolatile memory. Then, another control gate voltage for another logic function should be identified and stored. Once several series of control-gate voltages corresponding to various logic functions are identified and stored, the device can be used as a multifunctional device with functions selected by using the stored control-gate voltages.

The simplest logic gate is a two-input logic gate such as NAND, NOR, or exclusive-OR (XOR) gates. When a flexible two-input logic gate is considered, the logic function should be flexibly changed by the voltage applied to the control gates. Three gates are needed at least to realize such devices: two for input and one for control. The most important point is for the device to achieve as many logic functions as possible by changing the control-gate voltage. The variability of the function is thought to be strongly affected by the arrangement of nanodots because current transport paths play an important role in deciding the electrical characteristics of the device. In this paper, we assume the most simple nanodot arrays considering the fabrication of the array by the use of the established method and the use of conventional silicon technologies named pattern-dependent oxidation (PADOX) [12, 13]. The PADOX method converts a lattice of Si nanowires to an Si nanodot array, where the nanodots are arranged in vertical and horizontal directions, which provide parallel and series paths of current flow [11, 12]. To design the nanodot array, it is important to know which current path is more crucial. In this paper, the effect of nanodot arrangement on the functionality of a flexible two-input logic gate is investigated.

2. Nanodot-Array Device Structure and Simulation

Nanodot arrays typically have a variety of different dot arrangements. The most important point of any flexible device is accuracy in achieving the target function. Fluctuations of dot size and position, which are inevitable in nanodot array devices, cause fluctuations in tunnel resistances and in tunnel capacitances between dots and in gate capacitances between dots and gates. It is impossible to predict what the electrical characteristics will be, which makes it difficult to guarantee the functionality of the device. However, we propose using these fluctuations in a positive way to achieve a highly flexible device.

Here, a two-input, two-terminal logic device, in which output current or resistance between source and drain terminals, is changed by changing the combination of voltages applied to the two-input gates is considered. The device acts as a conventional two-input logic gate (such as a NAND, NOR, or XOR gate). One control gate to select the logic function of the device is attached. When the voltage applied to the control gate is changed, the logic function can be changed, for example, from NAND to XOR, and then to NOR [7, 12].

The electrical characteristics of the nanodot-array devices are calculated with different dot arrangements. When six-dot arrays are assumed, four kinds of dot arrangement can be typically made, as shown in Figures 2(a)–2(d). Here, we use nanodot arrangements assuming the fabrication by the PADOX method [11, 12]. The two reserves, the source and drain terminal, were attached to the dot array. These four dot arrangements are named series, 2×3, 3×2, and parallel. Every dot in the array is connected via a tunnel capacitor to the neighboring dots and source or drain terminal. As an example, Figure 3(a) shows the equivalent circuit of a 2×3 dot array connected with tunnel capacitors. In addition, three gates that couple capacitively to all the dots are also attached as shown in Figure 3(b). Note that the structure in which every gate couples to all the dots is effective in terms of achieving the most important two-input logic functions (AND, OR, NAND, NOR, XOR, and XNOR). One reason for this is that these important logic functions are symmetric: the output is the same between the two input combinations

Figure 2: Four types of dot arrangement of an array consisting of six nanodots sandwiched by the source and drain electrode. (a) Series, (b) 2 × 3, (c) 3 × 2, and (d) parallel.

Figure 3: (a) The equivalent circuit of a 2 × 3 nanodot array and (b) an equivalent circuit with gate capacitors. The device has two input gates corresponding to the V_{ga} and V_{gb} terminals and one control gate corresponding to the V_{cg} terminal.

of high-low and low-high [7]. Two of the three gates, V_{ga} and V_{gb}, were used as input gates to create a two-input logic gate. The other gate, V_{cg}, was used as a control gate to change the logic function of the device.

Here, fluctuations in these values were introduced as shown in Table 1. The average tunnel capacitance between islands, or between a dot and source or drain terminal, was assumed to be 2 aF. The average capacitance between a control gate and each nanodot was also assumed to be 2 aF, and the average capacitance between an input gate and a nanodot was 1 aF, so the average total capacitance of the typical dots is about 10 aF. This enables the device to operate at around 10 K, which is the temperature used for simulation. An average tunnel resistance of 2 MΩ and no offset charges were assumed. An important issue to achieve such a multi-functional device by the use of nanodot arrays is to introduce a fluctuation in these capacitances and resistances caused by the fluctuation of nanodot sizes and positions. In the actually fabricated devices, we can control the island size within about 20% fluctuation [13, 14]. A distribution of all capacitances was introduced so as to ensure a standard deviation of 0.2. This corresponds to the distribution in which 68% of capacitances are included within ±20% of the average, which is thought to be attained in actual SEDs. Tunnel resistance distribution was also introduced as a log-normal distribution with a standard deviation of 0.2. This means that 68% of the tunnel resistances are included within the resistance from 126 kΩ to 31.6 MΩ. More than 200 examples were created for each dot arrangement with different capacitances and tunnel resistances in accordance with the variation shown above by generating random numbers and simulated the electrical characteristics by a Monte Carlo simulation [7]. It should be noted that the too much fluctuated capacitances and tunnel resistances sometimes provide specific nanodot arrays which do not work as logic gates using small arrays consisting of six nanodots, even though the slight fluctuations are needed for achieving multifunctional device operation.

Table 1: Distribution of tunnel resistances, tunnel capacitances, and gate capacitances.

	Average	Distribution function	σ
Tunnel resistance	2 MΩ	Log normal	0.2
Tunnel capacitance	2 aF	Gaussian	0.2
Input-gate capacitance	1 aF	Gaussian	0.2
Control-gate capacitance	2 aF	Gaussian	0.2

The drain voltage V_d was set so that the average current I_d flowing between the source and drain terminal was constant at a high-temperature limit. To realize this condition, the V_d for series, 2 × 3, 3 × 2, and parallel are set to 42 mV, 12 mV, 6 mV, and 2 mV, respectively. Although the average drain current I_d at high temperature was 3 nA, the simulated

Figure 4: Simulated drain current I_d as a function of control-gate voltage V_{cg} of a "parallel" nanodot-array device. Parameters are a combination of input-gate voltages V_{ga} and V_{gb}. "1" corresponds to a "high" input voltage (60 mV) and "0" corresponds to a "low" input voltage (0 V). The arrows at A, B, and C correspond to the positions of V_{cg}, where the logic functions of NAND, NOR, and XOR are, respectively, achieved when the current threshold is set to 0.2 nA.

Figure 5: Occurrence frequencies of the six important logic functions (AND, OR, NAND, NOR, XOR, and XNOR) as a function of threshold current for a "parallel" nanodot-array device. We changed V_{cg} from 0 to 5 V.

average I_d at 10 K was about 0.5 nA due to the Coulomb blockade effect.

The two input-gate voltages, V_{ga} and V_{gb}, were set to 60 mV for the "high" state and 0 V for the "low" state. The input-gate voltage of 60 mV corresponds to 75% of the voltage needed for a half-period shift of the Coulomb oscillation if a single-electron transistor consisting of a dot without capacitance fluctuation is assumed [7]. The control-gate voltage V_{cg} ranged from 0 to 5 V.

3. Results and Discussion

Figure 4 shows a typical result of I_d-V_{cg} characteristics simulated for a device with a "parallel" nanodot arrangement in which tunnel resistances, tunnel capacitances, and gate capacitances were distributed by the method described above. The parameters are the four combinations of input-gate voltages, V_{ga} and V_{gb}. Here, "1" corresponds to the "high" input voltage (60 mV) and "0" corresponds to the "low" input voltage (0 V). The oscillation characteristics changed depending on the combination of the two input-gate voltages. This change was complicated due to the nonuniform capacitances and tunnel resistances. In other words, the control-gate voltage V_{cg} is what switched the characteristics of the array. Here, the drain current I_d is used as an output and introduces a current threshold to determine whether the current is "high" or "low." If the current threshold is set to 0.2 nA as shown by the broken line in Figure 4, and select a V_{cg} of around 0.04 V as indicated by the as indicated by arrow A in Figure 4, the output function is a NAND gate because the output current is low only for the input combination (V_{ga}, V_{gb}) = (1, 1). In the same way, if V_{cg} of around 0.22 V and 0.18 V are selected, as shown by arrows B and C in Figure 4, these functions are NOR and XOR gates, respectively. We can find every one of the important two-input logic functions—AND, OR, NAND, NOR, XOR, and XNOR—by changing V_{cg}.

It should be noted here that conventional CMOS circuits usually use voltage outputs. In addition, when the current threshold is used in the current output waveform characteristics shown in Figure 4, the on/off current ratio seems to be small. As shown in Figure 9 of [12], the current output can be converted to a voltage output with a relatively high on/off ratio by using a cascode MOSFET [15].

It is easily understood that the current threshold plays an important role in the occurrence frequency of each logic function: when the threshold is changed, the occurrence frequency is changed because OR and NAND frequently appear at the lower current threshold conditions while AND and NOR appear at the higher current threshold condition. Figure 5 summarizes the frequency of occurrence of each important logic function as a function of current threshold for a nanodot-array device of "parallel," where V_{cg} was changed from 0 to 5 V. If the current threshold is set from about 0.30 nA to 0.55 nA, any one of the important logic functions appears with a frequency higher than 1%. We call this current threshold region the "window" for 1%. A wide window is convenient for achieving a flexible logic gate. In order to define the width of the window, we introduce a standard frequency, as shown in Figure 5. The two arrows correspond to the windows for 1% and 4% frequency, respectively. The current threshold window for 4% frequency means that a 4% occurrence of all six of the important functions is guaranteed when the current threshold is set anywhere in the window.

Since the nanodot array has fluctuation in capacitance and tunnel resistance, the window also fluctuates. Figures 6(a)–6(c) show examples of the relation between the occurrence frequency of each important logic function and

Figure 6: Occurrence frequency of the six important logic functions as a function of current threshold for three different "series" nanodot-array devices: (a), (b), and (c). We changed V_{cg} from 0 to 5 V.

the current threshold calculated for three nanodot. arrays of "series" with different sets of capacitances and tunnel resistances. Although the frequency characteristics are all different, relatively wide windows are attained for all three arrays. We calculated more than 200 nanodot arrays with different sets of gate capacitances, tunnel capacitances, and tunnel resistances and confirmed that all arrangements have a window of 4%, as shown in Figure 6. We obtained the same results for the other dot arrangements (2 × 3, 3 × 2, and parallel) and confirmed that all arrays had at least a 4% window. An important point is that there were slight fluctuations in the position and width of the window, as shown in Figures 6(a)–6(c). When the array as a logic device is used, the current threshold has to be set at the initial setup of the logic device without measuring the I_d-V_{cg} characteristics. A wider window and a stable center of the window of the current threshold are preferable for prospecting the occurrence probability of the logic functions. If the probability of occurrence of the six important logic functions is 1, we can always change to a different important logic function by changing V_{cg}.

We introduced a "normalized window width" that is normalized on the basis of the averaged value of the center of the window. Here, the center of the window of the current threshold is also normalized by the averaged value in order to compare the probability of the occurrence of six important logic functions in the four array arrangements. The electrical characteristics of more than 200 examples

Figure 7: (a) Normalized window width and (b) standard deviation of the normalized center of the current threshold of the window for the four nanodot arrangements of arrays. The parameter is the minimum frequency of the six important logic functions.

Figure 8: Occurrence probability of all the six important logic functions for the four nanodot arrangements of arrays when the current threshold is fixed at the most appropriate value for obtaining the highest probability. The parameter is the minimum frequency of the six important logic functions.

were calculated for each nanodot arrangement and the statistics of the normalized window width and the center of the window were evaluated. Figures 7(a) and 7(b) show the results of the averaged normalized window width and standard deviation of the normalized center of the current threshold of the window, respectively. The parameter is the minimum frequency of the six important logic functions, which guarantees the minimum frequency of the occurrence of the functions. Although the normalized window width becomes wider as the arrangement of the array changes from parallel to series, the standard deviation of the normalized center of the current threshold of the window also increases.

In order to determine the best arrangement of the dot array, the probability of the occurrence of all the six important logic functions was evaluated. Figure 8 shows the results when the current threshold was fixed at the most appropriate value for obtaining the highest probability to meet the minimum frequency. The best nanodot arrangement seems to be the 3 × 2 or 2 × 3 nanodot arrays. If a frequency of occurrence of 1% is permitted, the probability is almost 100%. This means that we can find any one of the six important logic functions with an appearance probability of at least 1% by changing the control-gate voltage from 0 V to 5 V. If a probability higher than 1% is claimed, some nanodot arrays do not work, which means that the appearance probability of all six logic functions is lower than the claimed value in some nanodot arrays. The nanodot array of series is not so bad if a relatively lower appearance probability of the six logic functions can be permitted. These results show that both parallel and series tunnel paths play an essential role for the operation as multifunctional logic gates, while the results suggest that the parallel paths are slightly important.

We also calculated the probability when the tunnel resistances have no fluctuation—namely, when they are constant at 2 MΩ—to investigate the origin of the results shown in Figure 8. As shown in Figure 9, all the nanodot-array arrangements recover the probability of the occurrence of the six logic functions. However, only the series with the frequency of 4% maintains a degraded state. If some dots in the series connections of nanodots have small capacitors, the charging energy becomes high, which inhibits the tunneling of electrons and makes the current lower. The large charging energy of the smallest dot makes the current level low in

Figure 9: Occurrence probability of all the six important logic functions for the four nanodot arrangements of arrays without tunnel resistance fluctuation. The parameter is the minimum frequency of the six important logic functions.

the nanodot array of series, which limits the possibility of obtaining a wider current threshold window for high-occurrence probability. In the other arrays, since there are other parallel current paths, current levels are kept relatively high. When the fluctuation of tunnel resistance is introduced, and when both sides of the tunnel resistances of one of the dots in the parallel array is low, the current level increases, which also makes the current threshold window narrower. The tunnel resistance fluctuation degrades the appearance probability of the six logic functions. Consequently, it is important that the arrays have some parallel and some series connections in order to maintain current levels and to provide almost the same logic characteristics with a similar threshold current.

4. Conclusion

The Monte Carlo simulation was used to investigate flexible logic-gate devices consisting of a nanodot array assuming the fabrication by the use of the PADOX method in which lattice-like arrangement of nanodot arrays are attained easily. We changed the arrangement of the nanodots to clarify the importance of the parallel and series tunnel paths and then studied the variability of the logic functions of a device operating as a two-input logic gate. We introduced fluctuations in tunnel resistances, tunnel capacitances, and gate capacitances and then calculated the electrical characteristics of more than 200 sets for each nanodot arrangement as a function of the control voltage V_{cg}. We evaluated the appearance probability of the six important logic functions and clarified that both parallel and series tunnel paths play an essential role for the operation as multifunctional logic gates. The results also suggest that the parallel paths seem to be more critical than the series ones.

Acknowledgments

The authors are grateful to A. Fujiwara, Y. Ono, H. Inokawa, K. Nishiguchi, T. Kaizawa, and T. Oya for their invaluable discussions. This work was partly supported by JSPS KAKENHI (2156081, 22240022, and 24360128).

References

[1] H. Grabert and M. H. Devoret, *Single Charge Tunneling*, Plenum, New York, NY, USA, 1992.

[2] M. A. Kastner, "Artificial atoms," *Physics Today*, vol. 46, pp. 24–31, 1993.

[3] K. K. Likharev, "Single-electron devices and their applications," *Proceedings of the IEEE*, vol. 87, no. 4, pp. 606–632, 1999.

[4] Y. Takahashi, Y. Ono, A. Fujiwara, and H. Inokawa, "Silicon single-electron devices," *Journal of Physics Condensed Matter*, vol. 14, no. 39, pp. R995–R1033, 2002.

[5] Y. Ono, A. Fujiwara, K. Nishiguchi, H. Inokawa, and Y. Takahashi, "Manipulation and detection of single electrons for future information processing," *Journal of Applied Physics*, vol. 97, no. 3, Article ID 031101, 19 pages, 2005.

[6] C. Wasshuber, H. Kosina, and S. Selberherr, "A comparative study of single-electron memories," *IEEE Transactions on Electron Devices*, vol. 45, no. 11, pp. 2365–2371, 1998.

[7] T. Kaizawa, T. Oya, M. Arita, Y. Takahashi, and J. B. Choi, "Multifunctional device using nanodot array," *Japanese Journal of Applied Physics*, vol. 45, no. 6A, pp. 5317–5321, 2006.

[8] H. Fukutome, Y. Momiyama, T. Kubo, Y. Tagawa, T. Aoyama, and H. Arimoto, "Direct evaluation of gate line edge roughness impact on extension profiles in sub-50-nm n-MOSFETs," *IEEE Transactions on Electron Devices*, vol. 53, no. 11, pp. 2755–2763, 2006.

[9] T. Skotnicki, J. A. Hutchby, T. J. King, H. S. P. Wong, and F. Boeuf, "The end of CMOS scaling: toward the introduction of new materials and structural changes to improve MOSFET performance," *IEEE Circuits and Devices Magazine*, vol. 21, no. 1, pp. 16–26, 2005.

[10] A. Chin and S. P. McAlister, "The power of functional scaling: beyond the power consumption challenge and the scaling roadmap," *IEEE Circuits and Devices Magazine*, vol. 21, no. 1, pp. 27–35, 2005.

[11] Y. Takahashi, A. Fujiwara, K. Yamazaki, H. Namatsu, K. Kurihara, and K. Murase, "Multigate single-electron transistors and their application to an exclusive-OR gate," *Applied Physics Letters*, vol. 77, no. 5, pp. 637–639, 2000.

[12] T. Kaizawa, M. Arita, A. Fujiwara et al., "Single-electron device with si nanodot array and multiple input gates," *IEEE Transactions on Nanotechnology*, vol. 8, no. 4, pp. 535–541, 2009.

[13] Y. Takahashi, H. Namatsu, K. Kurihara, K. Iwadate, M. Nagase, and K. Murase, "Size dependence of the characteristics of si single-electron transistors on SIMOX substrates," *IEEE Transactions on Electron Devices*, vol. 43, no. 8, pp. 1213–1217, 1996.

[14] H. Namatsu, Y. Takahashi, K. Yamazaki, T. Yamaguchi, M. Nagase, and K. Kurihara, "Three-dimensional siloxane resist for the formation of nanopatterns with minimum linewidth fluctuations," *Journal of Vacuum Science and Technology B*, vol. 16, no. 1, pp. 69–76, 1998.

[15] H. Inokawa, A. Fujiwara, and Y. Takahashi, "A multiple-valued logic and memory with combined single-electron and metal-oxide-semiconductor transistors," *IEEE Transactions on Electron Devices*, vol. 50, no. 2, pp. 462–470, 2003.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 621531, 10 pages
http://dx.doi.org/10.1155/2013/621531

Review Article

Advances in Optical and Magnetooptical Scatterometry of Periodically Ordered Nanostructured Arrays

Martin Veis and Roman Antos

Institute of Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague, Czech Republic

Correspondence should be addressed to Martin Veis; veis@karlov.mff.cuni.cz

Received 26 November 2012; Accepted 27 December 2012

Academic Editor: Yue Li

Copyright © 2013 M. Veis and R. Antos. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We review recent advances in optical and magnetooptical (MO) scatterometry applied to periodically ordered nanostructures such as periodically patterned lines, wires, dots, or holes. The techniques are based on spectroscopic ellipsometry (SE), either in the basic or generalized modes, Mueller matrix polarimetry, and MO spectroscopy mainly based on MO Kerr effect measurements. We briefly present experimental setups, commonly used theoretical approaches, and experimental results obtained by SE and MO spectroscopic analyses of various samples. The reviewed analyses are mainly related to monitoring optical critical dimensions such as the widths, depths, and periods of the patterned elements, their real shapes, and their line edge or linewidth roughness. We also discuss the advantages and disadvantages of the optical spectroscopic techniques compared to direct monitoring techniques.

1. Introduction

Recent advances in nanotechnologies [1, 2] have yielded periodically ordered nanostructures with shapes of unlimited complexity, ultrahigh depth and lateral resolution, high aspect ratios, and various material compositions, all of which require further development of characterization techniques. Such techniques should measure the critical dimensions (CDs) of patterned lines, wires, dots, or holes with high accuracy and resolution, and also be capable of detecting tiny sidewall features of deep pattern trenches or other geometric parameters such as the line edge roughness (LER) or linewidth roughness (LWR) of patterned lines or wires.

The direct techniques for monitoring the geometric properties of laterally patterned nanostructures are scanning electron microscopy (SEM) and scanning probe methods such as scanning tunneling microscopy (STM), restricted to samples with metallic surfaces, atomic force microscopy (AFM), or magnetic force microscopy (MFM), restricted to samples with magnetic surfaces. Although these techniques have some disadvantages and restrictions (SEM requires cutting a sample to image its cross-section, while the scanning probe methods are affected by the probe-sample contact and special surfaces as mentioned), their recent development helped to overcome some of them. For instance, if an AFM probe uses a special tip with a flared apex radius [3] (so-called a CD tip) instead of a conventional tip, then the AFM measurement can yield an accurate relief profile, provided by an appropriate postprocessing algorithm which removes the tip's influence [4]. The direct techniques are also suitable for determining the LER/LWR parameters just by the statistical analysis of the scanned image [5, 6]. However, the probe-sample contact still hinders the analysis and especially disables the LER measurement at the sharp bottom of patterned grooves.

The optical and magnetooptical (MO) spectroscopic techniques such as spectroscopic ellipsometry (SE) and magnetooptical Kerr effect (MOKE) measurements are not affected by the probe-sample contact. They are, however, indirect techniques that require both simulations and measurements of the optical spectra, from whose comparison, using a fitting procedure with the least square method, the requested parameters can be determined with the precision proportional to the amount of experimental data. The method is usually called optical or MO scatterometry.

In this paper we review some recent advances in the characterization of periodically patterned nanostructures by scatterometry based on SE and MOKE spectroscopy. We first introduce the experimental techniques used to measure SE

and MO spectra, then we briefly list the most common theoretical approaches and their recent improvements, and finally we review some important results achieved on patterned nanostructures. For better demonstration, we also include an example of AFM, SE, and MO investigation of a magnetic grating.

2. Experimental Techniques

When polarization-sensitive measurements are employed to obtain experimental data, it is favourable to describe the polarization state of light by a proper mathematical approach. If depolarization effects are not considered, the Jones matrix formalism is frequently used for the description of polarized light and its transformation by polarizing optical elements. The optical and MO behavior of the sample can be macroscopically described within the Jones matrix formalism in the Cartesian representation (with the s- and p-polarization bases), using the 2×2 Jones reflection matrix

$$\mathbf{R} = \begin{bmatrix} r_{ss} & r_{sp} \\ r_{ps} & r_{pp} \end{bmatrix}, \tag{1}$$

where r_{ij} are Fresnel amplitude reflection coefficients.

According to quantities measured, we can distinguish between photometric and ellipsometric experimental techniques. Spectrophotometry measures the amount of energy reflected or transmitted by the sample, so it provides the spectrally resolved information about $|r_{ss}|^2$ or $|r_{pp}|^2$. Typically, the light generated by a lamp is driven to the sample trough input optics and a polarizer. Then the reflected light intensity is detected by a photomultiplier or another type of photodetector. The main disadvantage of this technique is the time instability of the light flux and it also needs a proper calibration by reference reflectors.

Spectroscopic ellipsometry is an experimental technique that measures the change of incident light polarization upon its reflection (or sometimes transmission). The exact nature of polarization change is determined by the material and geometry of the nanostructured array. If the material of the sample is isotropic, then the Jones reflection matrix is diagonal and there is no interaction between the s and p waves. The diagonal elements are related to the array structure and its optical properties. The ellipsometric angles Ψ and Δ are then defined by following equation:

$$\varrho = \frac{r_{pp}}{r_{ss}} = \tan \Psi e^{j\Delta}. \tag{2}$$

Spectral dependence of Ψ and Δ obtained by SE carries the important information about the geometry of nanostructured arrays. Its analysis, however, requires advanced theoretical approaches, which are described in the next section. The principle of determining unknown parameters of an analyzed structure, called fitting, is minimizing the differences between simulated and measured values throughout the spectrum and all angles of incidence. More precisely, the error is here evaluated as the angular distances between measured and simulated point plotted on the Poincaré sphere, which is specified by the azimuthal angle 2Ψ and the polar angle Δ, that is, $\varepsilon_j = \mathbf{S}_{e,j} \cdot \mathbf{S}_{m,j}$, where the subscript "$e, j$" means the jth experimental value, "m, j" means jth modeled value, and the vectors $\mathbf{S} = [\sin 2\Psi \cos \Delta, \sin 2\Psi \sin \Delta, \cos 2\Phi]$ denote the Stokes vectors of the experimental and modeled points on the sphere, respectively. For the sake of fitting, the sum of least squares $\varepsilon_{LS}^2 = \sum_j \varepsilon_j^2$ is searched. However, finally the average error $\varepsilon = (\sum_{j=1}^{M} \varepsilon_j)/M$ is presented.

Typical ellipsometric experimental setup is the high power arc lamp-polarizer-sample-compensator-analyzer. This so-called PSCA optical sequence is widely used in standard ellipsometric setups. Detailed information about the main ideas of ellipsometry including basic notions on polarization and experimental techniques is treated in the book written by Azzam and Bashara [7]. Here, we restrict ourselves to the description of a specific four-zone ellipsometric configuration which was used in various scatterometric experiments [8–10]. This experiential setup is depicted in Figure 1. An optical sequence of this null ellipsometer is polarizer-sample-compensator-analyzer (PSCA), where the compensator is a phase-retarding tool. The Jones vector of the light at the output of the analyzer (and the intensity detected by the detector as well) depends on the rotation angles of polarizer, compensator, and analyzer: α, β, γ. By searching the right values of α and β at a fixed γ, the null ellipsometry provides a zero intensity of the light at the output. In the presented setup, the compensator is a quarter-wave plate operating at two opposite positions $\gamma^{(\pm)} = \pm\pi/2$. Taking this under consideration one has generally four null intensity positions of the optical setup. Therefore, it is favourable to divide the Poincaré sphere into four zones. From each zone, it is possible to derive the requested Ψ and Δ quantities. To eliminate slight misalignments in the setup of polarizing components, the ellipsometric quantities are taken in all zones and finally their averages are calculated:

$$\begin{aligned} \Psi &= \frac{1}{4}\left(\overline{\alpha_1} - \overline{\alpha_2} + \overline{\alpha_3} - \overline{\alpha_4}\right), \\ \Delta &= \frac{1}{4}\left(\overline{\beta_1} + \overline{\beta_2} - \overline{\beta_3} - \overline{\beta_4}\right), \end{aligned} \tag{3}$$

where $\overline{\alpha}_i = \alpha_i - \pi/2$ and $\overline{\beta_i} = \beta_i - \pi/2$ are the null positions of the polarizer and analyzer corresponding to the ith zone.

When an external magnetic field is applied to a ferromagnetic sample, it induces magnetooptical anisotropy. The off-diagonal elements of the Jones reflection matrix become in general nonzero, which indicates the conversion between s incident and p reflected (r_{ps}) as well as p incident and s reflected (r_{sp}) waves. Although the Jones reflection matrix has generally four elements, it can be simplified if the magnetic field is applied in the certain directions (e.g., perpendicular to the sample) [11].

There are two basic classes of experimental techniques which are employed for studies of weak MO effects. The first class is measuring the direct change of the intensity of light at the output of an optical element sequence. The second class, more sophisticated one, is based on the modulation of azimuth or ellipticity of incident light. In combination with a synchronic detection system, modulation techniques

Figure 1: Experimental setup of four-zone null ellipsometer for scatterometric experiments.

increase the signal-to-noise ratio. However, both classes are used in different specific situations (Kerr microscopy, Kerr vector magnetometry, Kerr spectroscopy, etc.).

There are two basic techniques using the time modulation of the light polarization. First, an intensity-based method is based on the modulation of ellipticity of a light wave using the photoelastic modulator. This method allows fast measurement, which makes it suitable for studying dynamics of magnetization processes. Because it is an intensity method, the calibration of the equipment is required in each measurement, which makes it inconvenient for spectroscopic experiments. The second experimental technique employs the Faraday rotation in glass for the modulation of the azimuth of the polarization ellipse. Such a modulator, called the Faraday cell, consists of a fused quartz rod with optically polished faces, inserted into a solenoid coil. Owing to the sinusoidal time dependence of the modulation current in the coil generated by a high power audio amplifier, the azimuth of the light wave passing through the cell is harmonically modulated in time. One can imagine the Faraday cell as a rotator with time-dependent angle of rotation. A typical sequence of optical elements in a null MO spectrometer based on the azimuth modulation technique (depicted in Figure 2) is high power arc lamp-monochromator-polarizer-*dc* compensating Faraday rotator-*ac* modulating Faraday rotator-phase plate (for Kerr ellipticity measurements)-sample-analyzer-photomultiplier. In the small angle approximation, the complex MOKE is measured as the ratio:

$$\frac{r_{sp}}{r_{ss}} \approx \theta_K + i\epsilon_K \tag{4}$$

or

$$-\frac{r_{ps}}{r_{pp}} \approx \theta_K + i\epsilon_K, \tag{5}$$

where the indecent light beam is s- or p-polarized, respectively. Here θ_K and ϵ_K denote the Kerr rotation and ellipticity. Compensating *dc* Faraday cell automatically turns the plane of polarization by a certain angle to adjust detected intensity approximately to zero. Therefore, it compensates all changes produced by MO effects in the sample or by rotation of the polarizer. This Faraday cell is controlled by negative feedback loop. Measured signal on the output is then proportional to the magnetooptical effect of the sample and it decreases with increasing amplification of the feedback regulator. The negative feedback is introduced by means of analog output signal from the lock-in detector. This signal is used to control the current supply for the compensating cell.

Such compensation technique with azimuth modulation has several advantages over the other experimental methods. Azimuth modulation with synchronic detection notably increases the signal-to-noise ratio. The intensity dependence at the output is a linear function of the deviation from crossed polarizers. Crossing of the polarizers can be completely automatic (controlled by the negative feedback loop) and very precise without mechanical input. The value of the measured angle is not dependent on the intensity of output light (null method). Therefore if a highly stable current supply for the *dc* compensating Faraday cell is used, very small MOKE angles down to the order of one millidegree can be measured. On the other hand, the usage of Faraday cells limits the photon energy range of the measured spectrum. Typically, the energy range is from 1.2 to 6 eV.

3. Theoretical Approaches

Periodic nanostructures or diffraction gratings can be classified by various means. According to the number of dimensions, they are one-, two-, or three-dimensional (1D, 2D, or 3D), where the third dimension generalizes a simple multilayer profile of the nanostructure within its depth. According to the pattern shape, there are sinusoidal and sine-like gratings (usually fabricated by holographic lithography) and lamellar gratings (usually made by exposure through masks combined with e-beam or ion-beam milling), and so forth. According to the used material, there are transparent and absorbing gratings, or isotropic and anisotropic gratings. The latter contain anisotropic materials, for example, magnetically ordered metals.

It is obvious that different modeling methods are suitable for different kinds of gratings. There is a variety of theoretical approaches, approximate and rigorous ones. Optics of shallow gratings, for example, can be advantageously simulated by an approximate theory based on local thin-film/multilayer approximation, neglecting the effect of patterned edges of

nanoelements. This method, based on Fourier optics analysis of the sample illumination, is sometimes ambiguously referred to as the scalar diffraction theory. In this paper we call it the local modes method because it also works on anisotropic gratings requiring the fully vectorial electromagnetic approach [12]. Another type of nanostructures are subwavelength gratings, for example, wire-grid polarizers, which can be modeled by the effective medium theory where the periodic medium is regarded as an effective homogeneous medium.

General nanostructures, in particular structures with a larger period and deep trenches, require rigorous numerical methods based on electromagnetic theory. Among those, there are direct numerical approaches such as the finite difference method [13], finite elements method [14], or the finite difference time/frequency domain (FDTD/FDFD) method [15, 16], each of which can be used for any (a) periodic nanostructure. Then there are approaches originally used in other fields or applications, for example, the plane wave expansion method, Korringa-Kohn-Rostoker [17] and other methods based on Green's functions, method of fictitious sources [18], variational methods [19], or diffractive approaches. Finally, there are methods originally developed for diffraction gratings [20, 21], which can be classified as differential, integral, and modal methods (according to the chosen numerical algorithm). They are based on the Fourier expansion of the electromagnetic fields and either the material parameters (the coupled-wave method and Fourier modal method) or the relief functions (Chandezon's coordinate transformation method [22], appropriate for sinusoidal gratings).

The coupled-wave method, usually called the rigorous coupled-wave analysis (RCWA) [23], is one of the most used approaches to simulate the optical response of general periodic nanostructures and is also used in simulations presented in this paper. During the latter half of the last century, it underwent a remarkable progress towards high accuracy and generality. Since Kogelnik's paper [24], which used only two waves in a volume grating, the method was generalized and improved to simulate with high-precision deep, 2D, arbitrary-relief, and anisotropic gratings and their various combinations. The improvements have been achieved by improving propagational algorithms, from the transfer-matrix algorithm, through the R-matrix algorithm, to the presently most used scattering-matrix algorithm [25]. Further enhancements of the methods have been performed by modifying the Fourier factorization procedures according to the field discontinuities at the pattern boundaries [26–30], and other modern enhancements such as the adaptive spatial resolution (ASR) [31].

4. Results Obtained by Scatterometry

4.1. Purely Optical Scatterometry. Optical scatterometry is most frequently based on SE and sometimes is combined with spectrophotometry. The SE spectra are almost always measured in the specular reflection, which corresponds to the zeroth order of the grating diffraction. In the case of 1D gratings, the plane of incidence is usually chosen perpendicular to the grating grooves, which corresponds to planar diffraction (the entire problem is then solved in one plane for each independent polarization, which reduces the computation time). Using the specular SE, various authors have successfully determined linewidths, periods, depths, and other fine profile features, as already reviewed by Huang and Terry [32]. It has been shown that some of the features detected by scatterometry are not detectable by scanning probe methods (e.g., sharp bottom corners of grooves) and are difficult to observe on SEM images.

Obvious advantages of scatterometry (besides it is non-destructive) are higher sensitivity, no contact with any mechanical tool, and possibility to monitor features beneath the relief such as native oxide overlayers or thermally induced overlayers developed in an oxygen/nitrogen atmosphere. Recently, Ghong et al. [33] have demonstrated the influence of the native oxide overlayer on the SE spectra measured on 1D and 2D silicon gratings. Similarly, Yu et al. [34] used SE to monitor a coating process when a resist layer was deposited over a silicon grating.

On the other hand, scatterometry has some disadvantages: spectral measurements are indirect, and the measured spectra sometimes require very difficult analyses to reveal the real profile of the structure, which should be approximately known before starting the fitting procedure (to use it as an initial value). Moreover, the spectra can contain too many unknown parameters, or at least some vaguely known parameters. For these reasons, it is important to study carefully the influence of the geometric and material parameters on the spectral dependences of the optical response [35, 36]. Furthermore, Kim et al. [37] have shown that the detailed theoretical analysis of the SE dependence on the geometric parameters can also help one to determine asymmetric profiles of gratings, although the SE response is same when light illuminates the asymmetric grooves from either the left or the right side.

Another disadvantage of scatterometry is the long computation time during the fitting procedure when complicated structures are analyzed. Therefore, for computation it is desirable to retain as few Fourier components of the periodic functions as possible but to still have good approximation [8].

To overcome the problem of many parameters and to increase the sensitivity of SE measurements, novel ellipsometric configurations have been proposed. For instance, Liu and Terry Jr. [38] have developed immersion scatterometry which used SE in an immersion mode (in water), which increased the refractive index of the grating's ambient medium and thus increased the numerical aperture of the optical apparatus.

Other configurations that increase the sensitivity and the number of detectable parameters are generalized ellipsometry [39, 40] and Mueller matrix polarimetry [32]. Both methods are capable to deal with anisotropic samples, where anisotropy might exist either due to the presence of anisotropic materials (such as ordered uniaxial or biaxial nanocrystals) or due to the order of nanoelements, where both cases yield small cross-polarization effects not detectable by the conventional SE. Using both methods,

Foldyna et al. [41, 42] have accurately determined the depth and the top width of 2D-periodic square holes patterned in the photoresist film deposited on a silicon substrate and discussed possibilities of determining further parameters from the same spectra.

Unlike generalized ellipsometry, the Mueller matrix polarimetry works not only with cross-polarization effects, but also can detect the depolarization effects caused by surface roughness or LER and LWR. Foldyna et al. [43] demonstrated the application of this method to monitor the LWR.

As an example of scatterometric analysis based on SE measurement, consider a rectangular-relief grating patterned on the top of a 32 nm thick permalloy (NiFe) film deposited on a Si substrate, whose AFM measurement is displayed in Figure 3 (the details of fabrication are described in [44]). The comparison of the nominal geometric parameters (those intended by the grating manufacturer) with parameters determined by AFM and scatterometry (based on SE performed at three angles of incidence, 60, 70, and 80°, the last of which is displayed in Figure 4, using Permalloy's material parameters from [45]) is listed in Table 1.

Here the AFM measurement (in the conventional tip mode) provides a direct image of the grating's relief profile, but the horizontal values (period and linewidth) are affected by a 9% error due to wrong scale. According to our experiences, the period of patterns made by lithographic processes is always achieved with high precision, so that we scale the horizontal AFM parameters to obtain the nominal 1000 nm period and to keep the same period-to-linewidth ratio (the vertical depth 21.7 nm is kept without change). The scaled AFM linewidth (329.3 nm, measured at the bottom) now corresponds well to the linewidth determined by scatterometry (307.2 nm); the 22 nm difference is probably due to the finite size of the apex of the AFM tip. Since the presented ellipsometric spectrum is not sensitive to the grating period (due to the shallow relief), it was not fitted but just verified by the spectral positions of Wood anomalies (the tiny discontinuities in the spectra).

Finally, the 2.6 nm difference between the AFM and scatterometric values of the relief depth is most probably due to some negligence of the used optical model such as the native top NiFe oxide overlayer or inaccurate NiFe optical parameters. This is also the reason why it is difficult to determine the real error of the fitted parameters (or the possible range of their accurate values). Instead, the error of the fitted optical parameters (Ψ and Δ) is usually listed (determined as the average difference on the Poincaré sphere in degrees), which approximately reflects the quality of the fit. This error is in our case $\varepsilon = 2.8°$.

4.2. Magnetooptical Scatterometry. Another way how to increase accuracy or the number of detectable parameters is measuring higher diffraction orders or additional spectra such as MO spectroscopy, which can be also regarded as a generalized SE method applicable to magnetic gratings.

Laterally patterned magnetic nanostructures [46] were originally investigated with respect to their micromagnetic properties, that is, the switching behavior [47] and later also spin-dynamical processes [48]. Besides MFM [49] and spin-polarized STM [50], MO experiments were also employed. Single-wavelength MOKE measurements in specular reflectin and higher diffraction orders became the basis for the technique called diffracted MOKE (D-MOKE) [47, 51], which provides an approximate geometrical distribution of magnetization within a periodic magnetic nanostructure. In the D-MOKE measurement, this information is distributed among the beams diffracted by the nanostructure's periodicity (where higher diffraction orders are more sensitive to the vicinity of the edges of magnetized elements).

A more precise magnetization distribution can be measured by microscopic MOKE (M-MOKE), which does not require the periodic arrangement of magnetic elements. In the wide-field mode [52], the direct magnified image of a single element or a tiny array of elements is provided being sensitive to one chosen magnetization component. In the scanning mode [48], the surface is scanned while the magnetization vector is determined at each point by analyzing asymmetries in the optical Fourier transform image.

The essential advantage of both D- and M-MOKE measurements and the reason for their popularity is again the simplicity of the data analysis, providing the direct or nearly direct magnetic image of the illuminated sample. However, these methods are affected by limitations of the optical imaging and by imperfections of the investigated patterns. For instance, the periodicity of an analyzed structure comparable to the wavelength of detection light makes it almost impossible to record the sufficient number of higher diffraction orders for a proper D-MOKE analysis. Next, the M-MOKE is limited by the detection resolution, also affected by the nonzero wavelength and by the numerical aperture of the objective lens. And finally, the M-MOKE wide-field and scanned images are strongly affected by the so-called edge effects of the lateral patterning, that is, the effects of internal diffraction by the edges of the patterned elements. The edge effects blur the recorded image and thus erase the information about magnetization near the vicinity of the magnetized elements. Particularly important edge effects affecting the MOKE approaches are the cross-polarization effects, observed when the angle of the incidence plane is oblique to the edges, and the depolarization effects, mainly caused by the LER.

Table 1: Comparison of grating geometrical parameters obtained by AFM and scatterometry, together with nominal ones (intended by the manufacturer). All the dimensions are in nanometers.

Parameter	Nominal	AFM	Scaled AFM	Scatterometry
Period	1000	1091.5	1000*	1000**
Linewidth	500	359.4	329.3	307.2***
NiFe thickness	32	—	—	—
Relief depth	16	21.7	21.7	24.3***

*Fixed value.
**Just verified from the position of the Wood anomaly.
***The average error of the fit on Poincaré sphere is $\varepsilon = 3.8°$.

Figure 2: Experimental setup for MOKE measurements utilizing azimuth modulation in the photon energy range from 1.2 to 6 eV. L1, L2, L3, and L4 denote quartz lenses.

Figure 3: AFM measurement on a NiFe grating.

The aim to use the MOKE techniques even beyond those limitations demands to investigate those effects by a method which would accurately distinguish between the magnetization response and the effects due to optical imaging and fabrication imperfections. Several papers [9, 10, 12, 44] have already shown that this demand is satisfied by MO spectroscopic scatterometry, which can be applied as accurate quality control of lithographic manufacturing or as a tool quantitatively determining the LER, native oxide, and other effects, so that it could be later utilized for extending the D- and M-MOKE analyses to higher-resolution patterns. It is worth pointing out that MO spectroscopic analyses could take place after the development of proper modeling methods for anisotropic gratings, which are considerably more difficult than those for isotropic ones [53–56].

In particular, [9] demonstrates that MOKE spectra measured in zeroth and −1st diffraction orders can be used to determine the thicknesses of native oxide overlayers developed on the top of a magnetic grating (made here as periodic NiFe wires capped by a protection Cr overlayer, fabricated on the top of a Si substrate). It was shown that the zeroth order was particularly sensitive to the SiO_2 overlayer developed on the top of the Si substrate before fabricating the grating. On the other hand, the −1st order was more sensitive to the Cr_2O_3 overlayer developed on the top of the Cr capping.

It was further shown [10] that applying p-polarized incident light in the MOKE measurement helps one to determine the quality of the edges of the patterned wires by a numerical quantity denoted η, which is proportional to the smoothness of the edges ($\eta = 1$ means that the edges are perfect, whereas $\eta = 0$ means that the LER and LWR are so large that the patterned area is randomly disordered). Measurements of η on two examples of gratings displayed in Figure 5 yielded the values $\eta = 7.0$ (Figure 5(a)) and $\eta = 0.53$ (Figure 5(b)), which clearly corresponds with the obvious quality of the samples. The parameter η can be, therefore, identified with the grating's LER.

Figure 4: Spectroellipsometric parameters Ψ and Δ measured (dots) and simulated (solid curves) on the NiFe rectangular-relief grating with the angle of incidence of 80°. The geometric parameters for the simulation were chosen those in the last column of Table 1.

Figure 5: AFM measurements of two Cr/NiFe wire samples made on a Si substrate, both with different LER.

To illustrate difficulties coupled with too high sensitivity of the MO spectroscopy, Figure 6 shows a comparison of measured and simulated MOKE parameters, the Kerr rotation and ellipticity in the polar magnetic configuration, using again the material parameters from [45] and the grating's geometrical dimensions determined by SE. The discrepancy between the theory end experiment in some spectral ranges are again due to possible inaccuracy of the material parameters and/or the native NiFe oxide overlayer.

5. Conclusions

We have reviewed some recent advances in optical and MO characterization techniques (mainly based on SE and MOKE spectroscopy) applied to various grating structures and discussed their advantages and disadvantages as compared to direct monitoring techniques such as SEM, AFM, STM (spin polarized STM for magnetic samples), MFM, D-MOKE, and M-MOKE. The spectroscopic techniques require

Figure 6: MOKE parameters (polar Kerr rotation and ellipticity) measured (dots) and simulated (solid curves) on the permalloy rectangular-relief grating, the same as presented in Figures 3 and 4.

more difficult and time-consuming postprocessing analysis of measured experimental data. However, they are more sensitive, nondestructive, and capable of detecting more unknown parameters. Besides monitoring optical CDs, they can also evaluate such parameters like LER or LWR.

Acknowledgment

The work was supported by Czech Science Foundation Grant no. P204/10/P346.

References

[1] C. Lu and R. H. Lipson, "Interference lithography: a powerful tool for fabricating periodic structures," *Laser & Photonics Reviews*, vol. 4, no. 4, pp. 568–580, 2010.

[2] S. Brose, S. Danylyuk, L. Juschkin et al., "Broadband transmission masks, gratings and filters for extreme ultraviolet and soft X-ray lithography," *Thin Solid Films*, vol. 520, no. 15, pp. 5080–5085, 2012.

[3] H. Liu, M. Klonowski, D. Kneeburg, G. Dahlen, M. Osborn, and T. Bao, "Advanced atomic force microscopy probes: wear resistant designs," *Journal of Vacuum Science and Technology B*, vol. 23, no. 6, pp. 3090–3093, 2005.

[4] G. Dahlen, M. Osborn, N. Okulan, W. Foreman, A. Chand, and J. Foucher, "Tip characterization and surface reconstruction of complex structures with critical dimension atomic force microscopy," *Journal of Vacuum Science and Technology B*, vol. 23, no. 6, pp. 2297–2303, 2005.

[5] J. Thiault, J. Foucher, J. H. Tortai, O. Joubert, S. Landis, and S. Pauliac, "Line edge roughness characterization with a three-dimensional atomic force microscope: transfer during gate patterning processes," *Journal of Vacuum Science and Technology B*, vol. 23, no. 6, pp. 3075–3079, 2005.

[6] Y. Ma and F. Cerrina, "Effect of a surface inhibition layer on line edge roughness," *Journal of Vacuum Science and Technology B*, vol. 23, no. 3, pp. 1096–1101, 2005.

[7] R. A. M. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North Holland Publishing, North-Holland, The Netherlands, 1977.

[8] R. Antos, J. Pistora, J. Mistrik et al., "Convergence properties of critical dimension measurements by spectroscopic ellipsometry on gratings made of various materials," *Journal of Applied Physics*, vol. 100, no. 5, Article ID 054906, 2006.

[9] R. Antos, J. Mistrik, T. Yamaguchi, S. Visnovsky, S. O. Demokritov, and B. Hillebrands, "Evidence of native oxides on the capping and substrate of permalloy gratings by magneto-optical spectroscopy in the zeroth- and first-diffraction orders," *Applied Physics Letters*, vol. 86, no. 23, Article ID 231101, 3 pages, 2005.

[10] R. Antos, J. Mistrik, T. Yamaguchi, S. Visnovsky, S. O. Demokritov, and B. Hillebrands, "Evaluation of the quality of permalloy gratings by diffracted magneto-optical spectroscopy," *Optics Express*, vol. 13, no. 12, pp. 4651–4656, 2005.

[11] S. Visnovsky, *Optics in Magnetic Multilayers and Nanostructures*, CRC Press, Taylor & Francis, Boca Raton, Fla, USA, 2006.

[12] R. Antoš, J. Mistrík, M. Aoyama, T. Yamaguchi, S. Visnovsky, and B. Hillebrands, "Magneto-optical spectroscopy on permalloy wires in 0th and 1st diffraction orders," *Journal of Magnetism and Magnetic Materials*, vol. 272, part 3, supplement 1, pp. 1670–1671, 2004.

[13] P. Vincent, "A finite-difference method for dielectric and conducting crossed gratings," *Optics Communications*, vol. 26, no. 3, pp. 293–296, 1978.

[14] T. Delort and D. Maystre, "Finite-element method for gratings," *Journal of the Optical Society of America A*, vol. 10, no. 12, pp. 2592–2601, 1993.

[15] H. Ichikawa, "Electromagnetic analysis of diffraction gratings by the finite-difference time-domain method," *Journal of the Optical Society of America A*, vol. 15, no. 1, pp. 152–157, 1998.

[16] S. D. Wu and E. N. Glytsis, "Volume holographic grating couplers: rigorous analysis by use of the finite-difference frequency-domain method," *Applied Optics*, vol. 43, no. 5, pp. 1009–1023, 2004.

[17] A. Modinos, N. Stefanou, and V. Yannopapas, "Applications of the layer-KKR method to photonic crystals," *Optics Express*, vol. 8, no. 3, pp. 197–202, 2001.

[18] F. Zolla and R. Petit, "Method of fictitious sources as applied to the electromagnetic diffraction of a plane wave by a grating in conical diffraction mounts," *Journal of the Optical Society of America A*, vol. 13, no. 4, pp. 796–802, 1996.

[19] O. P. Bruno and F. Reitich, "Numerical solution of diffraction problems: a method of variation of boundaries," *Journal of the Optical Society of America A*, vol. 10, no. 6, pp. 1168–1175, 1993.

[20] R. Petit, Ed., *Electromagnetic Theory of Gratings*, Springer, Berlin, Germany, 1980.

[21] E. G. Loewen and E. Popov, *Diffraction Gratings and Applications*, CRC Press, New York, NY, USA, 1997.

[22] L. Li and J. Chandezon, "Improvement of the coordinate transformation method for surface-relief gratings with sharp edges," *Journal of the Optical Society of America A*, vol. 13, no. 11, pp. 2247–2255, 1996.

[23] M. G. Moharam and T. K. Gaylord, "Rigorous coupled-wave analysis of planar-grating diffraction," *Journal of the Optical Society of America*, vol. 71, no. 7, pp. 811–818, 1981.

[24] H. Kogelnik, "Coupled wave theory for thick hologram gratings," *The Bell System Technical Journal*, vol. 48, no. 9, pp. 2909–2947, 1969.

[25] N. P. K. Cotter, T. W. Preist, and J. R. Sambles, "Scattering-matrix approach to multilayer diffraction," *Journal of the Optical Society of America A*, vol. 12, no. 5, pp. 1097–1103, 1995.

[26] P. Lalanne and G. M. Morris, "Highly improved convergence of the coupled-wave method for TM polarization," *Journal of the Optical Society of America A*, vol. 13, no. 4, pp. 779–784, 1996.

[27] P. Lalanne, "Convergence performance of the coupled-wave and the differential methods for thin gratings," *Journal of the Optical Society of America A*, vol. 14, no. 7, pp. 1583–1591, 1997.

[28] P. Lalanne, "Improved formulation of the coupled-wave method for two-dimensional gratings," *Journal of the Optical Society of America A*, vol. 14, no. 7, pp. 1592–1598, 1997.

[29] L. Li, "Use of Fourier series in the analysis of discontinuous periodic structures," *Journal of the Optical Society of America A*, vol. 13, no. 9, pp. 1870–1876, 1996.

[30] R. Antos, "Fourier factorization with complex polarization bases in modeling optics of discontinuous bi-periodic structures," *Optics Express*, vol. 17, no. 9, pp. 7269–7274, 2009.

[31] G. Granet, "Reformulation of the lamellar grating problem through the concept of adaptive spatial resolution," *Journal of the Optical Society of America A*, vol. 16, no. 10, pp. 2510–2516, 1999.

[32] H. T. Huang and F. L. Terry Jr., "Spectroscopic ellipsometry and reflectometry from gratings (Scatterometry) for critical dimension measurement and in situ, real-time process monitoring," *Thin Solid Films*, vol. 455-456, no. 1-2, pp. 828–836, 2004.

[33] T. H. Ghong, J. S. Byun, S. H. Han, J. M. Chung, and Y. D. Kim, "Analysis of 2D periodic nanostructures with an oxide overlayer via spectroscopic ellipsometry," *Journal of Nanoscience and Nanotechnology*, vol. 11, supplement I, no. 7, pp. 6514–6517, 2011.

[34] Z. Yu, J. Hwu, Y. Liu, G. Gauzner, K. Lee, and D. Kuo, "Study of spin-coated resist coverage on nanoscale topography using spectroscopic ellipsometry," *Journal of Applied Physics*, vol. 110, no. 1, Article ID 014303, 2011.

[35] R. Antos, I. Ohlidal, J. Mistrik et al., "Spectroscopic ellipsometry on lamellar gratings," *Applied Surface Science*, vol. 244, no. 1–4, pp. 225–229, 2005.

[36] R. Antos, J. Pistora, I. Ohlidal et al., "Specular spectroscopic ellipsometry for the critical dimension monitoring of gratings fabricated on a thick transparent plate," *Journal of Applied Physics*, vol. 97, no. 5, Article ID 053107, 7 pages, 2005.

[37] T. J. Kim, S. H. Han, T. H. Ghong, J. S. Byun, J. M. Chung, and Y. D. Kim, "Study on an asymmetric nanostructure by using a rigorous coupled-wave analysis," *Journal of the Korean Physical Society*, vol. 56, no. 41, pp. 1278–1281, 2010.

[38] E. Liu and F. L. Terry Jr., "Immersion scatterometry for improved nano-scale topography measurements," *Physica Status Solidi A*, vol. 205, no. 4, pp. 784–788, 2008.

[39] M. Schubert, "Generalized ellipsometry and complex optical systems," *Thin Solid Films*, vol. 313-314, pp. 323–332, 1998.

[40] L. Halagačka, K. Postava, M. Foldyna, and J. Pištora, "Precise phase-modulation generalized ellipsometry of anisotropic samples," *Physica Status Solidi A*, vol. 205, no. 4, pp. 752–755, 2008.

[41] M. Foldyna, A. De Martino, E. Garcia-Caurel et al., "Monitoring critical dimensions of bidimensional gratings by spectroscopic ellipsometry and mueller polarimetry," *Physica Status Solidi A*, vol. 205, no. 4, pp. 806–809, 2008.

[42] M. Foldyna, A. De Martino, E. Garcia-Caurel et al., "Critical dimension of biperiodic gratings determined by spectral ellipsometry and Mueller matrix polarimetry," *The European Physical Journal of Applied Physics*, vol. 42, no. 3, pp. 351–359, 2008.

[43] M. Foldyna, T. A. Germer, B. C. Bergner, and R. G. Dixson, "Generalized ellipsometry of artificially designed line width roughness," *Thin Solid Films*, vol. 519, supplement 1, no. 9, pp. 2633–2636, 2011.

[44] R. Antos, M. Veis, E. Liskova et al., "Optical metrology of patterned magnetic structures: deep versus shallow gratings," in *Metrology, Inspection, and Process Control for Microlithography XIX*, vol. 5752 of *Proceedings of SPIE*, pp. 1050–1059, San Jose, Calif, USA, March 2005.

[45] G. Neuber, R. Rauer, J. Kunze et al., "Temperature-dependent spectral generalized magneto-optical ellipsometry," *Applied Physics Letters*, vol. 83, no. 22, pp. 4509–4511, 2003.

[46] J. I. Martin, J. Nogues, K. Liu, J. L. Vicent, and I. K. Schuller, "Ordered magnetic nanostructures: fabrication and properties," *Journal of Magnetism and Magnetic Materials*, vol. 256, no. 1–3, pp. 449–501, 2003.

[47] M. Grimsditch and P. Vavassori, "The diffracted magneto-optic Kerr effect: what does it tell you?" *Journal of Physics Condensed Matter*, vol. 16, no. 9, pp. R275–R294, 2004.

[48] W. K. Hiebert, A. Stankiewicz, and M. R. Freeman, "Direct observation of magnetic relaxation in a small permalloy disk by time-resolved scanning Kerr microscopy," *Physical Review Letters*, vol. 79, no. 6, pp. 1134–1137, 1997.

[49] T. Shinjo, T. Okuno, R. Hassdorf, K. Shigeto, and T. Ono, "Magnetic vortex core observation in circular dots of permalloy," *Science*, vol. 289, no. 5481, pp. 930–932, 2000.

[50] A. Wachowiak, J. Wiebe, M. Bode, O. Pietzsch, M. Morgenstern, and R. Wiesendanger, "Direct observation of internal spin structure of magnetic vortex cores," *Science*, vol. 298, no. 5593, pp. 577–580, 2002.

[51] J. B. Kim, Y. H. Lu, M. H. Cho et al., "Diffracted magneto-optical Kerr effect of a Ni magnetic grating," *Journal of Applied Physics*, vol. 106, no. 9, Article ID 093103, 2009.

[52] A. Neudert, J. McCord, R. Schäfer, and L. Schultz, "Subnanosecond vortex transformation in ferromagnetic film elements observed by stroboscopic wide-field Kerr microscopy," *Journal*

of Applied Physics, vol. 97, no. 10, part 2, Article ID 10E701, 3 pages, 2005.

[53] K. Rokushima and J. Yamakita, "Analysis of anisotropic dielectric gratings," *Journal of the Optical Society of America*, vol. 73, no. 7, pp. 901–908, 1983.

[54] S. Visnovsky and K. Yasumoto, "Multilayer anisotropic biperiodic diffraction gratings," *Czechoslovak Journal of Physics*, vol. 51, no. 3, pp. 229–247, 2001.

[55] M. H. Cho, Y. Lu, J. Y. Rhee, and Y. P. Lee, "Rigorous approach on diffracted magneto-optical effects from polar and longitudinal gyrotropic gratings," *Optics Express*, vol. 16, no. 21, pp. 16825–16839, 2008.

[56] M. H. Cho, H. Zheng, Y. Lu, Y. Lee, and W. Cai, "Improved rigorous coupled-wave analysis for polar magnetic gratings," *Computer Physics Communications*, vol. 182, no. 2, pp. 360–365, 2011.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 619682, 8 pages
http://dx.doi.org/10.1155/2013/619682

Research Article

Effect of Liquid Ga on Metal Surfaces: Characterization of Morphology and Chemical Composition of Metals Heated in Liquid Ga

Eun Je Lee, Min Goo Hur, Jeong Mun Son, Jeong Hoon Park, and Seung Dae Yang

Radiation Instrumentation Research Division, Korea Atomic Energy Research Institute, 1266 Sinjeong-dong, Jeollabuk-do, Jeongeup-si 580-185, Republic of Korea

Correspondence should be addressed to Min Goo Hur; hur09@kaeri.re.kr

Received 18 October 2012; Revised 21 December 2012; Accepted 21 December 2012

Academic Editor: Yue Li

Copyright © 2013 Eun Je Lee et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This study investigates the effect of liquid gallium (Ga) on metal foils made of titanium (Ti), niobium (Nb), and molybdenum (Mo). The Ti, Nb, and Mo foils were heated in liquid Ga at 120°C for a maximum of two weeks. After heating, the changes in the morphology and the chemical composition of the metal foils were analyzed by using a field emission scanning electron microscope, energy-dispersive X-ray spectrometer, X-ray diffractometer, and X-ray photoelectron spectrometer. The results of the analysis indicated that the Nb foil showed the minimum adhesion of liquid Ga to the surface while the maximum amount of liquid Ga was observed to adhere to the Ti foil. In addition, the Nb foil was oxidized and the Mo foil was reduced during the heating process. Considering these effects, we conclude that Mo may be used as an alternative encapsulation material for Ga in addition to Nb, which is used as the conventional encapsulation material, due to its chemical resistance against oxidation in hot liquid Ga.

1. Introduction

^{68}Ga has attracted great attention in such medical research areas as positron emission tomography (PET) because it decays mainly via positron emission and has a short half-life (~68 min) [1]. Therefore, the production of ^{68}Ge, the long-lived (half-life of ~288 days) parent radioisotope of ^{68}Ga, has become an important issue. ^{68}Ge can be produced by proton irradiation of a Ga target, or by alpha irradiation of a Zn target. However, the use of a Zn target induces difficulty in chemical processing after the irradiation because a third element (Zn) is involved, and, thus, the use of a Ga target has attracted additional research interest. Various forms of Ga, for example, Ga_2O [1], Ga_2O_3 [2], Ga_4Ni [3], and natural Ga [4] have been used for the production of ^{68}Ge by proton irradiation. Specifically, encapsulation is required when a natural Ga target is used because the natural Ga has relatively low melting point (~30°C) and is therefore easily liquefied by the temperature increase resulting from the bombardment of energetic protons. According to a report by Noriter et al., the maximum temperature produced in this process has been estimated to reach as high as 148°C in simulations under irradiation conditions of 29.5 MeV in proton energy and 250 μA in beam current [5]. When the encapsulation material is determined, its resistance to corrosion or embrittlement caused by liquid Ga is one of the most important criterion because the damage of encapsulation by liquid Ga during the proton irradiation can induce serious breakage of accelerator vacuum system. In this research, Ti and Mo were chosen as candidate encapsulation materials in addition to Nb, the conventional choice for the encapsulation of Ga [4] because of the following reasons: Ti, Mo, and Nb are known to have satisfactory resistance to attack by Ga at temperatures up to 400°C [6]. Moreover, Ti is known to resist embrittlement by liquid Ga [7]. In addition, Ti and Nb are widely used metals in the ^{18}O water target for ^{18}F production by proton irradiation because of their hardness and inertness [8], and Mo is used as a window material for the ^{124}Xe target in ^{123}I production by proton irradiation [9]. Therefore, we could conclude that Ti and Mo are suitable candidate materials to this paper. Furthermore, a temperature of 120°C was chosen for the experiments; in our institute, we plan to produce ^{68}Ge

(a) pristine (b) 1 day (c) 3 days

(d) 5 days (e) 9 days (f) 14 days

Figure 1: FESEM images of pristine Ti foil (a) and Ti foils heated in liquid Ga for 1 day (b), 3 days (c), 5 days (d), 9 days (e), and 14 days (f).

by proton irradiation with a <200 μA beam current, so we expect that the maximum temperature will not exceed 120°C. To investigate whether Ti and Mo can be used as alternative materials to Nb in the Ga target for ^{68}Ge production, we carried out heating experiments with Ti, Nb, and Mo foils in liquid Ga at 120°C and investigated the effect of liquid Ga on the morphology and chemical composition of those metals in this paper. The amount of residual Ga after heating and washing was also measured because fine separation between Ga and an encapsulation material is important in real application.

2. Experimental

2.1. Material Preparation. Ga (Strategic Metal Investments, 99.9%) was melted by heating at a temperature slightly above its melting point (~40°C). Next, 2 mL of Ga was transferred to each of several vials (Thermo Scientific Reacti-Vial number 13223). Ti (Goodfellow, thickness: 0.075 mm, 99.6+%), Nb (Goodfellow, thickness: 0.1 mm, 99.9%), and Mo (Goodfellow, thickness: 0.05 mm, 99.9%) foils were cut into samples with sizes of 5 mm × 25 mm and dipped into the liquid Ga in the vials.

2.2. Heating Experiment. After the preparation of the vials containing liquid Ga and a sample of metal foils, the vials were placed on the heating device (Reacti-Therm Heating/Stirring Module, Thermo Scientific). The heating temperature was set to 120°C, and the heating time was varied from 1 day to 14 days (Figure S1) (see Supplementary Material available online at http://dx.doi.org/10.1155/2013/619682). After the heating experiments, the metal foils were taken out of the vials and carefully washed with ethanol several times to remove any residual Ga on the metal foil surfaces. After washing, the samples were put into a vacuum oven and then dried at 40°C for 2 hours.

2.3. Characterization. The surface morphology of the metal foils heated in the liquid Ga was characterized with a field emission scanning electron microscope (FESEM, Hitachi S-4800). Energy dispersive X-ray spectroscopy (EDS) analysis was carried out using a FESEM (Nova230, FEI) instrument equipped with an energy-dispersive X-ray spectrometer. The chemical compositions of the pristine and heated metal foils were investigated by X-ray photoelectron spectroscopy (XPS) using an Mg and Al Kα X-ray source in a Sigma Probe (Thermo VG) spectrometer. The XPS spectra were curve fitted with a mixed Gaussian-Lorentzian shape using the XPSPEAK analysis software [10]. The Shirley function was used to remove the background prior to curve fitting. All of the XPS spectra were charge compensated to C 1s at 285.0 eV. The crystallinity of the pristine and heated metal foils was examined with an X-ray diffractometer (XRD, RIGAKU, D/MAX-2500).

3. Results and Discussion

3.1. Surface Morphology. The surfaces of the Ti, Nb, and Mo foils were observed using FESEM. The surface of the pristine Ti foil appeared slightly rough, as shown in Figure 1(a). When the heating time of the Ti foil in the liquid Ga was increased, the amount of material adhered to the Ti foil was monotonically increased (Figures 1(b)–1(f)). The material that adhered to the surface of Ti foil was in the form of both nanoparticles with a size of several hundred nm

(a) Pristine (b) 1 day (c) 3 days

(d) 5 days (e) 9 days (f) 14 days

Figure 2: FESEM images of pristine Nb foil (a) and Nb foils heated in liquid Ga for 1 day (b), 3 days (c), 5 days (d), 9 days (e), and 14 days (f).

(a) Pristine (b) 1 day (c) 3 days

(d) 5 days (e) 9 days (f) 14 days

Figure 3: FESEM images of pristine Mo foil (a) and Mo foils heated in liquid Ga for 1 day (b), 3 days (c), 5 days (d), 9 days (e), and 14 days (f).

(see arrowed area in Figures 1(c) and 1(d)) and aggregates. Particularly, when the heating time was longer than nine days, lumps of aggregates with a size of several μm were easily observed on the Ti foil surface (see arrowed area in Figures 1(e) and 1(f)). In the case of the Nb foil, the amount of the adhered material also was monotonically increased as the heating time increased. However, the amount of material adhered to the Nb foils was significantly reduced compared with the Ti foils. When the heating time was increased up to three days, there was little material (in the form of either nanoparticles or aggregates) adhered to the Nb foil surface (Figures 2(a)–2(c)). After heating for more than five days, nanoparticles were found on the Nb foil surface, and the number of nanoparticles increased as the heating time was

(a) (b) (c)

Figure 4: EDS peaks of Ti (a), Nb (b), and Mo (c) foils heated in the liquid Ga.

(a) Ti

(b) Nb

(c) Mo

Figure 5: FESEM images and corresponding EDS mapping data of Ti (a), Nb (b), and Mo (c) foils heated in liquid Ga.

Figure 6: XRD peaks of Ti (a), Nb (b), and Mo (c) foils heated in liquid Ga.

increased, as shown in Figures 2(d) and 2(e). Aggregates were also observed when the heating time was increased to 14 days (see arrowed area in Figure 2(f)). In the case of the Mo foil, the amount of adhered material was monotonically increased as the heating time increased, similar to the case of Ti and Nb (Figure 3). The amount of the adhered material was relatively abundant compared with that of Nb. In addition, the adhesion material in this case appeared mainly in the form of micro/nanoparticles (see arrowed area in Figure 3(e)) while the adhesion material was mainly in the form of aggregates for the Ti foil.

3.2. EDS Analysis. To identify the materials that adhered on the metal foil surfaces, the samples were analyzed using EDS. The EDS peaks measured from the Ti, Nb, and Mo foils after heating in the liquid Ga are shown in Figure 4. All samples exhibited peaks of the elements that compose the pristine foils: Ga peaks with intensities much smaller than those of the former peaks (Ti, Nb, and Mo), and small oxygen (O) peaks that possibly originated from the metal foil surfaces that were oxidized naturally or via the heating process. In addition, elemental mapping of the Ti, Nb, and Mo foils heated in liquid Ga was performed. Figure 5 displays the FESEM images showing the attached Ga on the metal foil surfaces and the corresponding EDS elemental mapping data (green: metal foil, red: attached Ga). This result revealed that a relatively small amount of Ga was attached to the metal surfaces by heating in the liquid Ga. According to the result of the EDS element analysis, the proportion of Ga was only a few weight percent for the Mo and Nb foils while much larger amount of Ga was attached to the Ti foil (Table S1). The Nb foil showed the minimum adhesion of Ga while the Ti foil exhibited the maximum adhesion of Ga.

3.3. XRD and XPS Analysis. To clarify whether Ga was either physically attached or chemically bonded on the metal foil surfaces, XRD and XPS data were collected and analyzed. The XRD peaks measured from the Ti foil heated in liquid Ga are shown in Figure 6(a). The peaks were centered at 34.94°, 38.21°, 40.03°, 52.83°, 62.83°, 70.44°, 76.03°, and 77.32°, corresponding to the (100), (002), (101), (102), (110), (103), (112), and (201) planes of pure Ti, respectively. However, no XRD Ga peaks were found. This result indicates that heating in liquid Ga at 120°C for two weeks did not affect the Ti foils,

Figure 7: XPS survey spectra of Ti (a), Nb (b), and Mo (c) foils before and after heating in the liquid Ga.

and the amount of Ga that adhered to the Ti foils was too small to be detected by XRD. The Nb and Mo foils exhibited XRD peaks with the same behavior. For the Nb foil, the XRD peaks were centered at 38.44°, 55.59°, and 69.66°, corresponding to the (110), (200), and (211) planes of pure Nb, respectively (Figure 6(b)). Similarly, the XRD peaks of Mo were centered at 40.42°, 58.58°, 73.61°, and 87.59°, corresponding to the (110), (200), (211), and (220) planes of pure Mo (Figure 6(c)).

The chemical composition changes in the metal foil surfaces were investigated using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra of the Ti, Nb, and Mo foils heated in the liquid Ga are shown in Figure 7. All of the pristine metal foils exhibited their characteristic peaks, a C 1s peak that possibly resulted from a surface contaminant, and the O peaks that most likely resulted from a natural oxidation. However, all of the XPS peaks of Ti (such as the Ti 2s, 2p, and Auger peaks) disappeared while the Ga peaks (such as the 2p, 3s, and 3p peaks) appeared after heating in the liquid Ga (Figure 7(a)). The change in survey spectra of the Ti foil may result from the formation of a thin Ga layer (> a few nm) on the Ti foil surface after the heating in the liquid Ga because these XPS signals originate from the material surface at a depth of only a few nm [11, 12], while the conventional XRD is able to gather data at a depth of several μm from the material surface due to the difference in the energy of the X-ray radiation. In the case of the Nb and Mo foils, only the small 3d peaks of Nb and Mo remained, and the Ga peaks appeared after heating in the liquid Ga (Figures 7(b) and 7(c)). It appears that Ga layer which adhered to the Ti foils was relatively thicker than that of the Nb and Mo foils.

The Ga 2p peaks of the Ti, Nb, and Mo foils were all centered at ~1118 and ~1145 eV, corresponding, respectively, to the typical $2p_{3/2}$ and $2p_{1/2}$ peaks of pure Ga (see Figure S2). This result showed that the Ga is only physically attached

Figure 8: 3d peaks of pristine Nb foil (a), Nb foil heated in the liquid Ga (b), pristine Mo foil (c), and Mo foil heated in liquid Ga (d).

to the metal foil surfaces, with no evidence of any chemical bonding.

However, a chemical change in the metal foil surfaces was observed. For the Ti foil, further analysis could not be carried out because all of the Ti peaks disappeared after heating in the liquid Ga. Detailed analysis of 3d spectra was performed for Nb and Mo. As shown in Figure 8(a), the 3d peak of the pristine Nb could be deconvoluted into four peaks centered at 202.3, 205.1, 207.4, and 210.2 eV, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ peaks of pure Nb, and the $3d_{5/2}$ and $3d_{3/2}$ peaks of Nb_2O_5, respectively. This result means that the surface of the Nb foil consisted of pure Nb and its natural oxide. In contrast, the two peaks centered at 202.3 and 205.1 eV disappeared, and only two other peaks centered at 207.4 and 210.2 eV remained after the heating in the liquid Ga, which implies that the material was transformed into a fully oxidized surface (Figure 8(b)). On the other hand, the 3d peak of the pristine Mo could be deconvoluted into two peaks centered at 232.7 and 235.8 eV, respectively, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ peaks of MoO_3, which is one of the oxide forms of Mo (Figure 8(c)). Interestingly, the Mo foil surface appeared to be reduced after heating in liquid Ga. After heating in the liquid Ga, the shape of the Mo 3d peak became more complicated, as shown in Figure 8(d). The peak could be deconvoluted into six peaks including the former two peaks and peaks centered at 227.8, 229.3, 230.9, and 232.5 eV, corresponding to the $3d_{5/2}$ peak of pure Mo and MoO_2 and the $3d_{3/2}$ peaks of pure Mo and MoO_2, respectively. This result indicated that a portion of the Mo(VI) was reduced to Mo(0) or Mo(IV).

4. Conclusions

This work investigated the effect of liquid Ga on Ti, Nb, and Mo foils at temperatures higher than the melting point of Ga. After the metal foils were heated in the liquid Ga at 120°C, a small amount of Ga remained on the metal foil surfaces even after several washing steps. Among the metal

foils used in this study, the Nb foil showed the minimum adhesion of Ga while the Ti foil exhibited the maximum adhesion of Ga. From the perspective of separation of Ga from the metal foils, we can conclude that Nb is the most attractive material among the three tested. In contrast, from the perspective of the chemical composition change, the Nb foil surfaces appeared to be oxidized after heating in the liquid Ga while the Mo foil surfaces were reduced. In conclusion, the conventional Nb encapsulation material of Ga exhibited the least Ga adhesion, a superior property, but Mo also could be used as the encapsulation material for Ga due to its chemical resistance against oxidation during the heating, even though a relatively larger amount of Ga was observed to adhere to its surface compared with Nb.

Acknowledgment

This work was supported by the Nuclear R&D Program of the National Research Foundation (NRF) funded by the Ministry of Education, Science, and Technology (MEST), Republic of Korea.

References

[1] C. Naidoo, T. N. van der Walt, and H. G. Raubenheimer, "Cyclotron production of ^{68}Ge with a Ga_2O target," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 253, no. 2, pp. 221–225, 2002.

[2] P. J. Pao, D. J. Silvester, and S. L. Waters, "A new method for the preparation of ^{68}Ga-generators following proton bombardment of gallium oxide targets," *Journal of Radioanalytical Chemistry*, vol. 64, no. 1-2, pp. 267–272, 1981.

[3] C. Loc'h, B. Maziere, D. Comar, and R. Knipper, "A new preparation of germanium 68," *International Journal of Applied Radiation and Isotopes*, vol. 33, no. 4, pp. 267–270, 1982.

[4] G. E. Meinken, S. Kurczak, L. F. Mausner, K. L. Kolsky, and S. C. Srivastava, "Production of high specific activity ^{68}Ge at Brookhaven National Laboratory," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 263, no. 2, pp. 553–557, 2005.

[5] F. M. Noriter, M. E. Fassbender, M. Dejohn et al., "Targetry at the LANL 100 MeV isotope production facility: lessons learned from facility commissioning," in *Americas Nuclear Energy Symposium*, LA-UR-04-6421, October 2004.

[6] L. R. Kelman, W. D. Wilkinson, and F. L. Yaggee, "Resistance of materials to attack by liquid metals," Argonne National Laboratory Report ANL-4417, 1950.

[7] M. H. Kamdar, "Embrittlement by liquid metals," *Progress in Materials Science*, vol. 15, no. 4, pp. 289–374, 1973.

[8] M. S. Berridge, K. W. Voelker, and B. Bennington, "High-yield, low-pressure [^{18}O] water targets of titanium and niobium for F-18 production on MC-17 cyclotrons," *Applied Radiation and Isotopes*, vol. 57, no. 3, pp. 303–308, 2002.

[9] L. C. A. Sumiya and V. Sciani, "Evaluation of irradiation parameters of enriched ^{124}Xe target for ^{123}I production in cyclotrons," *Applied Radiation and Isotopes*, vol. 66, no. 10, pp. 1337–1340, 2008.

[10] R. W. M. Kwok, "XPS Peak Fitting Program for WIN95/98 XPSPEAK version 4.1," 2000.

[11] C. Y. Tang, Y. N. Kwon, and J. O. Leckie, "Probing the nano- and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements," *Journal of Membrane Science*, vol. 287, no. 1, pp. 146–156, 2007.

[12] B. Berini, N. Keller, Y. Dumont et al., "Reversible phase transformation of $LaNiO_{3-x}$ thin films studied in situ by spectroscopic ellipsometry," *Physical Review B*, vol. 76, no. 20, Article ID 205417, 9 pages, 2007.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 365947, 7 pages
http://dx.doi.org/10.1155/2013/365947

Research Article

Fabrication of Self-Standing Silver Nanoplate Arrays by Seed-Decorated Electrochemical Route and Their Structure-Induced Properties

Guangqiang Liu,[1] Guotao Duan,[1] Lichao Jia,[1] Jingjing Wang,[1] Hongzhi Wang,[2] Weiping Cai,[1] and Yue Li[2]

[1] *Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China*
[2] *Center of Medical Physics and Technology, Hefei Institute of Physical Science, Chinese Academy of Sciences, Hefei 230031, China*

Correspondence should be addressed to Guangqiang Liu; liugq@issp.ac.cn

Received 3 September 2012; Accepted 12 December 2012

Academic Editor: Bingqiang Cao

Copyright © 2013 Guangqiang Liu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We present an electrochemical route to synthesize silver nanoplates on seed-decorated Indium tin oxide (ITO) glass substrate. The nanoplates are several tens of to several hundred nanometers in dimension. The density of nanoplates covered on the substrate can be controlled well by adjusting the amounts of seed. All the nanoplates are standing on the substrate uniformly even at very high density. Silver nanoplate arrays displayed an extraordinary superhydrophobicity after chemical modification and can serve as highly active surface-enhanced Raman scattering (SERS) substrates for microdetection. The arrays can also be used as electrodes for electrochemical capacitor with high power density.

1. Introduction

Surface morphology and assembly behavior of nanostructured materials decide their performances; therefore, their investigations have attracted much interest in recent years originated from their widespread applications in optics, electronics, optoelectronics, information storage, self-cleaning, catalysis biological, chemical sensing, surface-enhanced Raman scattering (SERS) effect, and so forth [1–10]. Among these, SERS is a typical instance, which is mainly determined by the surface morphology and structure of noble metal materials [11]. It means a dramatic enhancement of intensity of the Raman spectra of the molecule absorbed on the surface of metal [12–17]. Some reports have revealed that sharp protrusion and nanogaps in highly roughed metallic surface, so called active "hot" spots, are responsible for SERS, because of larger electromagnetic enhancement caused by local surface plasma resonance at these sites [18, 19]. In addition, other properties, that is, self-cleaning surface, use as electrode for electrochemical capacitor, are also determined by the surface morphology [20–28]. Self-cleaning surface should have static contact angles (CA) of water droplets larger than 150° and the slid angle (SA) smaller than 10°, which can be prepared by a combination of reducing the surface energy and enhancing the surface roughness [29–34]. The self-cleaning performance can be widely used for preventing the adhesion of water or snow on the surface of some objects. In electrochemical capacitor, electrochemical reaction occurred at the interface between electrode and electrolyte, so a large electrochemical interface of electrode is favorable to the enhancement of the power density [35]. In whole, assembly of nanostructured material with high rough surface is the key factor in the above applications.

Previously, we reported a spin-coated Ag seed growth method to fabricate standing silver nanoplate arrays with high rough surfaces [36]. But through this method, the obtained silver nanoplates are not sufficiently tightly anchored on indium tin oxide (ITO) substrate. Additionally, these nanoplates are not uniform in size and distribution when we need nanoplate array with a more high distribution density covered on the substrate for some applications. The main reason is poor uniform distribution of Ag seeds

Figure 1: Schematic illustration of formation of nanoplate arrays: (a); a layer of 3-aminopropyltrimethoxysilane (APTMS) absorbed on clean ITO (b) Ag seeds decorated on clean ITO; (c) growth of Ag nanoplate arrays by electrochemical method.

with a high density by spin-coating method. In this paper, we report a simple electrochemical approach decorated by Ag seeds to synthesize silver nanoplates with controllable density (roughness) covered on the ITO substrate. The obtained silver nanoplates are covered on the substrate uniformly with very high density. The whole procedure was shown in Figure 1. Firstly, we decorated a layer of 3-aminopropyltrimethoxysilane (APTMS) on clean ITO (Figure 1(a)), and then this substrate was immersed into as-prepared Ag colloid solution for decorating Ag seeds on the substrate (Figure 1(b)), followed growth of Ag nanoplates by electrochemical deposition route on the substrate directly. The as-prepared silver nanoplate arrays demonstrated structured enhanced SERS activity and a good superhydrophobic property after chemical modification with *n*-dodecanethiol, which has important potential application in fluidic device, self-cleaning surfaces, organic molecule detection, and so forth. In addition, the arrays can also be used as electrode for electrochemical capacitor with high power density.

2. Experiment

2.1. Decorating Seeds. The details of preparing silver seeds have been reported previously [36]. Briefly, 60 mM $AgNO_3$ of 0.5 mL and 35 mM sodium citrate of 1 mL were added into 98 mL distilled water. The mixed solution was stirred for five minutes. Then, an aqueous 20 mM $NaBH_4$ solution of 0.5 mL, which had been aged at room temperature for 2 h, was added quickly, stirred for 1 h, and then aged at room temperature for 24 h before use. ITO substrates were ultrasonically cleaned in acetone and then in ethanol for 1 h. Cleaned ITO substrates were placed into a dilute solution of 3-aminopropyltrimethoxysilane (APTMS) (0.3 mL of APTMS in 3 mL of methanol) for 12 hours and rinsed with methanol to remove redundant APTMS. The polymer-coated substrate was immersed in above Ag seeds colloid solution for different time, 4 h, 8 h, and 10 h respectively. Then, the substrates were taken out and dried with high-purity flowing nitrogen.

2.2. Electrochemical Deposition. Silver nitrate ($AgNO_3$, 99+%), and poly(vinyl pyrrolidone) (PVP, MW = 30 000) were purchased from Shanghai Chemical Reagent Co. All chemicals were analytically graded and were used without further purification. Typically, 0.05 g $AgNO_3$ and 0.25 g PVP were added to 50 mL of water followed by stirring till complete dissolution. Such aqueous solution was used as electrolyte for electrodeposition. The electrochemical deposition was carried out under current density 5 μA/cm^2 at room temperature. A graphite flake was used as anode and the Ag seed-decorated ITO substrate as cathode. After deposition for about 5 h, the substrate with products was taken out, cleaned with distilled water for several times and dried with high-purity flowing nitrogen for characterization and property study.

2.3. Characterization. The as-prepared samples were characterized by X-ray diffraction (XRD) (Philips X$'$pert-PRO, Cu Kα (0.15418 nm) radiation), field emission scanning electronic microscope (FESEM, sirion 200 FEG).

Before contact angle (CA) measurement, the substrate was immersed in ethanol solution of *n*-dodecanethiol (1×10^{-3} M) for about 10 h and washed in turn with ethanol and water and dried with nitrogen to coat a self-assembled monolayer of low free energy materials. Distilled water droplets with a volume of 5 μL were used in contact angle test.

For Raman spectral measurement, the samples were immersed in 4-aminothiophenol (4-ATP) solution with different concentration for 30 min, 10^{-6} mol/L, 10^{-8} mol/L, 10^{-10} mol/L, and 10^{-12} mol/L, respectively. After that, the substrates were taken out from the solution and rinsed with de-ionized water, and then dried with high-purity flowing nitrogen. The Raman spectra were recorded on a macroscopic confocal Raman spectrometer, using a laser beam with an excitation wavelength of 532 nm.

For electrochemical measurements, a typical three-electrode cell was employed. The electrolyte was 5 M KOH solution. An Hg/HgO electrode and a platinum electrode were used as the reference electrode and the counter electrode.

3. Results and Discussion

After electrodeposition on the ITO substrate coated with the Ag-seeds, the samples were characterized by XRD firstly, as shown in Figure 2(A) (curve (a), (b), (c) corresponding to samples obtained preimmersed Ag seeds colloid solution for 4 h, 8 h, 10 h), and the intensity of diffraction increase gradually with increasing immersing time. Four diffraction peaks (2θ) at 38.2, 44.3, 64.4, and 77.3° were observed, corresponding to the (111), (200), (220), and (311) of the face-centered cubic *(fcc)* structure of silver with space group *Fm3m* (JCPDS), respectively.

Figures 2(B)–2(D) display SEM image of as-prepared samples. We can see that these units are nanoplates with

Figure 2: XRD of the as-prepared sample with the polymer-coated substrate immersing in Ag seeds colloid solution for different time, 4 h (curve a), 8 h (curve b), and 10 h (curve c), respectively; FESEM images of the samples prepared with the polymer-coated substrate immersing in Ag seeds colloid solution for different time, 4 h (B), 8 h (C), 10 h (D).

the size in several tens to several hundred nanometers. Obviously, the densities of coverage of the nanoplates become dense with enlarging time of polymer-decorated ITO substrate into Ag colloid solution, and the density of coverage is about 7.2×10^7 plates/cm^2, 4.0×10^8 plates/cm^2, and 3.5×10^9 plates/cm^2, respectively. When the nanoplates are very dense, all nanoplates are standing on the ITO substrate uniformly and cross-linking together with each other, leading to a very rough surface (see Figure 2(D)), while some nanoplates are gathered together at high density fabricated by our previous method. But when the nanoplates are sparse, most of them are lying on the ITO substrate, and hence the surface roughness is low (Figure 2(B)). It demonstrates that we can also control the density of coverage of Ag nanoplates through decorating Ag seed layer method. That is, the roughness of the surface can be tuned.

4. The Application of Ag Nanoplate Arrays

4.1. Superhydrophobicity. The water droplet shapes on the surface of three samples (Figures 2(B)–2(D)) with different density is shown in Figure 3. The water CAs were 132°, 150° and 160° respectively, (Figures 3(a)–3(c)) and the SA is about 7° for nanoplates arrays with highest density (Figure 2(D)). It is obviously that surface roughness is directly related to the CA. With increasing of density of Ag nanoplates, the surface roughness is increasing, and the CA turned lager accordingly. The spherical water droplet (Figure 3(d)) also can further confirm the superhydrophobicity. We describe the CA in terms of the Cassie equation [37]:

$$\cos\theta_r = f_1 \cos\theta - f_2, \tag{1}$$

where θ_r and θ are the contact angles of a rough (textured) surface and a flat surface, respectively, f_1 and f_2 are the fractional interfacial areas of the Ag nanoplates arrays and the air interspaces among the Ag nanoplates arrays ($f_1 + f_2 = 1$). From this equation, it is easy to conclude that increasing the value of f_2 can increase CA. For a flat surface modified with the n-dodecanethiol, the CA is 108°, so f_2 is calculated to be 0.91. This means that the larger fraction of air (f_2) among the interspaces of standing Ag nanoplate arrays with higher density leads to superhydrophobicity of the surface. Another feature of a water-repellent surface from the dynamic viewpoint is a low sliding angle, which enables a water drop to easily roll down the surface. This means that these silver nanoplate arrays with a rough surface trap a large amount of air among nanoplate structures, leading to a very good superhydrophobicity with self-cleaning effect.

Figure 3: Photo images of water droplets on the surface of Ag nanoplates arrays with the polymer-coated substrate immersing in Ag seeds colloid solution for different time, 4 h (a), 8 h (b), and 10 h (c), respectively, and the water CAs were 132°, 150°, and 160°; (d) photograph of (c).

4.2. Surface-Enhanced Raman Scattering Effect. We use these three samples with different density of Ag nanoplates covered as substrates to study the SERS activity, as shown in Figure 4 corresponding to the Raman spectra of 4-ATP molecular (after immersion in 10^{-6} mol/L 4-ATP solution for 10 min). We can find the SERS activity raises with increase of the distribution density of Ag nanoplates arrays (integrating time 1 s). In order to further probe into the detection limit of SERS property of the substrate with highest density Ag nanoplate arrays (shown in Figure 2(D)), three different concentrations (10^{-8} M, 10^{-10} M, 10^{-12} M) of 4-ATP were examined. The Raman spectral intensity of 4-ATP turned weaker with decrease of the concentration of 4-ATP in a certain range (integrating time 1 s). But, even when the concentration of 4-ATP was decreased to 10^{-12} M, we still can distinguish Raman peaks of 4-ATP (see curve (c) in Figure 5). This evidence indicated that this rough surface built with Ag nanoplates arrays had an excellent SERS performance. We attribute this enhancement to the many protrusions of standing Ag nanoplates and interstitials or nanogaps is formed among these nanoplates, which provide many hot "spots" for SERS [38, 39]. Obviously, with increasing the density of Ag nanoplates, the "hot spots" increase correspondingly.

Figure 4: Raman spectra of the 4-ATP on different surface of Ag nanoplates arrays (Figure 2(D)) with the polymer-coated substrate immersing in Ag seeds colloid solution for different time, 4 h (a), 8 h (b), 10 h (c), respectively.

4.3. Electrochemical Properties of Silver Nanoplates Arrays. The cyclic voltammetry at different scan rate using silver nanoplates arrays with high density (Figure 2(D)) as electrode in 5 M KOH solution was shown in Figure 6. It can be noted that the shape of CV curves have no change and the redox peak is at the same position with different scan rates, which illustrate that the silver nanoplates electrodes has a good reversibility. Figure 7 shows the charge and discharge curve. After 25 cycles, the efficiency of charge/discharge

Figure 5: Raman spectra of the 4-ATP on the surface of Ag nanoplates arrays (Figure 2(D)) after immersed different concentration of 4-ATP solution for 30 min, (a) 10^{-8} M, (b) 10^{-10} M, and (c) 10^{-12} M.

Figure 6: The cyclic voltammetry at different scan rate with silver nanoplates arrays (Figure 2(D)) as electrode in 5 M KOH solution.

is not dropped, which exhibits that the silver nanoplates arrays have high stability using as electrode. In addition, the specific capacitance values can be calculated according to the following equation:

$$C_m = I \times \frac{t}{\Delta V \times m}. \quad (2)$$

Here, C_m is specific capacitance, I is charge/discharge current, t is the discharge time within the voltage difference (ΔV), and m is the mass of silver nanoplates. From Figure 7, we can calculate that the specific capacitance is 1270 F g^{-1}. This value is higher compared with other similar electrode [35]. We think that the increase in specific capacitance origins from high touching surface of standing Ag nanoplates with KOH solution.

Figure 7: The charge and discharge curve using Ag nanoplates arrays (Figure 2(D)) as electrode. After 25 cycles, the efficiency of charge/discharge is not dropped.

5. Conclusion

In summary, we prepared Ag nanoplates on ITO substrate by a seed-decorated electrochemical deposition approach. The density of Ag nanoplates can be controlled through the amount of Ag seed predecorated. The Ag nanoplates arrays with highest density can be dispersed uniformly on the substrate, which had high roughened surface and displayed an extraordinary superhydrophobicity after a chemical modification. Such Ag nanostructured array shows high SERS activity and hence is a good material for the microdetection device based on SERS effect. In addition, the Ag nanoplates arrays can be used as electrode for electrochemical capacitor with high power density.

Acknowledgments

The authors acknowledge the financial supports from Natural Science Foundation of China (Grants no. 51101149, 10974203, and 50831005); Anhui Provincial Natural Science Funds for Distinguished Young Scholar (Grant no. 1108085J20), and the National Basic Research Program of China (973 Program, Grant no. 2011CB302103).

References

[1] W. Fritzsche and T. A. Taton, "Metal nanoparticles as labels for heterogeneous, chip-based DNA detection," *Nanotechnology*, vol. 14, no. 12, pp. R63–R73, 2003.

[2] N. R. Jana, L. Gearheart, S. O. Obare, and C. J. Murphy, "Anisotropic chemical reactivity of gold spheroids and nanorods," *Langmuir*, vol. 18, no. 3, pp. 922–927, 2002.

[3] C. Salzemann, I. Lisiecki, A. Brioude, J. Urban, and M. P. Pileni, "Collections of copper nanocrystals characterized by

different sizes and shapes: optical response of these nanoobjects," *The Journal of Physical Chemistry B*, vol. 108, no. 35, pp. 13242–13248, 2004.

[4] S. H. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, "Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices," *Science*, vol. 287, no. 5460, pp. 1989–1992, 2000.

[5] N. I. Kovtyukhova and T. E. Mallouk, "Nanowires as building blocks for self-assembling logic and memory circuits," *Chemistry*, vol. 8, pp. 4354–4363, 2002.

[6] A. Tao, P. Sinsermsuksakul, and P. D. Yang, "Polyhedral silver nanocrystals with distinct scattering signatures," *Angewandte Chemie—International Edition*, vol. 45, no. 28, pp. 4597–4601, 2006.

[7] S. Habouti, M. Mátéfi-Tempfli, C.-H. Solterbeck, M. Es-Souni, S. Mátéfi-Tempfli, and M. M Es-Souni, "On-substrate, self-standing Au-nanorod arrays showing morphology controlled properties," *Nano Today*, vol. 6, no. 1, pp. 12–19, 2011.

[8] F. Xia and L. Jiang, "Bio-inspired, smart, multiscale interfacial materials," *Advanced Materials*, vol. 20, no. 15, pp. 2482–2858, 2008.

[9] S. K. Yang, W. P. Cai, G. Q. Liu, and H. B. Zeng, "From nanoparticles to nanoplates: preferential oriented connection of Ag colloids during electrophoretic deposition," *The Journal of Physical Chemistry C*, vol. 113, no. 18, pp. 7692–7696, 2009.

[10] S. K. Yang, W. P. Cai, L. C. Kong, and Y. Lei, "Surface nanometer-scale patterning in realizing large-scale ordered arrays of metallic nanoshells with well-defined structures and controllable properties," *Advanced Functional Materials*, vol. 20, no. 15, pp. 2527–2533, 2010.

[11] J. F. Li, Y. F. Huang, Y. Ding et al., "Shell-isolated nanoparticle-enhanced Raman spectroscopy," *Nature*, vol. 464, no. 7287, pp. 392–395, 2010.

[12] A. Tao, F. Kim, C. Hess et al., "Langmuir-Blodgett silver nanowire monolayers for molecular sensing using surface-enhanced Raman spectroscopy," *Nano Letters*, vol. 3, no. 9, pp. 1229–1233, 2003.

[13] Y. Xiong, J. M. McLellan, J. Chen, Y. Yin, Z. Y. Li, and Y. J. Xia, "Kinetically controlled synthesis of triangular and hexagonal nanoplates of palladium and their SPR/SERS properties," *Journal of the American Chemical Society*, vol. 127, no. 48, pp. 17118–17127, 2005.

[14] F. Yan, M. B. Wabuyele, G. D. Griffin, A. A. Vass, and T. Vo-Dinh, "Surface-enhanced Raman scattering detection of chemical and biological agent simulants," *IEEE Sensors Journal*, vol. 5, no. 4, pp. 665–670, 2005.

[15] D. A. Stuart, K. B. Biggs, and R. P. van Duyne, "Surface-enhanced Raman spectroscopy of half-mustard agent," *Analyst*, vol. 131, no. 4, pp. 568–572, 2006.

[16] G. T. Duan, W. P. Cai, Y. Y. Luo, Y. Li, and Y. Lei, "Hierarchical surface rough ordered Au particle arrays and their surface enhanced Raman scattering," *Applied Physics Letters*, vol. 89, no. 18, Article ID 181918, 3 pages, 2006.

[17] G. T. Duan, W. P. Cai, Y. Y. Luo, Y. Li, and Y. Lei, "Electrochemically induced flowerlike gold nanoarchitectures and their strong surface-enhanced Raman scattering effect," *Applied Physics Letters*, vol. 89, no. 21, Article ID 211905, 3 pages, 2006.

[18] S. M. Nie and S. R. Emory, "Probing single molecules and single nanoparticles by surface-enhanced Raman scattering," *Science*, vol. 275, no. 5303, pp. 1102–1106, 1997.

[19] J. Jiang, K. Bosnick, M. Maillard, and L. Brus, "Single molecule Raman spectroscopy at the junctions of large Ag nanocrystals," *The Journal of Physical Chemistry B*, vol. 107, no. 37, pp. 9964–9972, 2003.

[20] S. T. Wang, Y. L. Song, and L. Jiang, "Photoresponsive surfaces with controllable wettability," *Journal of Photochemistry and Photobiology C*, vol. 8, no. 1, pp. 18–29, 2007.

[21] X. Yao, Y. L. Song, and L. Jiang, "Applications of bio-inspired special wettablesurfaces," *Advanced Materials*, vol. 23, no. 6, pp. 719–734, 2011.

[22] K. S. Liu, X. Yao, and L. Jiang, "Recent developments in bio-inspired special wettability," *Chemical Society Reviews*, vol. 39, pp. 3240–3255, 2010.

[23] N. J. Shirtcliffe, G. McHale, S. Atherton, and M. I. Newton, "An introduction to superhydrophobicity," *Advances in Colloid and Interface Science*, vol. 161, no. 1-2, pp. 124–138, 2010.

[24] Z. Guo, W. Liu, and B.-L. Su, "Superhydrophobic surfaces: from natural to biomimetic to functional," *Journal of Colloid and Interface Science*, vol. 353, no. 2, pp. 335–355, 2011.

[25] Y. Li, C. C. Li, S. O. Cho, G. T. Duan, and W. P. Cai, "Silver hierarchical bowl-like array: synthesis, superhydrophobicity, and optical properties," *Langmuir*, vol. 23, no. 19, pp. 9802–9807, 2007.

[26] Y. Li, W. P. Cai, B. Q. Cao et al., "Two-dimensional hierarchical porous silica film and its tunable superhydrophobicity," *Nanotechnology*, vol. 17, no. 1, pp. 238–243, 2006.

[27] Y. Li, W. P. Cai, B. Q. Cao et al., "Superhydrophobicity of 2D ZnO ordered pore arrays formed by solution-dipping template method," *Journal of Colloid and Interface Science*, vol. 287, no. 2, pp. 634–639, 2005.

[28] V. Gupta and N. Miura, "Electrochemically deposited polyaniline nanowire's network a high-performance electrode material for redox supercapacitor," *Electrochemical and Solid-State Letters*, vol. 8, no. 12, pp. A630–A632, 2005.

[29] T. L. Sun, L. Feng, X. F. Gao, and L. Jiang, "Bioinspired surfaces with special wettability," *Accounts of Chemical Research*, vol. 38, no. 8, pp. 644–652, 2005.

[30] X. yao, Q. W. Chen, L. Xu et al., "Bioinspired ribbed nanoneedles with robust superhydrophobicity," *Advanced Functional Materials*, vol. 20, no. 4, pp. 656–662, 2010.

[31] F. Shi, Y. Y. Song, J. Niu, X. H. Xia, Z. Q. Wang, and X. Zhang, "Facile method to fabricate a large-scale superhydrophobic surface by galvanic cell reaction," *Chemistry of Materials*, vol. 18, no. 5, pp. 1365–1368, 2006.

[32] F. Shi, Z. Q. Wang, and X. Zhang, "Combining a layer-by-layer assembling technique with electrochemical deposition of gold aggregates to mimic the legs of water striders," *Advanced Materials*, vol. 17, no. 8, pp. 1005–1009, 2005.

[33] Y. Li, X. J. Huang, S. H. Heo et al., "Superhydrophobic bionic surfaces with hierarchical microsphere/SWCNT composite arrays," *Langmuir*, vol. 23, no. 4, pp. 2169–2174, 2007.

[34] Y. Li, E. J. Lee, and S. O. Cho, "Superhydrophobic coatings on curved surfaces featuring remarkable supporting force," *The Journal of Physical Chemistry C*, vol. 111, no. 40, pp. 14813–14817, 2007.

[35] Z. A. Hu, Y. X. Wang, Y. L. Xie, Y. Y. Yang, Z. Y. Zhang, and H. Y. Wu, "Ag nanowires and its application as electrode materials in electrochemical capacitor," *Journal of Applied Electrochemistry*, vol. 40, no. 2, pp. 341–344, 2010.

[36] G. Liu, W. Cai, L. Kong, G. Duan, and F. Lü, "Vertically cross-linking silver nanoplate arrays with controllable density based on seed-assisted electrochemical growth and their structurally enhanced SERS activity," *Journal of Materials Chemistry*, vol. 20, no. 4, pp. 767–772, 2010.

[37] A. B. D. Cassie and S. Baxter, "Wettability of porous surfaces," *Transactions of the Faraday Society*, vol. 40, pp. 546–551, 1944.

[38] H. H. Wang, C. Y. Liu, S. B. Wu et al., "Highly Raman-enhancing substrates based on silver nanoparticle arrays with tunable sub-10 nm gaps," *Advanced Materials*, vol. 18, pp. 491–495, 2006.

[39] S. J. Lee, A. R. Morrill, and M. Moskovits, "Hot spots in silver nanowire bundles for surface-enhanced Raman spectroscopy," *Journal of the American Chemical Society*, vol. 128, no. 7, pp. 2200–2201, 2006.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 802318, 7 pages
http://dx.doi.org/10.1155/2013/802318

Research Article

Visible Light Irradiation-Mediated Drug Elution Activity of Nitrogen-Doped TiO_2 Nanotubes

Seunghan Oh,[1] Kyung-Suk Moon,[1] Joo-Hee Moon,[2] Ji-Myung Bae,[1] and Sungho Jin[3]

[1] *Department of Dental Biomaterials and Institute of Biomaterial and Implant, College of Dentistry, Wonkwang University, Iksan, Jeonbuk 570-749, Republic of Korea*
[2] *Department of Dentistry, College of Dentistry, Wonkwang University, Iksan, Jeonbuk 570-749, Republic of Korea*
[3] *Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA*

Correspondence should be addressed to Seunghan Oh; shoh@wku.ac.kr and Sungho Jin; jin@ucsd.edu

Received 19 October 2012; Revised 23 December 2012; Accepted 24 December 2012

Academic Editor: Fengqiang Sun

Copyright © 2013 Seunghan Oh et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We have developed nitrogen-doped TiO_2 nanotubes showing photocatalytic activity in the visible light region and have investigated the triggered release of antibiotics from these nanotubes in response to remote visible light irradiation. Scanning electron microscopy (SEM) observations indicated that the structure of TiO_2 nanotubes was not destroyed on the conditions of 0.05 and 0.1 M diethanolamine treatment. The results of X-ray photoelectron spectroscopy (XPS) confirmed that nitrogen, in the forms of nitrite (NO_2^-) and nitrogen monoxide (NO), had been incorporated into the TiO_2 nanotube surface. A drug-release test revealed that the antibiotic-loaded TiO_2 nanotubes showed sustained and prolonged drug elution with the help of polylactic acid. Visible light irradiation tests showed that the antibiotic release from nitrogen-doped TiO_2 nanotubes was significantly higher than that from pure TiO_2 nanotubes ($P < 0.05$).

1. Introduction

Development of TiO_2 nanostructures has been a focus area in the fields of photocatalysis [1–3], solar cells [4], and biomedical applications [5–7]. TiO_2 is well known as a highly efficient photocatalyst and has been widely used for degrading organic pollutants for air purification and sterilization [8, 9]. However, the band gap of TiO_2 allows limited photocatalytic activity, which occurs solely in the narrow ranges of ultraviolet light. Many researchers have tried to develop visible light photocatalysts by modifying the structure of titanium dioxide. Metal doping is one of the typical modifications of TiO_2, and several kinds of metal elements, such as Cr, Co, Mo, Mn, and V, have been used to adjust the band gap of TiO_2 and promote its photocatalytic activity in the visible light range.

The unique advantages of TiO_2 nanostructures on Ti over microscale TiO_2 structures have been reported in the field of solar cells and biomaterials [10–15]. In addition, the morphology and crystallinity of TiO_2 nanotubes affect the adhesion, proliferation, and functionality of many types of cells [16–19]. For example, it is known that an array of TiO_2 nanotubes on Ti promotes osseointegration into animal bone *in vivo* [14, 20, 21].

Bacterial infection is one of the major reasons for the failure of orthopedic implants. An ideal solution to reduce bacterial infection is antibiotic drug therapy around 2 months after implant surgery. The delivery methods of antibiotics are generally systemic, intravenous, intramuscular, and topical. However, systemic antibiotic delivery is typically associated with certain side effects, including unwanted cytotoxicity. In recent years, various drug-delivery systems have been developed to facilitate drug effectiveness at the site of implantation [22, 23]. These drug-delivery devices release a proper dose of the drug at the site of action and thereby avoid undesirable side effects. However, these devices lack the ability to exert an on-off control over drug release. Consideration of release periods as well as the elution point of drugs is very important to reduce bacterial infection. Unwanted high doses of the drug lead to unavoidable toxic effects. Being able to trigger

the antibiotic release, for example, by using light stimulation, would be highly desirable to minimize complications and side effects for the orthopaedic implants. However, ultra violet (UV) light triggering TiO_2 photocatalytic activity is well known to be used for sterilization and to be harmful to mucous membrane in mouth. Therefore, the development of new TiO_2 showing photocatalytic activity at visible light region is required to minimize the side effect of UV light irradiation and promote the effect of remote-controlled drug release. In terms of the photocatalytic activity of TiO_2 nanotubes at visible light region, several studies reported that nitrogen or Fe-doped TiO_2 nanotubes showed excellent photocatalytic activity and degree of dye degradation compared to pure TiO_2 nanotubes by visible light irradiation [24–27].

In this study, we developed nitrogen-doped 100 nm TiO_2 nanotubes on Ti, performed surface analysis to examine the amounts and structure of nitrogen incorporated into Ti, and investigated the triggered release of antibiotic drug from nitrogen-doped TiO_2 nanotubes in response to remote visible light irradiation.

2. Materials and Methods

2.1. Fabrication of Nitrogen-Doped TiO_2 Nanotubes. As reported previously [28], a machined Ti sheet (0.2 mm thick, 99.5%; Hyundai Titanium Co., Republic of Korea) was electropolished by an electrochemical etching process and cleaned with acetone and deionized water. To prepare nitrogen-doped TiO_2 nanotube arrays on a Ti sheet, 0.05, 0.1, or 0.2 M diethanolamine (DEA; Sigma, MO, USA) was added into 0.5 w/v% hydrofluoric acid (48 w/v%; Merck, NJ, USA) in a mixture of water and acetic acid (98 w/v%; JT Baker, NJ, USA) in the volumetric ratio of 7 : 1. Anodization voltage and time were 20 V and 30 min, respectively.

Samples were then rinsed with deionized water, dried at 60°C for 24 h, and heat treated at 500°C for 2 h in an atmosphere of N_2. Morphological and surface analyses of nitrogen-doped TiO_2 nanotube arrays were performed by field emission scanning electron microscopy (FE-SEM, S4800; Hitachi/Horiba, Japan), transmission electron microscopy (TEM, Tecnai G2; FEI Co., USA, power: 300 kV), and X-ray photoelectron spectroscopy (XPS, K-Alpha ESKA system; Thermo, USA), respectively. Also, contact angle of experimental specimen was measured by contact angle meter (Theta Optical Tensiometer, KSV, Finland). The solvent of contact angle measurement was D.I. water.

2.2. Drug Release Test. Three antibacterial drugs, tetracycline (Sigma, MO, USA), cetylpyridinium chloride (CPC; Sigma, MO, USA), and chlorhexidine (Sigma, MO, USA), were mixed with polylactic acid (PLA; Sigma, MO, USA) and loaded into TiO_2 nanotubes. Tetracycline is an antibiotic drug that serves as a protein synthesis inhibitor. Chlorhexidine is a chemical antiseptic, while cetylpyridinium chloride is a strong bactericide. The amount of antibiotics released as a function of incubation time was measured by a microplate ELISA reader (Spectra Max 250; Thermo Electron Co., USA).

The amount of antibiotics released in response to visible right irradiation was also measured by the microplate ELISA reader. The source of visible light was a dental light curing unit (intensity, 1000 mW/cm^2; wavenumber of irradiated light, 470 nm; Elipar Free-Light 2; 3 M ESPE Co., USA).

2.3. Data Analysis. All data were expressed as mean ± standard deviation values and analyzed statistically by one-way ANOVA (SPSS 12.0; SPSS GmbH, Germany) and post hoc Duncan's multiple range test. Significant differences were considered if P values were less than 0.05.

3. Results and Discussion

As shown in Figures 1(a), 1(b), and 1(c), SEM images show the differences in appearance among N-doped 100 nm TiO_2 nanotubes with 0.05 M, 0.1 M, and 0.2 M of DEA. The micrographs of N-doped TiO_2 nanotubes show somewhat randomly organized nanotube geometry with different concentrations of DEA, in contrast to the SEM image of undoped TiO_2 nanotubes. However, the nanotubular structure was not formed on the Ti surface at a DEA concentration of 0.2 M. Therefore, we examined the characteristics of N-doped TiO_2 nanotubes at a DEA concentration of 0.1 M. TEM image (Figure 1(d)) of N-doped 100 nm TiO_2 nanotubes treated by 0.1 M DEA indicates that nanosized (100 nm thickness) porous layer was formed at top surface of TiO_2 nanotubes. High-magnification TEM image (Figure 1(e)) illustrates that the lattice spacing of newly formed layer is 0.35 nm, and this spacing is corresponding to the (101) planes of anatase TiO_2 as previously reported [29].

Figure 2 indicates X-ray diffraction (XRD) patterns of undoped and N-doped TiO_2 nanotubes. As shown, XRD mainly detected anatase TiO_2 and Ti crystalline phases. There was no dramatic difference in crystallinity between undoped and N-doped TiO_2 nanotubes after heat treatment. Therefore, we expect that DEA treatment had essentially no effect on the crystallinity of TiO_2 nanotubes in this study.

The XPS spectra of TiO_2 nanotubes and N-doped TiO_2 nanotubes are shown in Figure 3(a). In terms of pure TiO_2 nanotubes, Ti, O, and C elements were detected at 459.6, 531.2, and 285.5 eV, respectively. Among these elements, carbon is supposed to be contaminant deposited at the surface of TiO_2 nanotubes. The surfaces of N-doped TiO_2 nanotubes were composed of Ti, O, N, and C contaminants, and a very weak N signal was detected at the surface of N-doped TiO_2 nanotubes. The XPS analysis also resulted that the N amounts in undoped TiO_2 nanotubes and N-doped TiO_2 nanotubes were 0.57 and 3.39 atomic%, respectively. The atomic ratio of Ti to N of N-doped TiO_2 nanotubes was 5.13. As previously reported, the photocatalytic effect of N dopant was affected by both the N content of N-doped TiO_2 and the degree of nitrogen atoms reacting with TiO_2 precursor [30]. Therefore, N-doped TiO_2 nanotubes having high N amounts and the atomic ratio of Ti to N are supposed to result in enhanced photocatalytic activity by visible light irradiation.

Figure 1: SEM images of 100 nm TiO_2 nanotubes with (a) 0.05 M, (b) 0.1 M, and (c) 0.2 M of DEA treatment. (d) TEM and (e) high-magnification TEM images of 100 nm TiO_2 nanotubes with 0.1 M DEA treatment.

Top: 100 nm TiO_2 nanotubes
Bottom: N-doped 100 nm TiO_2 nanotubes

Figure 2: X-ray diffraction patterns of undoped and nitrogen-doped TiO_2 nanotubes treated by 0.1 M DEA.

Also, the N amount doped in TiO_2 structure is related to the intensity of photocatalytic activity at visible light region, and N amount is affected by the reaction temperature of dopant and TiO_2. Previous studies have reported 5–8 atomic% of nitrogen incorporation into the TiO_2 surface by chemical treatment and excellent photocatalytic activity in the visible light region [30–32]. These studies involved heat treatment of N-doped TiO_2 nanoparticles at temperatures of 800–900°C to maximize the concentration of nitrogen doping. However, we could not heat treat TiO_2 nanotubes above 500°C because heat treatment above 500°C resulted in the formation of rutile structure destroying the nanotubular structure of TiO_2. This limitation provides lower N amount of TiO_2 nanotubes compared to that of other TiO_2 nanoparticles. There are several researches obtaining highly N-doped TiO_2 nanomaterials without conventional sintering process. Xiang et al. developed nitrogen-, sulfur- or carbon- doped TiO_2 nanosheets with exposed (001) facets showing excellent photocatalytic activity at visible region by solvothermal process [29, 33, 34]. Also, solvothermal process is seemed to be one of the techniques enhancing N-doping into the structure of TiO_2 nanotubes without the destruction of nanotubular structure as previously reported [24, 26]. Further experiment is required to investigate the comparison of the photocatalytic activity between sintering process and solvothermal process for doping nitrogen into TiO_2 nanotubes.

The N 1s peaks were detected at the surface of N-doped TiO_2 nanotubes at 406.1 and 402.5 eV of binding energy, respectively (see Figure 3(b)). In terms of the location of nitrogen dopant in TiO_2 structure, many researches have reported that nitrogen species are doped into TiO_2 in different forms due to doping process, reaction technique, and nitrogen sources [24–27, 29, 33–38]. From the results of previous researches [35–37], typical N 1s peak of TiN species mainly in substitutional N was less than 397.5 eV, whilst interstitial N in TiN species showed above 400 eV of typical N 1s binding energy. From the results of XPS analysis, typical binding energies of 402.5 and 406.1 eV are assigned to NO and NO_2^- generating highest localized state for interstitial species, which are characteristics of interstitial N-doped TiO_2

Figure 3: (a) XPS spectra of TiO_2 nanotubes and N-doped TiO_2 nanotubes. (b) High resolution XPS spectra of N 1s for TiO_2 nanotubes and N-doped TiO_2 nanotubes.

Figure 4: (a) Cross-sectional views of water droplets on Ti, electropolished Ti, 100 nm TiO_2 nanotubes, and N-doped 100 nm TiO_2 nanotubes. (b) Graph showing water droplet contact angles at the surface of the nanotubes.

on the basis of previous studies [35–37, 39]. Thus, it is confirmed that nitrogen from DEA is effectively doped into TiO_2 nanotubes, and the N 1s peaks obtained from this study are assigned to interstitial N-doped TiO_2 nanotubes.

Figure 4(a) shows the cross-sectional views of water droplets on machined Ti, electropolished Ti, and undoped and N-doped TiO_2 nanotubes. Electropolishing did not change the hydrophilicity of Ti surface dramatically, but nitrogen doping did change the wettability of TiO_2 nanotubes by changing the hydrophilic surface to a super hydrophobic (>120°) surface. Therefore, we are investigating the effect of the super hydrophobicity of N-doped TiO_2 nanotubes on the behavior and functionality of human mesenchymal stem cells.

Presented in Figure 5 is the effect of PLA on the release behavior of antibacterial drugs such as tetracycline, CPC, and chlorhexidine. As shown in Figure 5(a), the experimental group with 10% tetracycline shows only an initial burst of drug release in the incubation period. However, all experimental groups with 1% PLA show sustained release of drugs as a function of incubation time. Therefore, we confirmed that 1% PLA could alter the elution behavior of all drugs and allow sustained and prolonged drug release regardless of the drug type.

Figure 6 shows the elution concentrations of the three antibacterial drugs loaded on the surface of undoped and N-doped TiO_2 nanotubes, respectively, after 30 seconds of visible light irradiation with the dental curing unit. In

Figure 5: The release amounts of antibacterial drugs as a function of incubation time. (a) 10% tetracycline mixed with/without 1% PLA. (b) 10% CPC and chlorhexidine mixed with 1% PLA.

Figure 6: (A) Dental light curing unit and visible light irradiation. (B) The concentration of drug released by visible light irradiation. (a) 10% Tetracycline, (b) 10% chlorhexidine, and (c) 10% CPC with 1% PLA.

the tetracycline and chlorhexidine elution tests, the release concentrations of drugs from N-doped TiO_2 nanotubes were significantly higher than those from undoped TiO_2 nanotubes ($P < 0.05$). However, the total amount of CPC released was much lower than the amounts of tetracycline and chlorhexidine, and there was no significant difference between CPC release from undoped and N-doped TiO_2 nanotubes.

On the basis of these results, we can summarize that nitrogen doping into the TiO_2 nanotubular structure was performed successfully by DEA treatment, even though the amount of nitrogen doping was lower than reported in other studies because of the lower heat treatment temperature used in this study. Moreover, drugs stored in N-doped TiO_2 nanotubes were released effectively by the visible light irradiation with the dental light curing unit.

4. Summary

The visible light irradiation-mediated drug elution activity of nitrogen-doped TiO_2 nanotubes has been investigated in this study. We found that nitrogen was effectively doped into the TiO_2 nanotubular structure, with the existence of NO_2^- (406.1 eV) detected by the XPS analysis playing an important role in the photocatalytic activity of TiO_2 in the visible light region. The results of the drug release test showed that PLA facilitated sustained and prolonged elution of drugs. We conclude that N-doped TiO_2 nanotubes are expected to overcome the limited usage of TiO_2, which shows photocatalytic activity only within the UV region, thereby allows the development of novel fusion technologies in the field of implant materials.

Conflict of Interests

The authors declare having no conflict of interests about all materials in this paper.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0024067). The authors also thank the Wonkwang University of Regional Innovation Center For Next Generation Industrial Radiation Technology for the use of FE-SEM and XRD.

References

[1] S. Liu and A. Chen, "Coadsorption of horseradish peroxidase with thionine on TiO_2 nanotubes for biosensing," *Langmuir*, vol. 21, no. 18, pp. 8409–8413, 2005.

[2] M. Paulose, K. Shankar, S. Yoriya et al., "Anodic growth of highly ordered TiO_2 nanotube arrays to 134 microm in length," *The Journal of Physical Chemistry B*, vol. 110, pp. 16179–16184, 2006.

[3] H. Zhang, P. Liu, X. Liu et al., "Fabrication of highly ordered TiO_2 nanorod/nanotube adjacent arrays for photoelectrochemical applications," *Langmuir*, vol. 26, no. 13, pp. 11226–11232, 2010.

[4] K. Shankar, G. K. Mor, H. E. Prakasam, O. K. Varghese, and C. A. Grimes, "Self-assembled hybrid polymer-TiO_2 nanotube array heterojunction solar cells," *Langmuir*, vol. 23, no. 24, pp. 12445–12449, 2007.

[5] M. Bigerelle, K. Anselme, B. Noël, I. Ruderman, P. Hardouin, and A. Iost, "Improvement in the morphology of Ti-based surfaces: a new process to increase *in vitro* human osteoblast response," *Biomaterials*, vol. 23, no. 7, pp. 1563–1577, 2002.

[6] B. D. Boyan, T. W. Hummert, D. D. Dean, and Z. Schwartz, "Role of material surfaces in regulating bone and cartilage cell response," *Biomaterials*, vol. 17, no. 2, pp. 137–146, 1996.

[7] C. G. Galbraith and M. P. Sheetz, "Forces on adhesive contacts affect cell function," *Current Opinion in Cell Biology*, vol. 10, no. 5, pp. 566–571, 1998.

[8] A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.

[9] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.

[10] C. S. Rustomji, C. J. Frandsen, S. Jin, and M. J. Tauber, "Dye-sensitized solar cell constructed with titanium mesh and 3-D array of TiO_2 nanotubes," *Journal of Physical Chemistry B*, vol. 114, no. 45, pp. 14537–14543, 2010.

[11] N. Wang, H. Li, W. Lü et al., "Effects of TiO_2 nanotubes with different diameters on gene expression and osseointegration of implants in minipigs," *Biomaterials*, vol. 32, no. 29, pp. 6900–6911, 2011.

[12] Y. T. Sul, "Electrochemical growth behavior, surface properties, and enhanced *in vivo* bone response of TiO_2 nanotubes on microstructured surfaces of blasted, screw-shaped titanium implants," *International Journal of Nanomedicine*, vol. 5, no. 1, pp. 87–100, 2010.

[13] L. Peng, A. D. Mendelsohn, T. J. LaTempa, S. Yoriya, C. A. Grimes, and T. A. Desai, "Long-Term small molecule and protein elution from TiO_2 nanotubes," *Nano Letters*, vol. 9, no. 5, pp. 1932–1936, 2009.

[14] C. Von Wilmowsky, S. Bauer, R. Lutz et al., "*In vivo* evaluation of anodic TiO_2 nanotubes; an experimental study in the pig," *Journal of Biomedical Materials Research—Part B*, vol. 89, no. 1, pp. 165–171, 2009.

[15] G. Balasundaram, C. Yao, and T. J. Webster, "TiO_2 nanotubes functionalized with regions of bone morphogenetic protein-2 increases osteoblast adhesion," *Journal of Biomedical Materials Research—Part A*, vol. 84, no. 2, pp. 447–453, 2008.

[16] K. S. Brammer, S. Oh, C. J. Cobb, L. M. Bjursten, H. V. D. Heyde, and S. Jin, "Improved bone-forming functionality on diameter-controlled TiO_2 nanotube surface," *Acta Biomaterialia*, vol. 5, no. 8, pp. 3215–3223, 2009.

[17] S. Oh, K. S. Brammer, Y. S. J. Li et al., "Stem cell fate dictated solely by altered nanotube dimension," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 106, no. 7, pp. 2130–2135, 2009.

[18] K. S. Brammer, S. Oh, J. O. Gallagher, and S. Jin, "Enhanced cellular mobility guided by TiO_2 nanotube surfaces," *Nano Letters*, vol. 8, no. 3, pp. 786–793, 2008.

[19] J. Park, S. Bauer, P. Schmuki, and K. Von Der Mark, "Narrow window in nanoscale dependent activation of endothelial cell growth and differentiation on TiO_2 nanotube surfaces," *Nano Letters*, vol. 9, no. 9, pp. 3157–3164, 2009.

[20] L. M. Bjursten, L. Rasmusson, S. Oh, G. C. Smith, K. S. Brammer, and S. Jin, "Titanium dioxide nanotubes enhance bone bonding *in vivo*," *Journal of Biomedical Materials Research—Part A*, vol. 92, no. 3, pp. 1218–1224, 2010.

[21] F. Zhang, Z. Zheng, Y. Chen, X. Liu, A. Chen, and Z. Jiang, "*in vivo* investigation of blood compatibility of titanium oxide films," *Journal of Biomedical Materials Research*, vol. 42, pp. 128–133, 1998.

[22] D. I. Axel, W. Kunert, C. Göggelmann et al., "Paclitaxel inhibits arterial smooth muscle cell proliferation and migration *in vitro* and *in vivo* using local drug delivery," *Circulation*, vol. 96, no. 2, pp. 636–645, 1997.

[23] G. Greenstein and A. Polson, "The role of local drug delivery in the management of periodontal diseases: a comprehensive review," *Journal of Periodontology*, vol. 69, no. 5, pp. 507–520, 1998.

[24] C.-C. Hu, T.-C. Hsu, and L.-H. Kao, "One-step cohydrothermal synthesis of nitrogen-doped titanium oxide nanotubes with enhanced visible light photocatalytic activity," *International Journal of Photoenergy*, vol. 2012, Article ID 391958, 9 pages, 2012.

[25] S. Li, S. Lin, J. Liao, N. Pan, D. Li, and J. Li, "Nitrogen-doped TiO_2 nanotube arrays with enhanced photoelectrochemical property," *International Journal of Photoenergy*, vol. 2012, Article ID 794207, 7 pages, 2012.

[26] J. Qian, G. Cui, M. Jing, J. Wang, M. Zhang, and J. Yang, "Hydrothermal synthesis of nitrogen-doped titanium dioxide and evaluation of its visible light photocatalytic activity," *International Journal of Photoenergy*, vol. 2012, Article ID 198497, 6 pages, 2012.

[27] Z. Xu and J. Yu, "Visible-light-induced photoelectrochemical behaviors of Fe-modified TiO_2 nanotube arrays," *Nanoscale*, vol. 3, pp. 3138–3144, 2011.

[28] S. Yeonmi and L. Seonghoon, "Self-organized regular arrays of anodic TiO_2 nanotubes," *Nano Letters*, vol. 8, no. 10, pp. 3171–3173, 2008.

[29] Q. Xiang, J. Yu, W. Wang, and M. Jaroniec, "Nitrogen self-doped nanosized TiO_2 sheets with exposed 001 facets for enhanced visible-light photocatalytic activity," *Chemical Communications*, vol. 47, no. 24, pp. 6906–6908, 2011.

[30] J. Ananpattarachai, P. Kajitvichyanukul, and S. Seraphin, "Visible light absorption ability and photocatalytic oxidation activity of various interstitial N-doped TiO_2 prepared from different nitrogen dopants," *Journal of Hazardous Materials*, vol. 168, no. 1, pp. 253–261, 2009.

[31] C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, "Enhanced nitrogen doping in TiO_2 nanoparticles," *Nano Letters*, vol. 3, no. 8, pp. 1049–1051, 2003.

[32] Y. Cong, J. Zhang, F. Chen, and M. Anpo, "Synthesis and characterization of nitrogen-doped TiO_2 nanophotocatalyst with high visible light activity," *Journal of Physical Chemistry C*, vol. 111, no. 19, pp. 6976–6982, 2007.

[33] Q. Xiang, J. Yu, and M. Jaroniec, "Nitrogen and sulfur co-doped TiO_2 nanosheets with exposed {001} facets: synthesis, characterization and visible-light photocatalytic activity," *Physical Chemistry Chemical Physics*, vol. 13, no. 11, pp. 4853–4861, 2011.

[34] J. Yu, G. Dai, Q. Xiang, and M. Jaroniec, "Fabrication and enhanced visible-light photocatalytic activity of carbon self-doped TiO_2 sheets with exposed 001 facets," *Journal of Materials Chemistry*, vol. 21, no. 4, pp. 1049–1057, 2011.

[35] H. Sun, Y. Bai, W. Jin, and N. Xu, "Visible-light-driven TiO_2 catalysts doped with low-concentration nitrogen species," *Solar Energy Materials and Solar Cells*, vol. 92, no. 1, pp. 76–83, 2008.

[36] S. Sakthivel and H. Kisch, "Photocatalytic and photoelectrochemical properties of nitrogen-doped titanium dioxide," *ChemPhysChem*, vol. 4, no. 5, pp. 487–490, 2003.

[37] Z. Wang, W. Cai, X. Hong, X. Zhao, F. Xu, and C. Cai, "Photocatalytic degradation of phenol in aqueous nitrogen-doped TiO_2 suspensions with various light sources," *Applied Catalysis B*, vol. 57, no. 3, pp. 223–231, 2005.

[38] J. Zhu, Z. Deng, F. Chen et al., "Hydrothermal doping method for preparation of Cr^{3+}-TiO_2 photocatalysts with concentration gradient distribution of Cr^{3+}," *Applied Catalysis B*, vol. 62, no. 3-4, pp. 329–335, 2006.

[39] N. C. Saha and H. G. Tompkins, "Titanium nitride oxidation chemistry: an X-Ray photoelectron spectroscopy study," *Journal of Applied Physics*, vol. 72, no. 7, pp. 3072–3079, 1992.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 263679, 6 pages
doi:10.1155/2012/263679

Research Article

Effect of Annealing on the Structure and Photoluminescence of Eu-Doped ZnO Nanorod Ordered Array Thin Films

Wen-Wu Zhong,[1] Da-Wei Guan,[2] Yue-Lin Liu,[3] Li Zhang,[1] Yan-Ping Liu,[1] Zhi-Gang Li,[1] and Wei-Ping Chen[1]

[1] *Department of Physics, Taizhou University, Taizhou 318000, China*
[2] *Department of Vessel Engineering, Wuhan Institute of Shipbuilding Technology, Wuhan 430050, China*
[3] *Department of Physics, Yantai University, Yantai 264005, China*

Correspondence should be addressed to Zhi-Gang Li, lizhigang@issp.ac.cn and Wei-Ping Chen, cwp@tzc.edu.cn

Received 18 October 2012; Accepted 7 December 2012

Academic Editor: Yue Li

Copyright © 2012 Wen-Wu Zhong et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Eu-doped ZnO nanorod ordered array thin films were synthesized on glass substrates with a ZnO seed layer via hydrothermal method. XRD reveals that the (002) diffraction peak of films annealed in hydrogen is sharper than that annealed in air. SEM reveals that the nanorods of films annealed in hydrogen are shortened and widened. TEM results demonstrate that the nanorods are single crystalline and the lattice spacing of 0.52 nm agrees with the *d* spacing of (001) crystal planes along *c*-axis. Room temperature photoluminescence (PL) reveals that the PL of films annealed in hydrogen is the strongest and shifts to lower wavenumber. The point defect of Eu-doped ZnO nanorod array thin film is transferred from O_i to O_{Zn} by annealing in hydrogen.

1. Introduction

Zinc oxide is an important member in the II–VI family with a wide band gap (3.37 eV) and a large excitonic binding energy (60 meV) [1–5]. Furthermore, ZnO is one of the environmental friendly materials, and the impurity-doped ZnO nanocrystals emitting visible light are expected to be appropriate materials for flat panel displays, florescence labels for biological imaging, and so on [6]. High quality II–VI semiconductor nanocrystals also become materials for doping of optically active impurities. The II–VI semiconductor nanocrystals doped with luminescence centers exhibit efficient luminescence even at room temperature [7–9].

Rare-earth ions are unique dopants, because they are optically and magnetically active in the semiconductor host crystals [10]. It is anticipated that in impurity-doped ZnO, strong interactions between the quantum-confined carriers and localized electrons on impurities will produce efficient photoluminescence (PL) [11, 12]. Eu is an attractive dopant for red emission in the range of 540–665 nm and the Eu-related luminescence lines are found to be a strong function of the structural quality and thermal cycling in the case of GaN [13].

In addition, nanorod thin films have some interesting properties. Among various synthesis methods, the hydrothermal method is attractive through which ZnO nanorods can be fabricated at low cost [14]. Despite various ZnO nanostructures that have been produced, few work has been executed on the synthesis of rod-like Eu-doped ZnO array thin films. In our work, via a low-temperature (70°C) hydrothermal synthesis, we present a nontoxic, large-scale, and low-cost method of preparing morphology-controlled Eu-doped nanorod ZnO array thin films on glass substrates with ZnO seed layer, and the effects of annealing atmosphere and Eu-doping on crystalline orientation and luminescence of the ZnO : Eu films are also investigated.

2. Experimental Details

2.1. Preparation of ZnO Seed Layer. The ZnO seed layer was prepared on glass substrates by the sol-gel spin-coating method. Zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was used as

Figure 1: X-ray diffraction patterns of the Eu-doped nanorod ZnO array thin films.

Figure 2: Secondary electronic microscopy micrographs of Eu-doped ZnO nanorod array thin films: (a) unannealed, (b) annealed in air, (c) annealed in hydrogen.

(a) (b) (c)

Figure 3: Low-resolution cross-sectional TEM image of the ZnO nanorods: (a) unannealed, (b) annealed in air, (c) annealed in hydrogen.

a basic chemical. Ethylene glycol monomethyl ether ($C_3H_8O_2$) and ethanolamine (C_2H_7NO) were used as solvent and stabilizer, respectively. The molar ratio of ethanolamine to zinc acetate was 1 : 1 and the concentration of the solution was 0.8 mol/L. The obtained mixture was stirred at 60°C for 4 h to yield a clear and homogeneous solution, which then served as the coating source after being cooled down to room temperature. The glass substrates were first cleaned in detergent, then in methanol and acetone using an ultrasonic cleaner, for 30 min each. Finally, the glass substrates were rinsed with deionized water and dried in oven. The coating solution was then dropped onto the glass substrate, which was rotated at 3000 rpm for 30 sec using KW-4A spin coater. After spin coating, the films were dried at 350°C for 20 min in a furnace to evaporate the solvent and remove organic residuals. This coating/drying procedure was repeated for three times before the films were inserted into a tube furnace and annealed at 550°C for 2 h in air.

2.2. Film Growth by Hydrothermal Method. At room temperature, diluted ammonia solution was dripped into the zinc nitrate solution under stirring, and requisite Eu_2O_3 was dissolved into dilute HNO_3. By mixing the above two solutions, we obtain one with Au-Zn molar ratio of 1 : 50, in which zinc nitrate was 0.54 g and the volume of solution was 40 mL. The glass substrates with the seed layer were immersed into the teflon lined stainless steel autoclaves filled with the resultant solution, and then the sealed vessels were put in the oven for heating at 70°C for 5 h. The grown films were rinsed with deionized water and dried in the air.

2.3. Characterization. The crystal graphic interpretations were performed on an X'Pert Pro XRD system with X-ray Mirror PFX at an operation voltage of 40 kV and a current of 40 mA, in which Cu Kα (λ = 0.154059 nm) was used and scanned in a 2θ range from 15° to 80°. Surface morphology and thickness of the film were studied via an FEI-SIRION

Figure 4: High-resolution TEM image of the ZnO array thin films together with the corresponding SAED pattern (inset): (a) unannealed, (b) annealed in air, (c) annealed in hydrogen.

scanning electron microscope (SEM). Transmission electron microscope (TEM) micrographs and selected-area electron diffraction (SAED) patterns were obtained on a PHILIPS-CM200 and JEM-2010 type TEM. The PL spectra were recorded from 330 to 800 nm at room temperature by a 325 nm excitation from Xe lamp (F-4500 Fluorescence Spectrophotometer).

3. Results and Discussion

3.1. Structure and Surface Morphology. Figure 1 shows the XRD patterns of the samples deposited on glass substrate with ZnO seed layer by hydrothermal synthesis under different annealing atmosphere. All the diffraction peaks can be indexed to a hexagonal wurtzite ZnO structure (a = 0.325 nm, c = 0.521 nm) and no peaks are detected from any impurities. The (002) reflection sharps up distinctly, indicating the c-axis of ZnO nanocrystals is oriented perpendicular to the plane of the ZnO seed layer. It can be also seen that the (002) diffraction peak is the strongest when the film is not annealed, and that which annealed in hydrogen is the second, while that annealed in air is the last. These results indicate that the prepared ZnO using the present method is highly crystallized.

Furthermore, in our experimental condition, a novel one-dimensional nanorod array thin film of ZnO was synthesized. The SEM micrographs of Eu doped ZnO nanorod array thin films are shown in Figure 2, in which Figures 2(a), 2(b), and 2(c) represent unannealed, annealed in air, and annealed in hydrogen of samples, respectively. From these pictures, it can be seen that nanorods are grown vertically oriented with seed layer. Notably, when the films were

Figure 5: PL spectra of Eu-doped ZnO nanorod array thin films.

annealed in hydrogen, the nanorods become shorter and wider. In addition, the typical EDS pattern of the nanorod indicates that the film consists of Zn, O, and Eu, and the molar ratio of Zn, O, and Eu is 48 : 0.4 : 51.6. The results reveal that the Eu atom might be doped into the nanorod in the form of substitution.

To characterize the crystallinity of the ZnO nanorods by TEM, we remove the products from the seed layer by ultrasonication in the ethanol. Figure 3 displays the TEM images of Eu doped ZnO nanorod array thin films. Among them, Figures 3(a), 3(b), and 3(c) denote the samples which are unannealed, annealed in air, and annealed in hydrogen, respectively. Those figures show that ZnO nanorods are straightforward with nonuniform diameter along their axis, and the ZnO nanorods are the widest when the films were annealed in hydrogen.

In Figure 4, we display the high-resolution TEM images and the corresponding SAED pattern of Eu doped ZnO nanorod array thin films. In a similar way, Figures 4(a), 4(b), and 4(c) denote the samples which are unannealed, annealed in air, and annealed in hydrogen, respectively. Those images further confirm that the nanorods are single crystalline and the obtained lattice spacing of 0.52 nm agrees with the d spacing of (001) crystal planes along c-axis, which is also supported by SAED patterns (inset in Figure 4).

3.2. PL Spectra. Figure 5 shows the PL spectra of the Eu-doped ZnO nanorod array thin films. We detected that the unannealed films have emission at 400, and 560 nm, the films annealed in air have emission at 400 nm, and the films annealed in hydrogen have emission at 390, and 520 nm. Furthermore, the figure confirms that the PL of films annealed in hydrogen is the strongest and shifts to lower wavenumber. Srikant and Clarke assigned the UV emission at ~395 nm to a shallow donor [15], and the nature of the shallow donor might be the complex defect of Zn_i [16]. The peak at ~520 nm remains controversial and is more preferably attributed to O_{Zn} [17, 18]. The origin of yellow and orange luminescence (>540 nm) is ascribed to O_i [19]. The above analysis verifies our assumption that the films unannealed have point defect O_i, and the films annealed in hydrogen have point defect O_{Zn}. In a word, the point defect of Eu-doped ZnO nanorod array thin film is transferred from O_i to O_{Zn} by annealing in hydrogen.

4. Conclusions

In summary, we present the fabrication of the Eu-doped ZnO nanorod ordered array thin films via hydrothermal method. Test results demonstrate that the (002) diffraction peak of films annealed in hydrogen is sharper than that annealed in air, and the nanorods of films annealed in hydrogen become shorter and wider. TEM results further demonstrate that the nanorods are single crystalline and the obtained lattice spacing of 0.52 nm agrees with the d spacing of (001) crystal planes along c-axis. Room temperature photoluminescence reveals that the PL of films annealed in hydrogen is the strongest and shifts to lower wavenumber. The point defect of Eu-doped ZnO nanorod array thin film is transferred from O_i to O_{Zn} by annealing in hydrogen.

Acknowledgments

The authors gratefully acknowledge the financial support of the project by National Natural Science Foundation of China (Grant nos. 51001078 and 51202155) and Zhejiang Provincial Natural Science Foundation of China (Grant nos. Y4110207 and Y4110547).

References

[1] B. Cao, Y. Li, G. Duan, and W. Cai, "Growth of ZnO nanoneedle arrays with strong ultraviolet emissions by an electrochemical deposition method," *Crystal Growth and Design*, vol. 6, no. 5, pp. 1091–1095, 2006.

[2] B. Cao, X. Teng, S. H. Heo et al., "Different ZnO nanostructures fabricated by a seed-layer assisted electrochemical route and their photoluminescence and field emission properties," *Journal of Physical Chemistry C*, vol. 111, no. 6, pp. 2470–2476, 2007.

[3] M. Kashif, U. Hashim, M. E. Ali et al., "Effect of different seed solutions on the morphology and electrooptical properties of ZnO nanorods," *Journal of Nanomaterials*, vol. 2012, Article ID 452407, 6 pages, 2012.

[4] L. Zhang, Y. K. Takahashi, A. Perumal, and K. Hono, "$L1_0$-ordered high coercivity (FePt)AgC granular thin films for perpendicular recording," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 18, pp. 2658–2664, 2010.

[5] Z. G. Li, Y. P. Liu, P. S. Liu, W. P. Chen, S. S. Feng, and W. W. Zhong, "Fabrication and morphology dependent magnetic properties of cobalt nanoarrays via template-assisted electrodeposition," *RSC Advances*, vol. 2, p. 3447, 2012.

[6] A. Ishizumi, Y. Takahashi, A. Yamamoto, and Y. Kanemitsu, "Fabrication and optical properties of Eu3+-doped ZnO nanospheres and nanorods," *Materials Science and Engineering B*, vol. 146, no. 1–3, pp. 212–215, 2008.

[7] A. Ishizumi, Y. Taguchi, A. Yamamoto, and Y. Kanemitsu, "Luminescence properties of ZnO and Eu^{3+}-doped ZnO nanorods," *Thin Solid Films*, vol. 486, no. 1-2, pp. 50–52, 2005.

[8] H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, and W. Cai, "Blue luminescence of ZnO nanoparticles based on non-equilibrium processes: defect origins and emission controls," *Advanced Functional Materials*, vol. 20, no. 4, pp. 561–572, 2010.

[9] H. Zeng, C. Zhi, Z. Zhang et al., ""White graphenes": boron nitride nanoribbons via boron nitride nanotube unwrapping," *Nano Letters*, vol. 10, no. 12, pp. 5049–5055, 2010.

[10] S. Taguchi, A. Ishizumi, T. Tayagaki, and Y. Kanemitsu, "Mn-Mn couplings in Mn-doped CdS nanocrystals studied by magnetic circular dichroism spectroscopy," *Applied Physics Letters*, vol. 94, no. 17, Article ID 173101, 2009.

[11] A. Ishizumi and Y. Kanemitsu, "Blinking behavior of surface-defect and impurity luminescence in nondoped and Mn2+-doped CdS nanocrystals," *Journal of the Physical Society of Japan*, vol. 78, no. 8, Article ID 083705, 2009.

[12] S. Taguchi, A. Ishizumi, and Y. Kanemitsu, "Multicarrier recombination and energy transfer in Mn-doped CdS nanocrystals studied by femtosecond pump-probe spectroscopy," *Journal of the Physical Society of Japan*, vol. 79, Article ID 063710, 2010.

[13] J. Shi, M. V. S. Chandrashekhar, J. Reiherzer et al., "Effect of growth temperature on Eu incorporation in GaN powders," *Journal of Crystal Growth*, vol. 310, no. 2, pp. 452–456, 2008.

[14] P. Suresh Kumar, P. Paik, A. Dhayal Raj et al., "Biodegradability study and pH influence on growth and orientation of ZnO nanorods via aqueous solution process," *Applied Surface Science*, vol. 258, no. 18, pp. 6765–6771, 2012.

[15] V. Srikant and D. R. Clarke, "On the optical band gap of zinc oxide," *Journal of Applied Physics*, vol. 83, no. 10, pp. 5447–5451, 1998.

[16] D. C. Look, J. W. Hemsky, and J. R. Sizelove, "Residual native shallow donor in ZnO," *Physical Review Letters*, vol. 82, no. 12, pp. 2552–2555, 1999.

[17] N. Han, P. Hu, A. Zuo, D. Zhang, Y. Tian, and Y. Chen, "Photoluminescence investigation on the gas sensing property of ZnO nanorods prepared by plasma-enhanced CVD method," *Sensors and Actuators B: Chemical*, vol. 145, no. 1, pp. 114–119, 2010.

[18] C. H. Tsai, W. C. Wang, F. L. Jenq, C. C. Liu, C. I. Hung, and M. P. Houng, "Surface modification of ZnO film by hydrogen peroxide solution," *Journal of Applied Physics*, vol. 104, no. 5, Article ID 053521, 2008.

[19] S. A. Studenikin, N. Golego, and M. Cocivera, "Fabrication of green and orange photoluminescent, undoped ZnO films using spray pyrolysis," *Journal of Applied Physics*, vol. 84, no. 4, pp. 2287–2294, 1998.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 854602, 6 pages
doi:10.1155/2012/854602

Research Article

Small-Sized Flat-Tip CNT Emitters for Miniaturized X-Ray Tubes

Hyun Jin Kim,[1] Jun Mok Ha,[1] Sung Hwan Heo,[2] and Sung Oh Cho[1]

[1] *Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea*
[2] *Particla Co. Ltd., Daejeon 305-701, Republic of Korea*

Correspondence should be addressed to Sung Oh Cho, socho@kaist.ac.kr

Received 18 October 2012; Accepted 7 December 2012

Academic Editor: Yue Li

Copyright © 2012 Hyun Jin Kim et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Small tip-type CNT emitters with the diameter of 0.8 mm were fabricated for miniaturized X-ray tubes. The CNT emitters were prepared by dropping CNTs and silver nanoparticles on a flat surface of a W metal tip followed by annealing at 800°C for 2 h under vacuum. The CNT emitters exhibit good field emission properties with the threshold electric field of 1.15 V/μm and the field enhancement factor of 12,050. CNTs were well attached to a flat W tip surface without coating on the side plane of the tip, and thus beam divergence could be minimized. Consequently, a miniaturized X-ray tube with the inner diameter of 5 mm was successfully demonstrated using the tip-type CNT emitter.

Nanostructured materials are widely used for electron emitters because of their good field-emission properties [1–7]. Among them, carbon nanotubes (CNTs) are mostly used as electron emitters because of their excellent electron emission property, chemical inertness, and high electrical and thermal conductivity [8–11]. Recently, miniaturized X-ray tubes [12–17] are being developed based on CNT emitters for the applications to brachytherapy [12, 16, 17], a cavity-inserted X-ray imaging [15, 18], nondestructive X-ray radiography, and a compact X-ray spectrometer [13, 15]. The diameter of miniaturized X-ray tubes is generally less than 10 mm, and a thermionic cathode of which operating temperature should be normally higher than 1000°C can induce a serious heating of the small X-ray tube. High operating temperature of miniaturized X-ray tubes limits the applications of the tubes, for example, to brachytherapy. Consequently, a cooling device is required for the operation, but the cooling device increases the size of the miniaturized X-ray tube. In this sense, CNT emitters are proper electron sources because electrons are generated through field emission, and hence the cold emission process does not increase the temperature of the X-ray tube. In addition, CNT emitters are also promising electron emitters for microfocus X-ray tubes [19]. X-ray image quality based on a microfocus X-ray tube is determined by the electron beam size of the tube. Therefore, the diameter of an electron beam source should be very small for the applications to miniaturized X-ray tubes or microfocus X-ray tubes.

Tip-shaped CNT emitters where CNTs are coated on a metal tip with the diameter less than 1 mm can satisfy the requirements of an electron beam source for miniaturized X-ray tubes or microfocus X-ray tubes. A few methods have been developed to prepare such tip-shaped CNT emitters. For example, a sharp-tip CNT emitter where CNTs are coated on a sharp metal tip that is chemically etched was developed. CNTs can be coated on the sharp metal tips by chemical vapor deposition (CVD) [19–22] or electrophoresis [23]. However CNT tips fabricated by these methods have a serious weakness for a real application to X-ray tubes: weak adhesion between CNTs and the metal substrate. X-ray tubes are operated at high voltages, and electrical breakdown can occur during the operation. CNT emitters must withstand electrical breakdown for a stable operation, but the CNTs coated on a metal tip by CVD or electrophoresis tend to be easily detached when breakdown occurs [24–27]. In addition, sharp geometry also has some disadvantages for

Figure 1: (a) SEM image of a flat-tip CNT emitter with CNTs coated on the side plane of a W tip. (b) Trajectories of electrons emitted at different positions of a flat-tip emitter. (c) Characterization of the electron beam diameter at the anode position using the emitter shown in (a) and a phosphorous screen.

Figure 2: (a) Schematic diagram to display the fabrication process of a flat-tip CNT emitter. (b) Optical image of a CNT drop on a W tip surface. (c) SEM image of a fabricated flat-tip CNT emitter. Inset: the magnified SEM image of the surface of the emitter. (d) Characterization of the electron beam diameter at the anode position using the emitter shown in (c) and a phosphorous screen.

Figure 3: Current density-electric field profile of the fabricated flat-tip CNT emitter. The inset is the F-N plot of the tip.

Figure 4: Schematic diagram of the miniaturized X-ray tube.

the applications to miniaturized X-ray tubes or high-power X-ray tubes. Due to the sharp and inclined geometry, electron emission positions are different and furthermore an electron beam is diverged radially. As a result, the beam quality is not so good and a device to focus the electron beam is necessary. Furthermore, the number of useful CNTs on a sharp metal tip is limited and hence each CNT must emit a high electron current to get an enough high total beam current for the practical application to an X-ray tube. As a result, CNTs can be easily damaged by high joule heating, reducing the lifetime of the CNT emitters. To overcome these, we proposed a flat-tip CNT emitter, where CNTs were coated on a flat end surface of a metal wire with a small (<1 mm) diameter. The electric field at the surface of a sharp-tip emitter is radially outward, but the electric field at the surface of a flat-tip emitter is parallel to the beam axis. Moreover, the useful number of CNTs on a flat surface is higher than that on a sharp surface. Consequently, an electron beam with a smaller diameter and a higher beam current can be obtained.

One problem that must be solved in the flat-tip CNT emitters is to prepare uniform CNTs on a small metal tip. Particularly, CNTs tend to be attached to the side surface of a metal tip because of the small geometry of the metal tip, as shown in the field-emission scanning electron microscope (FESEM) image of Figure 1(a). These CNTs attached to the side surface also act as electron emitters but badly affect the operation of an X-ray tube. Figure 1(b) displays the trajectories of electrons emitted at different positions of a flat emitter. The calculated was carried out using the EGN2 code [28]. In the calculation, a diode type composed of a flat-tip cathode emitter, a focusing electrode, and an anode was employed. The diameter of the emitter is 0.8 mm, and the emitter is inserted inside a focusing electrode. If there is no focusing electrode, the electron beam that is produced from an emitter is dramatically diverged. The distance between the emitter and the anode is 13 mm, and the applied voltage between the emitter and the anode is 50 kV. As shown in Figure 1(b), electrons emitted from a flat surface of the tip do not spread so much (electrons ① and ② in Figure 1(b)). An electron generated from the outermost position of a flat surface (electron ②, 0.4 mm far from the center of the tip) reaches the anode by 1.36 mm apart from the center. On the other hand, the electrons generated from the side surface of the tip diverge seriously even though a focusing electrode strongly prevents the divergence. An electron generated at 0.3 mm apart from the edge of the flat surface reaches the anode by 2.63 mm away from the center (electron ⑤). This was also experimentally verified. A diode gun as shown in Figure 1(a) was fabricated: a CNT tip emitter shown in Figure 1(a) was used for the electron emission. A phosphorous screen was installed at the anode position to measure the beam diameter at the anode position. Electrons were emitted from the CNT emitters through field emission and arrived at the phosphorous screen. The diameter of the electron beam at the phosphorous screen was ~5.5 mm. Due to the diverged electrons, the inner diameter of an X-ray tube cannot be reduced. An electrically insulating material should be used between the focusing electrode and the anode. An insulator with a smaller diameter must be used for a miniaturized X-ray tube. However, the diverged electrons can hit the insulator. This leads to the electrical charge builds upon the insulator and finally high voltage breakdown can occur. This prevents a stable operation of an X-ray tube. Consequently, if CNTs are coated on a side plane of a tip, the radial size of an X-ray tube cannot be decreased below a certain diameter because electrons generated from the side plane can induce an unstable operation.

For the realization of a smaller miniaturized X-ray tube, a method to develop CNT tip emitters without CNTs coated on the side plane of a tip was developed (Figure 2). At first, a CNT solution was prepared: the solution is composed of a 4 w% multiwalled CNTs (CM-95; Hanwha Nanotech Inc.) and 2 w% silver nanoparticles (NPs) (DGH; Advanced Nano Products Co., Ltd.) in a dichlorobenzene solvent. A 1 μL drop of the solution was carefully attached to the flat surface of a tungsten (W) wire. The end surface of the W wire was polished, and its diameter was 0.8 mm (Figure 2(a)). The dropped solution keeps a hemispherical morphology on the W surface because of a surface tension (Figure 2(b)). The solution was completely dried at ambient condition, which removes dichlorobenzene from the solution while leaving CNTs and Ag NPs on the tip surface. Subsequently, the tip with the CNTs and Ag NPs was thermally annealed at 800°C for 2 h under vacuum. The annealing process melts

Figure 5: (a) Current-voltage behavior of the miniaturized X-ray tube. (b) Energy spectrum of the X-rays produced from the miniaturized X-ray tube. The spectrum is normalized by the highest peak of 17.48 keV Mo $K_{\alpha 1}$ characteristics X-ray. (c) A radiograph of a line pair phantom.

Ag NPs to form Ag film on the W surface. This Ag film acts as an adhesive to strongly bind CNTs to the W surface. If the amount of the Ag NPs is properly chosen, one end of a CNT is emerged in the melted Ag film and the other end is exposed to the surface. An FESEM image displays the fabricated CNT tip emitter: CNTs are well attached to a flat W tip surface, and no CNTs are coated on the side plane of the tip (Figure 2(c)). The electron emission result using the fabricated CNT emitters shows that the diameter of an electron beam reaching at the anode was ~2.5 mm (Figure 2(d)), which was much decreased compared to Figure 1.

The emission property of the fabricated CNT tip emitter was characterized using a diode geometry. The same focusing electrode as shown in Figure 1 was used for the characterization. The cathode-anode distance was 1.3 mm. Figure 3 shows the measured current density-electric field profile of the emitter. The profile follows the Fowler-Nordheim (F-N) equation very well: a linear relationship between $\ln(J/E^2)$ and $1/E$ was observed as shown in the inset of Figure 3. The threshold electric field corresponding to an emission current density of 10 mA/cm^2 was 1.15 V/μm. The field emission enhancement factor derived from the F-N plot was approximately 12,050. These results indicate that the flat-tip CNT emitter exhibits a comparatively good field-emission performance.

In order to investigate the real device performance of the flat-tip CNT emitters, a miniaturized X-ray tube was fabricated using the CNT emitters. The schematic diagram of the miniaturized X-ray tube is shown in Figure 4. The X-ray tube consists of a flat-tip CNT emitter, a focusing electrode, and an X-ray target. The X-ray target acts as an anode. An alumina ceramic tube was used for an electrical insulator between the focusing electrode and the X-ray target. The inner diameter of the alumina tube was 5 mm, the outer diameter of the tube was 7 mm, and the total length of the X-ray tube was 40 mm. The X-ray target has a simple planar shape, and the target was prepared by coating molybdenum (Mo) on a thin beryllium X-ray window. All of the parts were vacuum tightly brazed in a vacuum furnace, and a getter was used to sustain a vacuum inside the X-ray tube. Consequently, the X-ray tube can be operated without an external vacuum pump. Figure 5(a) displays the measured current-voltage curve of the miniaturized X-ray tube. The X-ray tube could be stably operated up to 50 kV without any voltage breakdown after a short voltage conditioning [29]. The electron current reaching the X-ray target at 50 kV was 213 μA. Figure 5(b) shows the energy spectrum of the X-rays generated from the miniaturized X-ray tube. The energy spectrum was measured at 40 keV with an X-ray spectrometer (model: Amptek XR-100T-CdTe) that was 150 cm away from the X-ray target. In addition to the

broad bremsstrahlung X-rays, Mo characteristic X-rays of $K_{\alpha 1}$ at 17.48 keV and $K_{\beta 1}$ at 19.61 keV were clearly observed. Figure 5(c) shows a radiograph of a line pair phantom that was achieved by the miniaturized X-ray tube and a CMOS 197 photodiode array detector (Vatech Xmaru0505CF, pixel pitch 24 μm). Up to 10 line pairs/mm was clearly resolved.

In summary, we fabricated flat-tip CNT emitters for miniaturized X-ray tubes and successfully demonstrated the operation of a miniaturized X-ray tube with the inner diameter of 5 mm. The tip CNT emitter was prepared by coating CNTs on a flat surface of a W metal tip using Ag nanoparticles as an adhesive. The CNT emitters exhibit good field emission properties, and the beam divergence was minimized. We believe that flat-tip CNT emitters are very useful to realize smaller miniaturized X-ray tubes and high-brightness microfocus X-ray tubes.

Acknowledgments

This study was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea Government (MEST) (no. 2012-0005946) and the R&D Program of MKE/KEIT (10035553).

References

[1] J. Kong, N. R. Franklin, C. Zhou et al., "Nanotube molecular wires as chemical sensors," *Science*, vol. 287, no. 5453, pp. 622–625, 2000.

[2] Q. H. Wang, A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, E. W. Seelig, and R. P. H. Chang, "A nanotube-based field-emission flat panel display," *Applied Physics Letters*, vol. 72, no. 22, pp. 2912–2913, 1998.

[3] R. G. Ding, G. Q. Lu, Z. F. Yan, and M. A. Wilson, "Recent advances in the preparation and utilization of carbon nanotubes for hydrogen storage," *Journal of Nanoscience and Nanotechnology*, vol. 1, no. 1, pp. 7–29, 2001.

[4] Y. Qin, M. Hu, H. Li, Z. Zhang, and Q. Zou, "Preparation and field emission properties of carbon nanotubes cold cathode using melting Ag nano-particles as binder," *Applied Surface Science*, vol. 253, no. 8, pp. 4021–4024, 2007.

[5] L. Wang, Z. Sun, T. Chen, and W. Que, "Growth temperature effect on field emission properties of printable carbon nanotubes cathode," *Solid-State Electronics*, vol. 50, no. 5, pp. 800–804, 2006.

[6] J. L. Kwo, M. Yokoyama, W. C. Wang, F. Y. Chuang, and I. N. Lin, "Characteristics of flat panel display using carbon nanotube as electro emitters," *Diamond Related Materials*, vol. 9, no. 3–6, pp. 1270–1274, 2000.

[7] C. Niu, E. K. Sichel, R. Hoch, D. Moy, and H. Tennent, "High power electrochemical capacitors based on carbon nanotube electrodes," *Applied Physics Letters*, vol. 70, no. 11, pp. 1480–1482, 1997.

[8] W. A. de Heer, A. Chatelain, and D. Ugarte, "A carbon nanotube field-emission electron source," *Science*, vol. 270, no. 5239, pp. 1179–1180, 1995.

[9] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, "Self-oriented regular arrays of carbon nanotubes and their field emission properties," *Science*, vol. 283, no. 5401, pp. 512–514, 1999.

[10] X. Xu and G. R. Brandes, "A method for fabricating large-area, patterned, carbon nanotube field emitters," *Applied Physics Letters*, vol. 74, no. 17, pp. 2549–2551, 1999.

[11] Z. F. Ren and Z. P. Huang, "Synthesis of large arrays of well-aligned carbon nanotubes on glass," *Science*, vol. 282, no. 5391, pp. 1105–1107, 1998.

[12] G. Gutman, E. Strumban, E. Sozontov, and K. Jenrow, "X-ray scalpel—a new device for targeted x-ray brachytherapy and stereotactic radiosurgery," *Physics in Medicine and Biology*, vol. 52, no. 6, pp. 1757–1770, 2007.

[13] A. Dickler, "Xoft Axxent electronic brachytherapy—a new device for delivering brachytherapy to the breast," *Nature Reviews Clinical Oncology*, vol. 6, no. 6, pp. 138–142, 2009.

[14] L. N. Koppel and J. R. Marshall, "A miniature metal-ceramic x-ray source for spacecraft instrumentation," *Review of Scientific Instruments*, vol. 69, no. 4, pp. 1893–1897, 1998.

[15] F. Schneider, H. Fuchs, F. Lorenz et al., "A novel device for intravaginal electronic brachytherapy," *International Journal of Radiation Oncology Biology Physics*, vol. 74, no. 4, pp. 1298–1305, 2009.

[16] M. J. Rivard, S. D. Davis, L. A. DeWerd, T. W. Rusch, and S. Axelrod, "Calculated and measured brachytherapy dosimetry parameters in water for the Xoft Axxent X-Ray Source: an electronic brachytherapy source," *Medical Physics*, vol. 33, no. 11, pp. 4020–4032, 2006.

[17] J. C. Yanch and K. J. Harte, "Monte Carlo simulation of a miniature, radiosurgery x-ray tube using the ITS 3.0 coupled electron-photon transport code," *Medical Physics*, vol. 23, no. 9, pp. 1551–1558, 1996.

[18] P. Lovoi and J. F. Asmus, "An X-Ray microprobe for In-Situ stone and wood characterization," in *Proceedings of the Lasers in the Conservation of Artworks*, vol. 100, pp. 353–356, Springer, Berlin, Germany, 2005.

[19] S. H. Heo, A. Ihsan, and S. O. Cho, "Transmission-type microfocus x-ray tube using carbon nanotube field emitters," *Applied Physics Letters*, vol. 90, no. 18, Article ID 183109, 2007.

[20] Y. Sakai, A. Haga, S. Sugita et al., "Electron gun using carbon-nanofiber field emitter," *Review of Scientific Instruments*, vol. 78, no. 1, Article ID 013305, 2007.

[21] Y. Chen, D. T. Shaw, and L. Guo, "Field emission of different oriented carbon nanotubes," *Applied Physics Letters*, vol. 76, no. 17, pp. 2469–2471, 2000.

[22] S. K. Srivastava, V. D. Vankar, and V. Kumar, "Excellent field emission properties of short conical carbon nanotubes prepared by microwave plasma enhanced CVD process," *Nanoscale Research Letters*, vol. 3, no. 1, pp. 25–30, 2008.

[23] B. Gao, G. Z. Yue, Q. Qiu et al., "Fabrication and electron field emission properties of carbon nanotube films by electrophoretic deposition," *Advanced Materials*, vol. 13, no. 23, pp. 1770–1773, 2001.

[24] J. M. Bonard, C. Kinke, K. A. Dean, and B. F. Coll, "Degradation and failure of carbon nanotube field emitters," *Physical Review B*, vol. 67, no. 11, pp. 115406–115415, 2003.

[25] J. C. She, N. S. Xu, S. Z. Deng et al., "Vacuum breakdown of carbon-nanotube field emitters on a silicon tip," *Applied Physics Letters*, vol. 83, no. 13, pp. 2671–2673, 2003.

[26] X. H. Liang, S. Z. Deng, N. S. Xu, Jun Chen, N. Y. Huang, and J. C. She, "Noncatastrophic and catastrophic vacuum breakdowns of carbon nanotube film under direct current conditions," *Journal of Applied Physics*, vol. 101, no. 6, Article ID 063309, 2007.

[27] N. Y. Huang, J. C. She, J. Chen et al., "Mechanism responsible for initiating carbon nanotube vacuum breakdown," *Physical Review Letters*, vol. 93, no. 7, Article ID 075501, 2004.

[28] W. B. Herrmannsfeldt and G. A. Herrmannsfeldt, *EGN Electron Optics Program*, SLAC, Stanford, Calif, USA, 1993.

[29] J. L. Kwo, C. C. Tsou, M. Yokoyama et al., "Field emission characteristics of carbon nanotube emitters synthesized by arc discharge," *Journal of Vacuum Science and Technology B*, vol. 19, no. 1, pp. 23–26, 2001.

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 532847, 5 pages
doi:10.1155/2012/532847

Research Article

Effects of EDTA and Boric Acid on the Morphology of $CaCO_3$ Particles

Xingbo Shi,[1] Julin Wang,[1] and Xiaoping Cai[1,2]

[1] *National Carbon Fiber Engineering Research Center, Beijing University of Chemical Technology, Beijing 100029, China*
[2] *Jilin Petrochemical Co. Ltd., PetroChina, Jilin 132021, China*

Correspondence should be addressed to Julin Wang, julinwang@126.com

Received 31 July 2012; Accepted 30 November 2012

Academic Editor: Sung Oh Cho

Copyright © 2012 Xingbo Shi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Calcium carbonate ($CaCO_3$) particles with different morphologies were prepared using calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) aqueous solutions containing various amounts of ethylenediamine tetraacetic acid (EDTA) or boric acid. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The sphere-like $CaCO_3$ particle was inclined to be formed in EDTA or boric acid solution at room temperature. The surface of $CaCO_3$ is smooth in the presence of EDTA, and the crystal structure of $CaCO_3$ is majorly vaterite. However, the $CaCO_3$ has a rough surface in boric acid solution and pure calcite structure. The size of $CaCO_3$ particle decreases with the increase in the amount of EDTA or boric acid.

1. Introduction

Calcium carbonate ($CaCO_3$) is one of the most abundant materials on the planet and has been often used in ground form to produce polymer composites [1, 2]. Recently, there have been some interests in controlling the crystallization of $CaCO_3$ and the usage of various types of inorganic/organic additives in order to obtain unusual morphologies, crystal sizes, and control the outcoming polymorph type [3, 4]. Research on the controlling mineralization of $CaCO_3$ has focused on the following two approaches: (i) organic additives controlling the morphology and crystal structure of $CaCO_3$. These water-soluble additives include hydrophilic synthetic polymers [5, 6] and low-molecular mass organic additives [7–9], such as carboxylic or amino acids. The second approach is (ii) inorganic ions controlling the morphology and crystal structure of $CaCO_3$. It has been reported that crystallization of $CaCO_3$ is also affected by inorganic ions, such as Ba^{2+} and Co^{2+} [10–12].

In this work, $CaCO_3$ crystals were precipitated using aqueous mixtures of $CaCl_2$ and Na_2CO_3 in the presence of EDTA or boric acid. The $CaCO_3$ particles were characterized with XRD and SEM.

2. Experimental

Calcium chloride ($CaCl_2$), sodium carbonate (Na_2CO_3), ethylenediamine tetraacetic acid (EDTA), and boric acid were purchased from Beijing Chemical Works. These agents were all analytical reagent degree.

Alkaline condition: an aqueous solution containing 50 mL Na_2CO_3 (0.5 M) was stirred continuously for about 15 min at room temperature (25°C), and then different amounts of EDTA or boric acid (0.5 g, 1.0 g and 1.5 g) were added. The mixed solution was alkaline because of the small amount of EDTA or boric acid. 50 mL $CaCl_2$ (0.5 M) was gradually added into the above mixed solution and kept stirring for 60 min.

Acidic condition: the operation steps were same as above, the difference was only that 50 mL Na_2CO_3 (0.5 M) was added into the mixed solution of $CaCl_2$ and additives.

The precipitate was washed by deionized water and ethanol and then dried at 80°C for 24 h.

X-ray diffraction (XRD, 2500VB2+PC, Cu Kα radiation, Rigaku, Japan) was used to analyze the composition and crystal structure of the prepared micro-$CaCO_3$ products. The shapes of the products were characterized by scanning electron microscopy (SEM, S-4700, Hitachi, Japan).

Figure 1: SEM images and XRD patterns of $CaCO_3$ prepared in the presence of EDTA in alkaline condition. (A)–(C) SEM images of synthesized $CaCO_3$, (D) XRD patterns of product A (a), product B (b), and product C (c).

3. Results and Discussion

Figure 1 shows the SEM images and XRD patterns of the prepared $CaCO_3$ after adding different amounts of EDTA in alkaline condition. SEM image given in Figure 1(A) indicates that the particle, produced with addition of 0.5 g EDTA, is a majority of flower shapes with a size of 5 μm. The images in Figures 1(B) and 1(C) show that the products are composed of sphere-like particles in addition of 1.0 g or 1.5 g EDTA. The nanoparticle shown in Figure 1(C) (with a diameter of 0.5~2 μm) is smaller than those shown in Figure 1(B) (with a diameter of 1~3 μm). From the XRD patterns of the as-prepared $CaCO_3$ (Figure 1(D)), in comparison with their standard JCPDS files (calcite, 47-1743 and vaterite, 33-0268), the flower (Figure 1(D), (a)) and sphere-like (Figure 1(D), (b) and (c)) $CaCO_3$ particles are major vaterite structure.

Figure 2 shows the SEM images and XRD patterns of the synthesized $CaCO_3$ after adding different amounts of EDTA in acidic condition. Figure 2(A) indicates that the product is composed of a rodlike particle and a small part flower-like particle with a length of 3 μm with addition of 0.5 g EDTA. Figure 2(D) XRD patterns of the $CaCO_3$ demonstrate that pure calcite was produced (Figure 2(D), (a)). Figures 2(B) and 2(C) indicate that the products compose sphere-like $CaCO_3$ particle with a diameter of 1~2.5 μm in addition of 1.0 g or 1.5 g EDTA. The diffraction peaks (Figure 2(D), (b)) can be well indexed to the calcite and vaterite phase of $CaCO_3$. The diffraction peaks from (Figure 2(D), (c)) show that the hemispherical $CaCO_3$ is a pure vaterite structure.

Figure 3 shows the SEM images and XRD patterns of the synthesized $CaCO_3$ in the presence of boric acid in alkaline condition. Figure 3(A) indicates that the product is a sphere-like particle with a length of 2.5 μm and a rough surface in the presence of 0.5 g boric acid. Figures 3(B) and 3(C) indicate that the product is a cubic particle (size length of 500 nm or 300 nm) in the presence of 1.0 g or 1.5 g boric acid. The XRD patterns of the $CaCO_3$ can be indexed that the three kinds of products are composed of pure calcite structure (Figure 3(D)).

Figure 4 shows the SEM images and XRD patterns of the synthesized $CaCO_3$ in the presence of boric acid in acidic condition. Figures 4(A), 4(B), and 4(C) indicate that the products are sphere-like particle with a diameter of 2.5 μm, 1 μm, and 500 nm by adding 0.5 g, 1.0 g, and 1.5 g boric acid, respectively. The particle surface is rough. The XRD patterns of the $CaCO_3$ can be indexed that the three kinds of products are composed of pure calcite structure (Figure 3(D)).

Mann et al. [13] investigated the crystallization of $CaCO_3$ from supersaturated solutions. The formation of a Stern layer of Ca counterions favors the oriented nucleation of crystal faces consisting of only Ca atoms and the (0001) face of vaterite fits this criterion. Charge accumulation, however, cannot account for the structural selectivity of vaterite, as the (0001) face of calcite is also uni-charged. The trigonal planar carbonate anions are oriented parallel to the (0001) face of calcite, whereas in vaterite they are aligned perpendicularly, and the latter arrangement is equivalent to the orientation of the carboxylate headgroups with respect to the Ca-bound

Figure 2: SEM images and XRD patterns of $CaCO_3$ prepared in the presence of EDTA in acidic condition. (A)–(C) SEM images of synthesized $CaCO_3$, (D) XRD patterns of product A (a), product B (b), and product C (c).

Figure 3: SEM images and XRD patterns of $CaCO_3$ prepared in the presence of boric acid in alkaline condition. (A)–(C) SEM images of synthesized $CaCO_3$, (D) XRD patterns of product A (a), product B (b), and product C (c).

Figure 4: SEM images and XRD patterns of $CaCO_3$ prepared in the presence of boric acid in acidic condition. (A)–(C) SEM images of synthesized $CaCO_3$, (D) XRD patterns of product A (a), product B (b), and product C (c).

Figure 5: The chelation of EDTA and Ca^{2+}.

Figure 6: Formation mechanism of $CaCO_3$ with various shapes.

Stern layer. Thus, the stereochemical arrangement of the carboxylates in conjunction with Ca binding generates a two-layer subunit cell motif of the vaterite structure, rather than calcite. Subsequent addition of carbonate from solution will be similarly stereochemically directed extending the vaterite motif towards a stable nucleus. In our investigation, the electrostatic and stereochemical interactions of EDTA at the inorganic-organic interface are similar to the above mechanism. The chelation of EDTA with Ca^{2+} can be seen in Figure 5. The product was a major spherical $CaCO_3$ particle, which was induced by the addition of EDTA. The size of $CaCO_3$ decreased with increasing in the content of EDTA.

The size of $CaCO_3$ particle decreases with increase the amount of EDTA or boric acid, which can form nucleation point, and the larger size of $CaCO_3$ particle was obtained in the acidic conditions. The sphere-like $CaCO_3$ particle is obtained in the additives containing multicarboxyl or multihydroxyl. However, the carboxyl has a stronger induction than hydroxyl, so the surface of $CaCO_3$ was smooth formed in multicarboxyl compound. According the previous research [11], the formation mechanism of $CaCO_3$ with various shapes was shown in Figure 6.

4. Conclusion

The sphere-like $CaCO_3$ particles were obtained when the amount of EDTA was more than 1.0 g. The surface of $CaCO_3$ is smooth in the presence of EDTA, and the crystal structure of $CaCO_3$ is major vaterite. However, the sphere-like $CaCO_3$ particle was obtained when the amount of boric acid was less than 1.0 g. The $CaCO_3$ has a rough surface in boric acid solution and a pure calcite structure. The size of $CaCO_3$ particle decreases with increase in the amount of EDTA or boric acid, especially in alkaline condition.

Acknowledgment

This work is subsidized by the sci-tech innovation foundation of China National Petroleum Corporation (no. 2009D-5006-05-04).

References

[1] A. L. N. Da Silva, M. C. G. Rocha, M. A. R. Moraes, C. A. R. Valente, and F. M. B. Coutinho, "Mechanical and rheological properties of composites based on polyolefin and mineral additives," *Polymer Testing*, vol. 21, no. 1, pp. 57–60, 2002.

[2] M. C. G. Rocha, A. H. M. F. T. Silva, F. M. B. Coutinho, and A. L. N. Silva, "Study of composites based on polypropylene and calcium carbonate by experimental design," *Polymer Testing*, vol. 24, no. 8, pp. 1049–1053, 2005.

[3] R. R. Fay, "The goldfish ear codes the axis of acoustic particle motion in three dimensions," *Science*, vol. 225, no. 4665, pp. 951–954, 1984.

[4] H. Yang, W. Yao, L. Yang et al., "The self-assembly of $CaCO_3$ crystals in the presence of protein," *Journal of Crystal Growth*, vol. 311, no. 9, pp. 2682–2688, 2009.

[5] E. Altay, T. Shahwan, and M. Tanoğlu, "Morphosynthesis of $CaCO_3$ at different reaction temperatures and the effects of PDDA, CTAB, and EDTA on the particle morphology and polymorph stability," *Powder Technology*, vol. 178, no. 3, pp. 194–202, 2007.

[6] J. Rudloff and H. Cölfen, "Superstructures of temporarily stabilized nanocrystalline $CaCO_3$ particles: morphological control via water surface tension variation," *Langmuir*, vol. 20, no. 3, pp. 991–996, 2004.

[7] L. A. Gower and D. A. Tirrell, "Calcium carbonate films and helices grown in solutions of poly(aspartate)," *Journal of Crystal Growth*, vol. 191, no. 1-2, pp. 153–160, 1998.

[8] C. A. Orme, A. Noy, A. Wierzbicki et al., "Formation of chiral morphologies through selective binding of amino acids to calcite surface steps," *Nature*, vol. 411, no. 6839, pp. 775–779, 2001.

[9] M. Maas, H. Rehage, H. Nebel, and M. Epple, "A detailed study of closed calcium carbonate films at the liquid-liquid interface," *Langmuir*, vol. 25, no. 4, pp. 2258–2263, 2009.

[10] A. J. Xie, Y. H. Shen, X. Y. Li et al., "The role of Mg^{2+} and Mg^{2+}/amino acid in controlling polymorph and morphology of calcium carbonate crystal," *Materials Chemistry and Physics*, vol. 101, no. 1, pp. 87–92, 2007.

[11] G. Gao, P. Huang, K. Wang, R. He, and D. Cui, "Gram-scale synthesis and shape evolution of micro-$CaCO_3$," *Powder Technology*, vol. 205, pp. 270–275, 2011.

[12] K. B. Lee, S. B. Park, Y. N. Jang, and S. W. Lee, "Morphological control of $CaCO_3$ films with large area: effect of additives and self-organization under atmospheric conditions," *Journal of Colloid and Interface Science*, vol. 355, no. 1, pp. 54–60, 2011.

[13] S. Mann, B. R. Heywood, S. Rajam, and J. D. Birchall, "Controlled crystallization of $CaCO_3$ under stearic acid monolayers," *Nature*, vol. 334, no. 6184, pp. 692–695, 1988.