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Research Article

Variations of Optical and Structural Properties of Co_xO_y Thin Films with Thermal Treatment

A. B. C. Ekwealor,[1] S. U. Offiah,[2] S. C. Ezugwu,[3] and F. I. Ezema[1]

[1] *Department of Physics and Astronomy, University of Nigeria, Nsukka 410001, Nigeria*
[2] *National Centre for Energy Research and Development, University of Nigeria, Nsukka 410001, Nigeria*
[3] *Department of Physics and Astronomy, University of Western Ontario, 1151 Richmond St., London, ON, Canada N6A 3K7*

Correspondence should be addressed to A. B. C. Ekwealor; abcekwealor@yahoo.com

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The effects of thermal treatment on the optical and structural properties of cobalt oxide Co_xO_y thin films synthesized in the pores of PVP by chemical bath deposition technique were investigated. Films deposited were crystalline. The optical properties of the films were got from absorbance, transmittance reflectance, refractive index, absorption coefficient, and extinction coefficient measurements. The synthesized Co_xO_y films turned out to be cobalt oxyhydroxide , CoO(OH), nanocrystals. The crystals obtained were of size 41.84 nm; however, as annealing temperature increased, the size decreased to 16.28 nm. The absorption coefficient, refractive index, and extinction coefficient were found to increase with increase in annealing temperature though not sequentially. For the same energy ranges of the incident photons, the absorption coefficient and refractive index ranged from 0.2 to 1.8 and from 1.4 to 2.3, respectively. The energy band-gap of the films ranged from 1.96 eV to 2.22 eV.

1. Introduction

Five species of cobalt oxide (CoO_2, Co_2O_3, CoO(OH), Co_3O_4, and CoO) have been reported [1, 2]. Both Co_3O_4 and CoO(OH) are easily obtained by thermally decomposing cobalt salts under oxidizing reactions [3]. Cobalt oxides have applications in superconductivity in electronics, electrochemical properties in microbatteries and high density batteries [4]. Cobalt oxyhydroxide, CoO(OH), has a hexagonal structure in which a divalent metal cation is located at an octahedral site which is coordinated by six hydroxyl oxygen [2]. CoO(OH) has been proposed as an alternative material for CO detection at low temperatures, for improving Co_3O_4-based gas sensor [5]. Well-spread CoO(OH) can be used as the conductive network in rechargeable alkaline batteries [6]. CoO(OH) is a promising material for fuel cells [7] and capacitors [8]. Generally, cobalt oxide materials can be deposited using several techniques, such as precipitation, sputtering, pulsed laser deposition, spray pyrolysis, sol-gel, hydrothermal synthesis, and electrochemical deposition [9]. But chemical bath deposition (CBD) technique is one of the simplest, cheapest, cost saving, convenient, and highly reproducible techniques that can be used for this deposition. It has been well known as a prevalent low temperature aqueous technique for directly depositing large area thin films of semiconductors [10]. It can be used for deposition of both conducting and nonconducting layers from solutions by electrochemical processes, without application of external fields [11]. CBD has the following advantages: it allows films to be deposited on nonplanar substrates that might not be chemically or mechanically stable at high temperatures. It requires no sophisticated equipment such as vacuum systems. The starting chemicals are commonly available and cheap, and the preparation parameters can be easily controlled. However, CBD technique has not been extensively employed in the deposition of cobalt oxides and cobalt oxyhydroxide especially in the pores of PVP matrix. We therefore present, in this paper, the effect of annealing temperature on the optical and structural properties of cobalt oxyhydroxide thin films obtained by chemical bath deposition techniques.

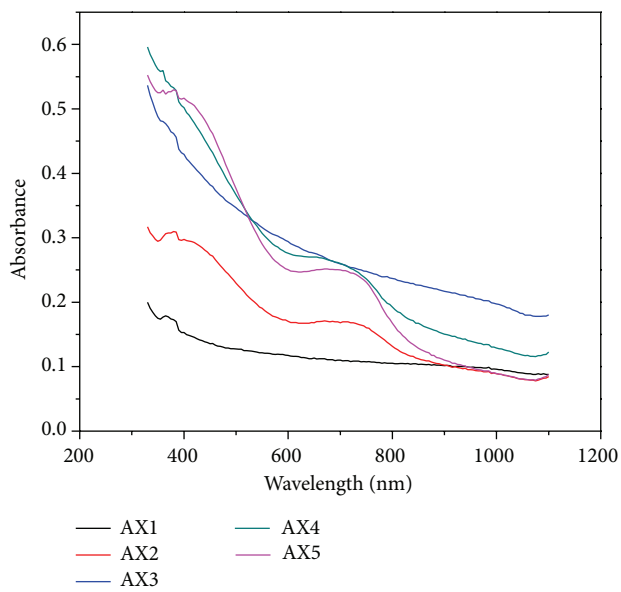

Figure 1: Absorbance spectra for Co_xO_y thin films with varying annealing temperatures.

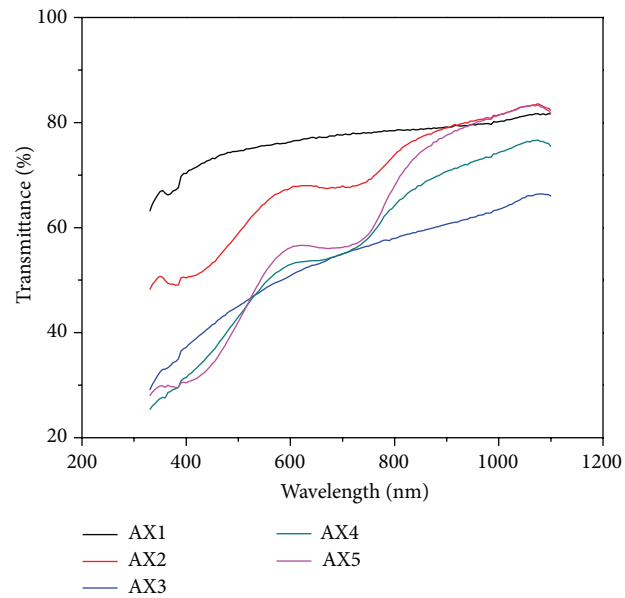

Figure 2: Transmittance spectra for Co_xO_y thin films with varying annealing temperatures.

2. Synthesis of Cobalt Oxide Co_xO_y

The chemical bath for this experiment was prepared by mixing and stirring 5 mL of 0.1 M $CoCl_2$, 5 mL of 1 M, triethanolamine (TEA) 1 mL of 13.4 M NH_3, and 40 mL of PVP in a 100 cm^3 beaker. The pH value of the solution was 8.1. To ensure equal parameters of deposition, 5 substrates were immersed in the same bath and supported by the wall of the beaker. The bath temperature was kept at 333 K and the substrates were left in the bath for five hours to allow for substantial deposition. The substrates were removed, rinsed in distilled water, and dried in an oven. One of them was left as deposited, while the others were annealed at temperatures of 373 K, 473 K, 573 K, and 673 K and were, respectively, designated with labels, AX1, AX2, AX3, AX4, and AX5.

The optical properties of the films were studied using absorption spectra in UV-VIS-NIR regions obtained from Unico UV-2102 PC spectrophotometer at normal incidence of light within the wavelength range 200 nm–1200 nm.

3. Results and Discussion

3.1. Optical Analysis. The absorbance of samples AX1 and AX2 is low, about 20%–32% in the wavelength region of UV-VIS, while that of samples AX3–AX5 is high, about 52%–60% in this region. These are evident in Figure 1 which gives a plot of absorbance against wavelength. The absorbance of all the samples, however, decreased to low values about 23%–10% in the NIR region. It is apparent from this figure that absorbance increased with annealing temperature. The low absorbance in the UV-VIS region for as deposited film and that annealed at low temperatures can be attributed to poor crystalline structure of the films. When annealed at higher temperatures, the films became better crystallized [12] and absorbed more of the incident radiation.

It can be seen in Figure 2 which is a graph of transmittance against wavelength that the transmittance of samples AX1 and AX2 is fairly high, about 48%–62% for the wavelengths in UV-VIS regions, while that of samples AX3–AX5 is low, about 25%–30% for the wavelengths in these regions. The transmittance of all the samples however increased to about 58%–84% in the NIR region. Here transmittance is observed to decrease with increased annealing temperature.

The reflectance of all samples AX1–AX5 is low (<25%) in the UV-VIS regions and decreased to lower values in the NIR region. This can be observed in Figure 3 which is a plot of reflectance against wavelength.

The energy band-gap of the films was determined from the relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) given by $(\alpha h\nu) = A(h\nu - E_g)^n$ [13], where A is a constant, E_g is the band-gap energy of the material, and n depends on nature of transition. For direct allowed transition, $n = 1/2$, for direct forbidden transition, $n = 3/2$, and for indirect allowed transition, $n = 2$. The possible transitions were determined from plots of $(\alpha h\nu)^n$ against $h\nu$ given in Figure 4. By extrapolating the straight portions of the graphs on hν axis, the band-gaps were obtained from the intercepts since $E_g = h\nu$ when $(\alpha h\nu)^n = 0$. From Figure 4, it can be seen that the direct band-gap energy values of the Co_xO_y films range from about 1.96 eV to 2.22 eV. Again, increased annealing of the films is found to increase their band-gaps.

The plot of absorption coefficient against photon energy is given in Figure 5. This reveals that absorption coefficient of the films increased progressively from 0.2 to about 1.8 within the energy range of 1.0 eV to 4.0 eV. It also shows that

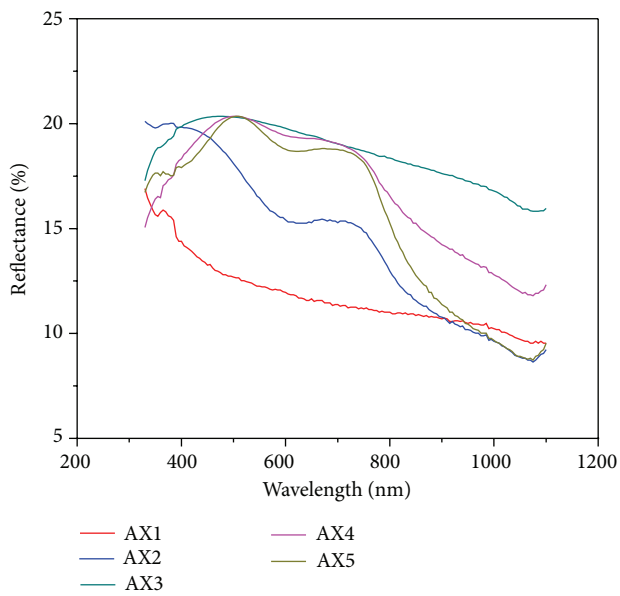

Figure 3: Reflectance spectra for Co_xO_y thin films with varying annealing temperatures.

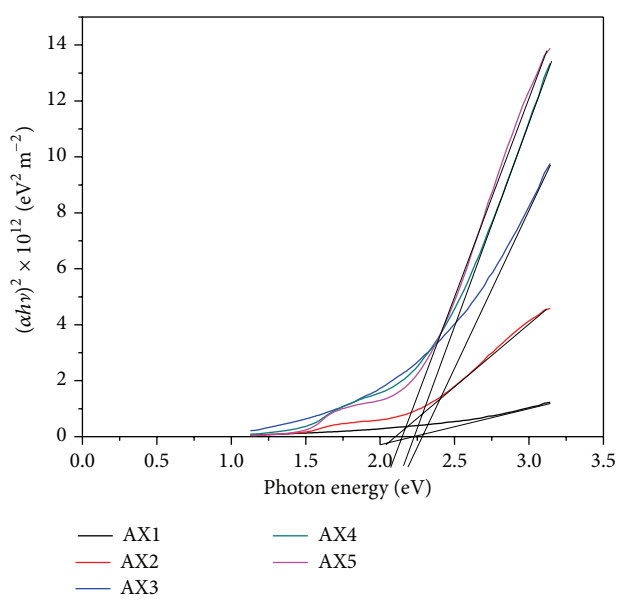

Figure 4: Band-gap spectra for Co_xO_y thin films with varying annealing temperatures.

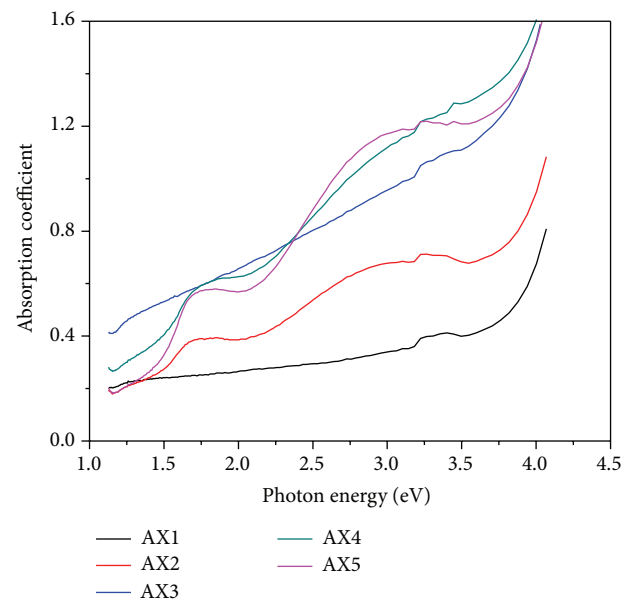

Figure 5: Absorption coefficient spectra for Co_xO_y thin films with varying annealing temperatures.

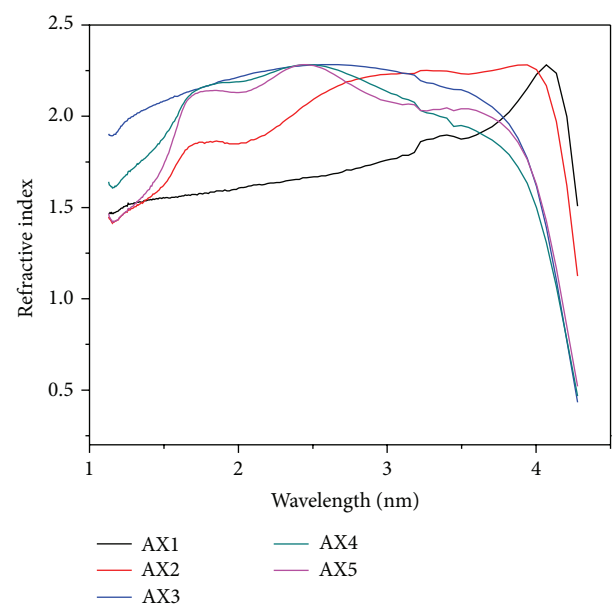

Figure 6: Refractive index spectra for Co_xO_y thin films with varying annealing temperatures.

absorption coefficient of the films increased with increased annealing temperature.

The refractive index of the films could be seen to range from about 1.40 to 2.25 for photon energy range of 1.0–4.0 eV in Figure 6 which gives the refractive index plot with photon energy. Thin films with refractive index lower than 1.9 have been reported to be employable as antireflecting material [14]. The as deposited film has refractive index lower than this value for the aforementioned energy range and so could serve for this purpose. Figure 6 also shows that refractive index of the films increased with increased annealing temperature though nonsequentially.

The extinction coefficient versus photon energy plot shown in Figure 7 shows that the extinction coefficient of the films increased irregularly with increase in annealing temperature. It can also be observed that, for the as deposited films and those annealed at lower temperatures, the extinction coefficient increased remarkably, but, for higher annealing temperatures, the variation was slight.

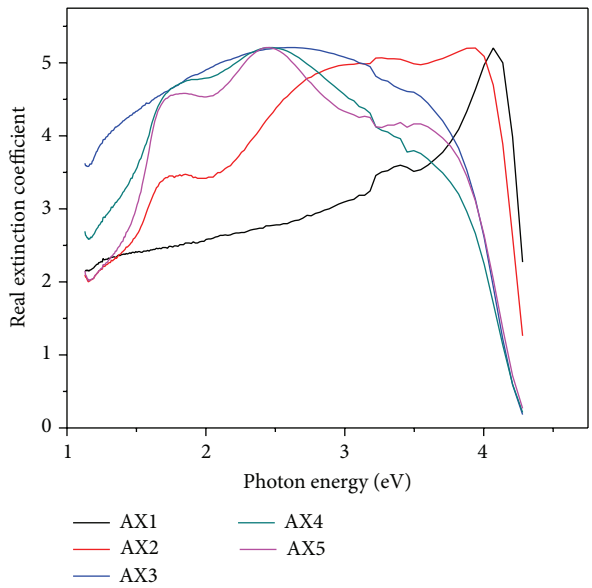

Figure 7: Extinction coefficient spectra for Co_xO_y thin films with varying annealing temperatures.

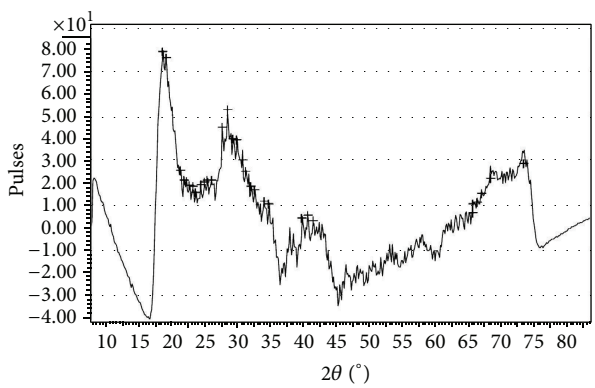

Figure 8: XRD diffractogram for as deposited CoO(OH) films.

3.2. Structural Characterization. The XRD spectra for the synthesized films with varying annealing temperatures given by Figures 8–10 show that the synthesized films is cobalt oxyhydroxide, CoO(OH) (also known as Heterogenite-3). From Figure 8, which gives the spectra for the as deposited film, peaks were obtained at $2\theta = 41.20^\circ$ and 68.50°, corresponding to diffraction lines produced by (006) and (018) planes (JCPDS card number 07-0169).

The film annealed at 473 K given by Figure 9 shows peaks at $2\theta = 20.23^\circ$, 38.91°, 68.45°, and 69.30° corresponding to (003), (012), (018), and (113) planes, respectively.

The film annealed at 573 K given by Figure 10 shows peaks at $2\theta = 38.93^\circ$ and 65.40° corresponding to diffraction lines produced by (012) and (110) planes, respectively.

3.3. Determination of Film Size. Using Scherer's formula given by [15], $D = 0.9\lambda/\beta\cos\theta$, where λ is wavelength of the X-ray, β is full width at half maximum (FWHM) of the

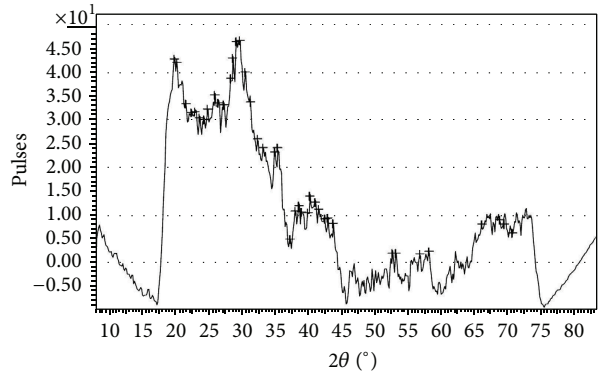

Figure 9: XRD diffractogram for CoO(OH) films annealed at 473 K.

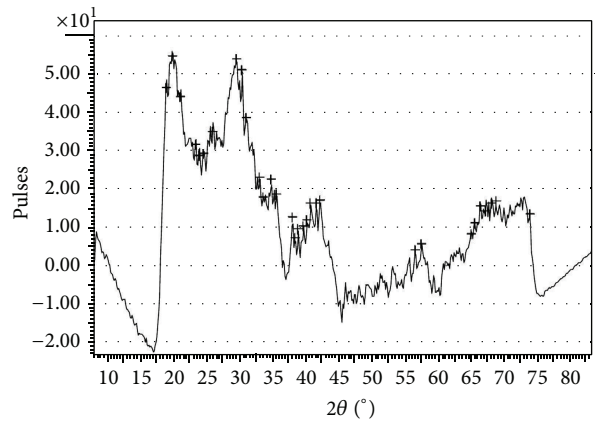

Figure 10: XRD diffractogram for CoO(OH) films annealed at 573 K.

peak with the highest intensity, and θ is the diffraction angle, and the grain sizes were obtained to be of range 16.28 nm–41.84 nm for varied annealing temperatures.

4. Conclusion

Cobalt oxyhydroxide CoO(OH) thin films have been prepared by CBD technique. The structural property study showed that the films have crystalline nanostructure. Their optical properties studies revealed that they have strong absorbance in the visible region of the electromagnetic spectrum when treated with high temperatures and their refractive index ranged from 1.40 to 2.25, thus making them suitable for applications as antireflection coatings. They have direct band-gap values which ranged from 1.96 eV to 2.22 eV. These narrow band-gaps make them suitable for application as good absorber layers for photocells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] H. Yamaura, K. Moriya, N. Miura, and N. Yamazoe, "Mechanism of sensitivity promotion in CO sensor using indium oxide and cobalt oxide," *Sensors and Actuators B*, vol. 65, no. 1–3, pp. 39–41, 2000.

[2] C.-W. Tang, C.-B. Wang, and S.-H. Chien, "Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS," *Thermochimica Acta*, vol. 473, no. 1-2, pp. 68–73, 2008.

[3] T. Pauporte, L. Mendoza, M. Cassir, M. C. Bernard, and J. Chivot, "Direct low-temperature deposition of crystallized CoOOH films by potentiostatic electrolysis," *Journal of the Electrochemical Society*, vol. 152, no. 2, pp. C49–C53, 2005.

[4] C. M. Lampert and C. G. Granqvist, *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, vol. 4 of *SPIE Institutes for Advanced Optical Technologies*, SPIE Optical Engineering Press, Bellingham, Wash, USA, 1990.

[5] R. J. Wu, J.-G. Wu, T.-K. Tsai, and C.-T. Yeh, "Use of cobalt oxide CoOOH in a carbon monoxide sensor operating at low temperatures," *Sensors and Actuators B*, vol. 120, no. 1, pp. 104–109, 2006.

[6] R. van Zee, Y. Hamrick, S. Li, and W. Weltner Jr., "Cobalt, rhodium, and iridium dioxide molecules and walsh-type rules," *The Journal of Physical Chemistry*, vol. 96, no. 18, pp. 7247–7251, 1992.

[7] C. Mansour, T. Pauporté, A. Ringuedé, V. Albin, and M. Cassir, "Protective coating for MCFC cathode: low temperature potentiostatic deposition of CoOOH on nickel in aqueous media containing glycine," *Journal of Power Sources*, vol. 156, no. 1, pp. 23–27, 2006.

[8] H. Zheng, F. Tang, M. Lim et al., "Electrochemical behavior of carbon-nanotube/cobalt oxyhydroxide nanoflake multilayer films," *Journal of Power Sources*, vol. 193, no. 2, pp. 930–934, 2009.

[9] I. Kelpšaitė, J. Baltrušaitis, and E. Valatka, "Electrochemical deposition of porous cobalt oxide films on AISI 304 type steel," *Materials Science*, vol. 17, no. 3, pp. 236–243, 2011.

[10] R. S. Mane and C. D. Lokhande, "Chemical deposition method for metal chalcogenide thin films," *Materials Chemistry and Physics*, vol. 65, no. 1, pp. 1–31, 2000.

[11] K. L. Chopra and S. R. Das, *Thin Film Solar Cells*, Plenum Press, London, UK, 1983.

[12] M. O. Nwodo, S. C. Ezugwu, F. I. Ezema, R. U. Osuji, and P. U. Asogwa, "Effect of thermal annealing on the optical and structural, properties of PbO thin film," *Journal of Optoelectroncs and Biomedical Materials*, vol. 3, no. 4, pp. 95–100, 2011.

[13] J. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, Eaglewood, NJ, USA, 1971.

[14] R. A. Chikwenze and M. N. Nnabuchi, "The effect of Pb^{2+} precursor concentration on the optical and solid state properties of annealed PbSe thin films grown by solution growth method," *Journal of Optoelectronics and Advanced Materials*, vol. 12, no. 12, pp. 2363–2368, 2010.

[15] E. Vigil, L. Saadoun, J. A. Ayllón, X. Domènech, I. Zumeta, and R. Rodríguez-Clemente, "TiO_2 thin film deposition from solution using microwave heating," *Thin Solid Films*, vol. 365, no. 1, pp. 12–18, 2000.