

Research Article

Origin of Difference in Photocatalytic Activity of ZnO (002) Grown on a- and c-Face Sapphire

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The oriented (002) ZnO films were grown on a- and c-face sapphire by pulsed laser deposition. The X-ray diffraction analysis revealed that the oriented (002) ZnO films were epitaxially grown on the substrate successfully. The sample on a-face sapphire had higher crystal quality. However, the photocatalytic activity for Rhodamine B degradation of ZnO film on c-face sapphire was higher than that on a-face sapphire. The Raman spectrum and XPS analysis suggested that the sample on a-face sapphire had higher concentration of defects. The result of the contact angle measurement revealed that the sample on c-face sapphire had higher surface energy. And the investigation of the surface conductance implied that the higher light conductance was helpful for the photocatalytic activity.

1. Introduction

Semiconductor photocatalysis has attracted many attentions due to the extensive potential applications in renewable energy production and environmental remediation [1]. Many semiconductor oxides were evaluated for the photocatalytic activity for water splitting or organic compound decomposition [2–5]. Among the binary metal oxide photocatalysts, ZnO was studied extensively, especially for the samples with nanoplate, nanorod, microrod, and dumbbell-shape morphology [6–10]. Recently, ZnO photoanodes with the (100) preferential orientation have been shown to generate hydrogen under solar photon illumination [11]. However, the key factor of the given plane impacting the photocatalytic activity was not addressed due to the limit of the samples. This question would help us understand and improve the photocatalytic activity of the sample exposed one certain facet.

The ZnO sample exposed crystal plane was controllable when it was fabricated by pulsed laser deposition (PLD) via selecting the proper substrate [12–15]. The ZnO with the (001) plane could be grown on both a- and c-face sapphire [13, 15]. Although their crystal plane was the same, they

often exhibit different physical and chemical properties [16]. Consequently, in this study, the ZnO samples oriented (002) plane was prepared on a-plane and c-plane sapphire by PLD and investigated for photocatalytic activity. The sample on c-plane sapphire showed higher activity than that on a-plane sapphire. The observations revealed that the crystallinity and defects did not affect the photocatalytic activity positively, while the surface free energy and surface conductance had the positive effect.

2. Experimental

The ZnO thin films were deposited on a-plane and c-plane sapphire substrates by PLD. The fabrication conditions for the ZnO layer were as follows: laser repetition rate 3 Hz, target and substrate distance 50 mm, laser energy 300 mJ, O₂ partial pressure about 2.0×10^{-2} Pa, substrate temperature 873 K, and deposited time 0.5 h.

The thickness of ZnO thin films grown on a-plane and c-plane sapphire was estimated with the aid of ellipsometer (type II, Taijing Tuopu Co., China). The thickness of ZnO thin film grown on a-plane and c-plane sapphire was estimated

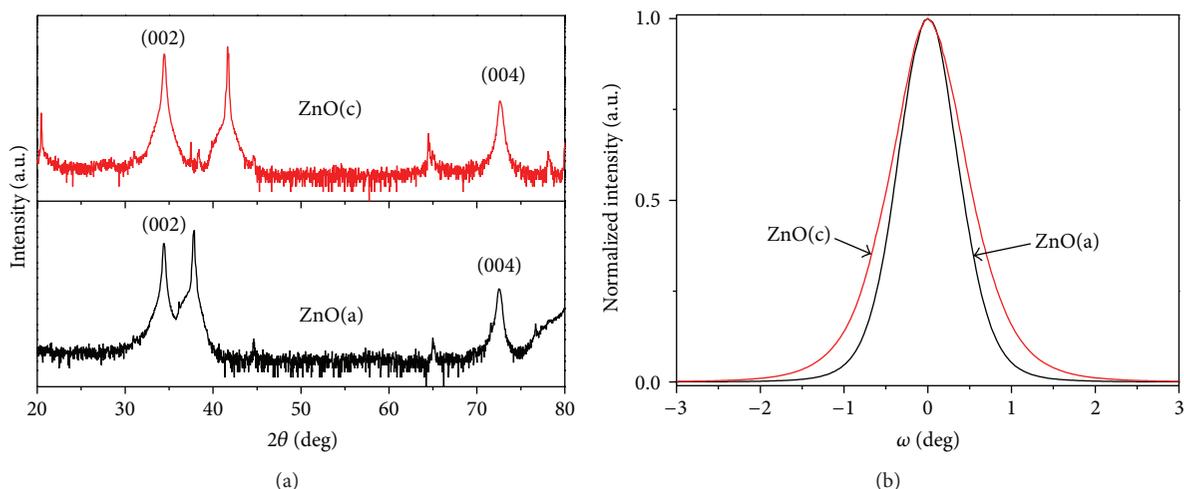


FIGURE 1: X-ray diffraction (XRD) patterns (a) and ω -scan spectra (b) of ZnO thin films grown on a-plane and c-plane sapphire.

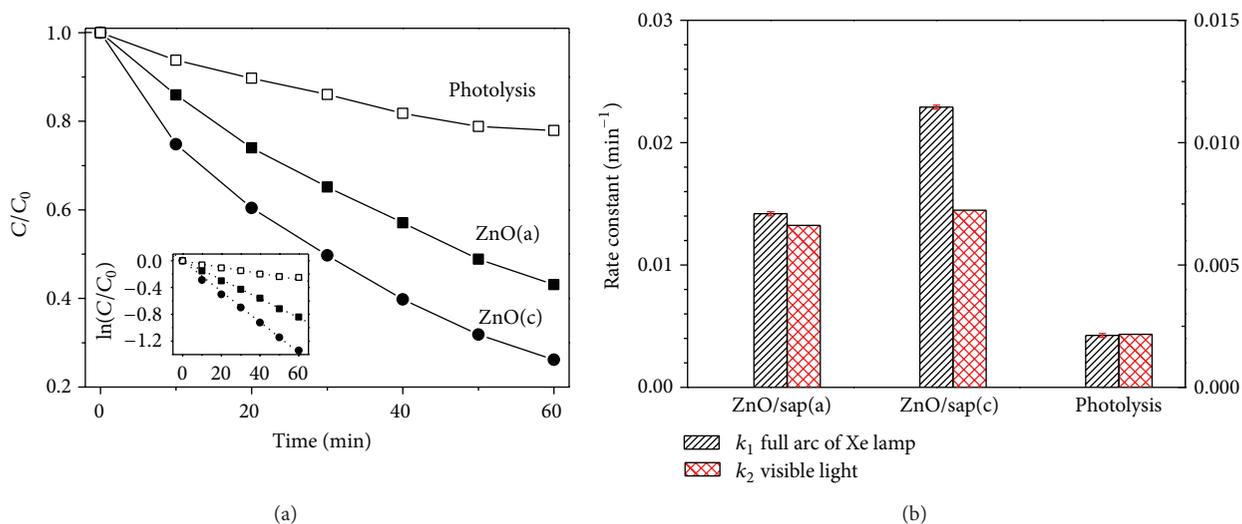


FIGURE 2: (a) Variation in RhB concentration over ZnO thin films grown on a-plane and c-plane sapphire; the inset of a is the plot of first order kinetics. (b) Rate constant in the degradation of RhB over ZnO thin films grown on a-plane and c-plane sapphire under full arc and visible light irradiation of Xe lamp.

to be ~ 270 nm. The crystal structures of samples were determined by an X-ray diffractometer (DX-2500 diffractometer, Fangyuan) with Cu $K\alpha$ radiation ($\lambda = 0.154145$ nm) in θ - 2θ mode. The carrier density was obtained from the Hall measurement. The surface morphology was observed by atomic force microscopy (AFM, SPA400, Japan). The transmittance spectrum was recorded with a UV-Vis spectrophotometer (Varian Cary 5000) using the air as the reference and transformed to the absorption spectra automatically. In the case of X-ray photoelectron spectroscopy (Thermo ESCALAB 250, USA), an Al anode with a monochromator was used to reduce the background signal. The binding energy was referenced to the C 1s peak taken at 284.8 eV. Raman scattering spectrum

was measured using a laser Raman spectrophotometer (RM-1000, Renishaw). Surface conductivity was measured on the samples covered by the plane fork electrode with the fork width of 0.1 mm under full arc of 450 W Xe lamp irradiation.

The photocatalytic activities of the as-prepared samples were evaluated by the Rhodamine B (RhB) under full arc and visible light irradiation of 300 W Xe lamp. The photocatalytic reaction was carried out over the sample with the area of 1 cm^2 in a 1 mL RhB solution in a sealed quartz cuvette with the light path length of 3 mm. There was no stirring during reaction. The initial concentration of RhB solution was about $10\text{ mg}\cdot\text{L}^{-1}$. After 30 min dark reaction, the variation in RhB concentration was in situ recorded in the interval of 10 min

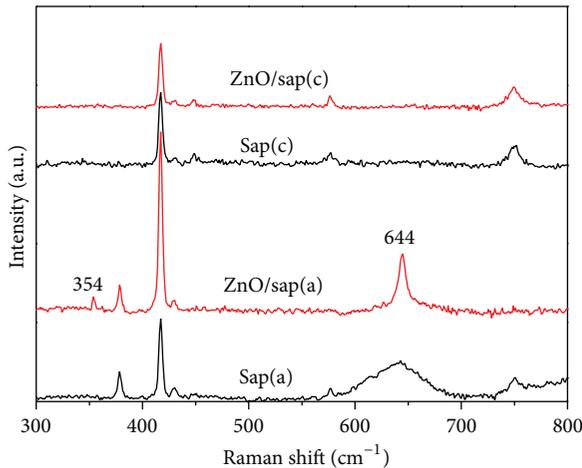


FIGURE 3: Raman spectra obtained from ZnO thin films grown on a-plane and c-plane sapphire.

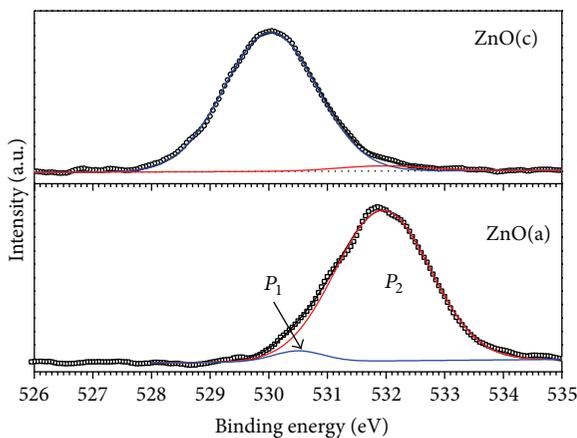


FIGURE 4: O 1s XPS line obtained from ZnO thin films grown on a-plane and c-plane sapphire.

using a UV-Vis spectrophotometer (UV2550, Shimadzu, Japan) by measuring the absorption spectrum.

3. Results and Discussion

The X-ray diffraction (XRD) patterns of ZnO thin films grown on a-plane and c-plane sapphire were shown in Figure 1(a). Obviously, the oriented ZnO films along with (002) were fabricated successfully. The lattice parameter along the c-axis for this ZnO film on a- and c-plane sapphire was 5.2096 and 5.2022 Å, respectively. For simplicity, hereafter, the samples on a-plane and c-plane sapphire were denoted as ZnO(a) and ZnO(c), respectively. The crystal qualities for the prepared samples are characterized by the ω -scan spectra, as shown in Figure 1(b). The full width at half maximum (FWHM) is 0.86° for ZnO(a) and 1.08° for ZnO(c), which is close to the previous results obtained from the samples prepared by PLD [17]. The smaller FWHM of ZnO(a) indicated that its crystal quality was better than that of

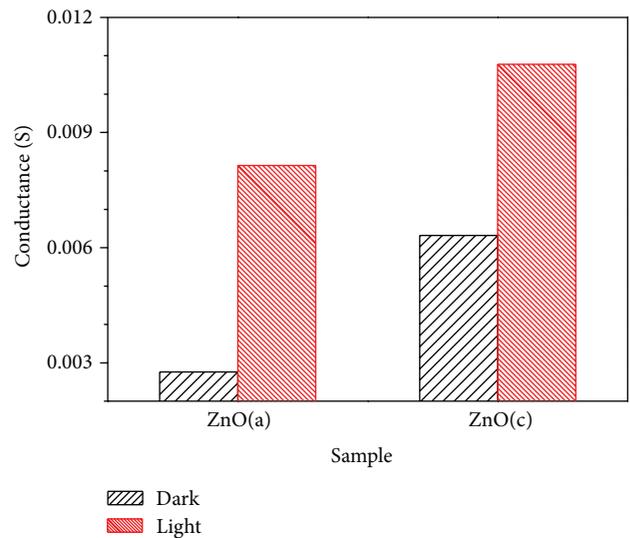


FIGURE 5: Conductance of ZnO thin films grown on a-plane and c-plane sapphire.

ZnO(c). The a-plane sapphire was nonpolarized, while the c-plane was polarized. The polarized substrate would offer an electric field during the deposition. The ZnO (002) was polarized plane. Therefore, the fact of better crystal quality of ZnO(a) was considered to be caused by the polarization of substrate.

Photocatalytic activity for the decomposition of RhB in an aqueous solution was evaluated in the presence of ZnO films under full arc and visible light irradiation of Xe lamp. Figure 2(a) is the variation in RhB concentration which was obtained from monitoring the main peak at ~554 nm. The 74% RhB was degraded by ZnO(c) after one hour irradiation, while 57% by ZnO(a). Additionally, the self-degradation of RhB was about 22%. When the reagent solution was dilute, the reaction rate (r) could be expressed as $r = kC$, where k is the apparent rate constant and C is the instantaneous concentration of the reactant. The plot of $\ln(C/C_0)$ versus time was shown in the inset of Figure 2(a). The reactions exhibited the first order reaction kinetics for ZnO(a) and ZnO(c). Consequently, the apparent rate constant was used to compare the photocatalytic activity. Figure 2(b) shows the apparent rate constant for RhB under full arc (k_1) and visible light irradiation (k_2), where the apparent rate constant under visible light irradiation was applied to characterize the self-sensitized degradation of RhB. The visible light activity was considered to be caused by the self-sensitized degradation of RhB because ZnO was a UV active photocatalyst. From Figure 2(b), it could be seen that the activity under full arc irradiation was larger than that under visible light, indicating that the RhB degradation was really related to the light excitation. Both ZnO samples showed higher activity than the photolysis, demonstrating that the ZnO played an important role in the degradation of RhB. The proportion of the self-sensitized degradation of RhB in the total degradation was very important to understand the real photocatalytic activity of ZnO. The ratio of k_2 to k_1 was used to estimate

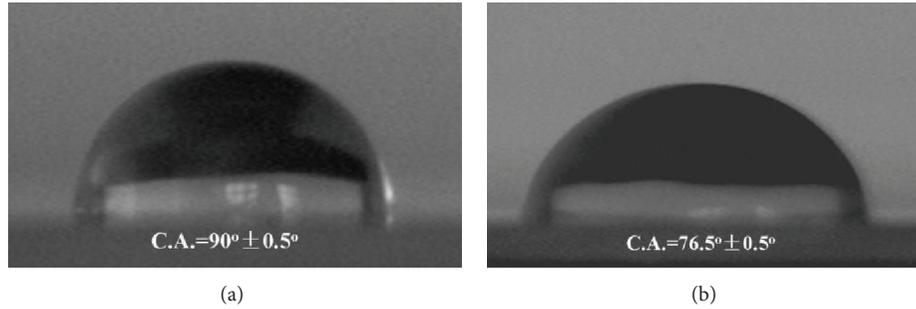


FIGURE 6: Contact angle obtained from ZnO thin films grown on a-plane and c-plane sapphire.

the proportion of the self-sensitized degradation of RhB in the total degradation. The larger k_2/k_1 ratio implied the higher proportion of the self-sensitized degradation of RhB, indicating the lower activity of ZnO. The ratio of k_2 to k_1 for ZnO(c) was 31%, which was the smallest compared to 46% for ZnO(a) and 51% for photolysis, implying that the RhB degradation due to ZnO(c) excitation was dominant in the total degradation.

The photocatalytic activity was affected by the bulk and surface properties. ZnO(a) had a better crystallinity than ZnO(c), revealing that the crystallinity was not the key factor to determine the photocatalytic activity in these samples. Also the optical band gap estimated from the absorption spectra was the same, but the absorption coefficient of ZnO(c) was larger than that of ZnO(a). The average roughness was estimated to be 1.1 nm for sample on a-face sapphire and 8.6 nm for sample on c-face sapphire. The sample on c-face sapphire showed higher activity than that on a-face sapphire, indicating that the larger roughness and absorption coefficient were helpful for photocatalytic activity.

To obtain the key factors to impact the photocatalytic activity of ZnO (001) plane, we had examined the optical properties, surface properties, and electrical property of the prepared samples.

The Raman spectra were shown in Figure 3. Except for the peaks of substrate, the new peaks at 644 cm^{-1} and 354 cm^{-1} were observed in ZnO(a), while now new peak was obtained in ZnO(c). The peak at 644 cm^{-1} was caused by the defects, such as the Zn interstitials or oxygen vacancies [18]. The appearance of 644 cm^{-1} peak indicated that some effects existed in ZnO(a). And almost the same profile between the ZnO(a) and substrate implied that few defects were in ZnO(c).

The O 1s XPS line was usually used to characterize the existence of oxygen vacancy [19]. The O 1s XPS line obtained from ZnO(a) and Zn(c) was shown in Figure 4. The O 1s region was fitted by two peaks with Gauss distribution, and these peaks located at 531.95 and 530.5 eV for ZnO(a) and at 531.95 and 530.03 eV for ZnO(c). The fitting of O 1s region with two-peak contribution indicated that at least two kinds of oxygen species were presented in the near surface domain of the ZnO films. The peak P_1 at about 530 eV was due to crystal lattice oxygen of ZnO, while the peak P_2 at

about 532 eV was due to chemisorbed oxygen on the film surfaces [20, 21]. These previous studies implied that the surface adsorbed oxygen could hide the signal of crystal lattice oxygen [21]. The more the adsorbed oxygen was, the weaker the signal of crystal lattice oxygen was. Moreover, the intensity of the peak P_2 was connected to the concentration of oxygen vacancies [19]. Consequently, we considered that the amount of the defects in ZnO(a) was more than that in ZnO(c). Taking into account the results of Raman spectra, it seems that the defects are not positive to the photocatalytic activity.

Surface conductivity, especially under light irradiation, was very important to the photoelectric processing in semiconductor. The surface conductivity in the dark and under full arc of Xe lamp irradiation was measured. The surface conductivity under light irradiation was larger than that in the dark, as shown in Figure 5, which was consistent with the previous report [22]. Moreover, the rate constants for RhB degradation increased with the increase in the conductivity under light irradiation. The light irradiation would bring much larger electron mobility than that in the dark [22]. The photocatalytic reaction contained light absorption, generation of e-h pairs, charge transfer, and chemical reaction on surface, apart from all kinds of recombination. After the generation of e-h pairs coming from the light excitation, the electron would transfer to the surface of photocatalyst. The higher surface conductance would be helpful to the charge transfer. According to the above description, it was thus reasonable to understand that the sample with the larger surface conductivity showed the higher activity.

Surface free energy could be evaluated from the contact angle measurement because the specimens did not have the special microstructure. Generally, the smaller the contact angle is, the higher the surface free energy is. The results of contact angle measurement for all the tested samples were shown in Figure 6. The contact angle for ZnO(a) was $90^\circ \pm 0.5^\circ$ and that for ZnO(c) was $76.5^\circ \pm 0.5^\circ$. The smaller contact angle for ZnO(c) revealed that it had higher surface free energy. Bi et al. proposed that the higher photocatalytic activity of Ag_3PO_4 could be obtained in the sample that exposed the face with the higher surface energy [23]. Therefore, the surface free energy was considered to be closely relative to the photocatalytic activity.

4. Conclusions

The ZnO samples oriented (002) plane was prepared successfully on a-plane and c-plane sapphire by PLD. The ZnO on c-plane sapphire showed higher activity than that on a-plane sapphire. The crystallinity and amount of defects did not have positive contribution on the photocatalytic activity, but the higher surface free energy and conductance had positive effects on the photocatalytic activity. The quantitative relationship between these factors and activity was being investigated.

Conflict of Interests

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

Acknowledgments

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