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Influence of Gas Flow Rate for Formation of Aligned Nanorods in ZnO Thin Films for Solar-Driven Hydrogen Production

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ZnO thin films have been deposited in mixed Ar/N_2 gas ambient at substrate temperature of 500°C by radiofrequency sputtering of ZnO targets. We find that an optimum N_2-to-Ar ratio in the deposition ambient promotes the formation of well-aligned nanorods. ZnO thin films grown in ambient with 25% N_2 gas flow rate promoted nanorods aligned along *c*-axis and exhibit significantly enhanced photoelectrochemical (PEC) response, compared with ZnO thin films grown in an ambient with different N_2-to-Ar gas flow ratios. Our results suggest that chamber ambient is critical for the formation of aligned nanostructures, which offer potential advantages for improving the efficiency of PEC water splitting for H_2 production.

INTRODUCTION

Photoelectrochemical (PEC) systems based on transition-metal oxides such as TiO_2, ZnO, and WO_3 have received extensive attention due to their potential application for H_2 production in aqueous solution by solar energy.[1–9] TiO_2 has been extensively studied for such applications. ZnO has a similar bandgap (~3.3 eV) and band-edge positions as compared with TiO_2. Furthermore, ZnO has a direct bandgap and higher electron mobility than TiO_2.[8] Thus, ZnO can be a potential candidate for PEC splitting of water for H_2 production.[9]

To improve the PEC response, a photoelectrode should have a high contact area with the electrolyte to provide more interfacial reaction sites. The morphological features of thin films such as grain size, grain shape, and surface area have profound influence on the performance of thin-film electrodes. Thus, electrodes with nanostructures have been applied to improve PEC properties.[10–12] However, most of these nanostructures are not single crystals and contain defects. It is known that defects typically act as recombination centers that can kill photon-generated electron–hole pairs before they can reach surfaces for reactions. Therefore, single-crystal nanostructures are highly desirable. For ZnO, various forms of single-crystal nanostructures such as nanowires, nanobelts, and nanorods have been reported.

It has been reported that ZnO nanorods were synthesized using catalysts, and recently, catalyst-free ZnO nanorods have been synthesized by various chemical and physical techniques such as metal-organic vapor-phase epitaxy (MOVPE), plasma-enhanced chemical vapor deposition (PECVD), and pulsed laser deposition (PLD).[10–13] In our earlier studies,[14,15] we found that single-crystal ZnO nanorods aligned along the *c*-axis can be synthesized by radiofrequency (RF) sputter deposition in mixed Ar and N_2 ambient, and ZnO films with aligned nanorods exhibited improved PEC performance as compared with ZnO films without nanorods.

So far, RF sputtering has not been considered as widely as other methods for growth of ZnO nanorods. Detailed examination of the deposition conditions for ZnO nanorod growth and study of ZnO nanorods for PEC application are needed.

In this paper, we report on the influence of the N_2-to-Ar gas flow rate ratio on the formation of aligned nanorods in ZnO thin films and their PEC performance. We find that deposition in optimum N_2-to-Ar ratio ambient leads to formation of single-crystal ZnO nanorods aligned along the *c*-axis. ZnO films with aligned nanorods exhibit significantly enhanced PEC response compared with ZnO thin films deposited in ambient with different N_2-to-Ar ratios. Our results suggest that the deposition ambient can be used to control the morphology of ZnO thin films

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and that aligned single-crystal nanorods can be potentially beneficial for PEC performance.

EXPERIMENTAL PROCEDURES

ZnO thin films were deposited by reactive RF sputtering of a ZnO target in ambient with different nitrogen-to-argon gas flow rate ratios. The nitrogen-to-argon ratio was varied from 0% to 75%. We refer to these samples as ZnO(0%N_2), ZnO(12.5%N_2), ZnO(25%N_2), ZnO(50%N_2), and ZnO(75%N_2). Transparent conducting F-doped SnO_2 (FTO)-coated glass (20–23 Ω/) was used as the substrate to allow PEC measurements. Prior to deposition, the substrates were ultrasonically cleaned by an acetone-methanol-deionized (DI) water sequence. The distance between the ZnO target and substrate was about 10 cm, and the substrates were rotated at 30 RPM to enhance deposition uniformity. The base pressure was below 1×10^{-6} Torr, and the working pressure was 5×10^{-3} Torr. The chamber ambient was mixed N_2 and Ar with gas flow ratio of $N_2/(Ar + N_2)$ = 0–75%. Prior to sputtering, presputtering cleaning was performed for 20 min to eliminate possible contaminants from the target. Sputtering was then conducted at RF power of 200 W. During deposition, the substrate temperature was maintained at 500°C. All the deposited samples were controlled to have similar film thickness of 0.5 ± 0.05 μm as measured by stylus profilometry.

Structural characterization was performed by x-ray diffraction (XRD) measurements, using an x-ray diffractometer (XGEN-4000, SCINTAG Inc.), operated with a Cu-K_α radiation source at 45 kV and 37 mA. The N concentration in the ZnO films was evaluated by x-ray photoelectron spectroscopy (XPS). Monochromatic Al-K_α radiation was used for all data sets, and the analyzer was set to 59 eV pass energy. Argon-ion sputtering (3 keV, 0.8 μA mm^{-2}, 120 s) was used to clean samples prior to analysis. The surface morphology was examined by atomic force microscopy (AFM) conducted in tapping mode with a silicon tip, and field-emission scanning electron microscopy (FE-SEM). The ultraviolet–visible (UV–Vis) absorption spectra of the samples were measured by an n&k analyzer 1280 (n&k Technology, Inc.) to investigate the optical properties.

PEC measurements were performed in a three-electrode cell with a flat quartz-glass window to facilitate illumination of the photoelectrode surface.[16–20] The sputter-deposited films were used as the working electrode. Pt plate and Ag/AgCl electrode were used as counter and reference electrodes, respectively. A 0.5 M Na_2SO_4 mild aqueous solution was used as the electrolyte for the stability of the ZnO films.[18–22] PEC response was measured using a fiber-optic illuminator (150-W tungsten halogen lamp) with an ultraviolet (UV)/infrared (IR) filter. Light intensity was measured by a photodiode power meter, using which the total light intensity with the UV/IR filter was fixed at 125 mW/cm^2.

RESULTS AND DISCUSSION

Figure 1 shows XRD curves for the ZnO thin films deposited at different nitrogen-to-argon ratios at substrate temperature of 500°C. We reported earlier that aligned nanorods can be formed in mixed N_2/Ar chamber ambient at substrate temperature of 500°C. The crystallinity of the ZnO thin films increases gradually with increasing nitrogen content in the chamber ambient up to 25%. Above 25% nitrogen, the crystallinity starts decreasing. Of all these chamber ambients, ZnO thin film deposited at 25% nitrogen showed greatly enhanced (002) peak. The ZnO thin film grown at 75% nitrogen exhibited the least crystallinity. The measured full-width at half-maximum (FWHM) of (002) peak of ZnO thin films decreased as the N_2 percentage in the chamber ambient increased from 0% to 25%, and started increasing again as the N_2 gas flow rate was increased above 25%. The FWHM of (002) peak for ZnO(0%N_2), ZnO(12.5%N_2), ZnO(25%N_2), and ZnO(50%N_2) was 0.25, 0.17, 0.14, and 0.18, respectively. It is known from recent reports that incorporated *N* atoms can deteriorate the crystal structure and modify the growth mode.[23–25] However, for substrate temperature above 300°C, no significant N can be incorporated. The rapid decrease of the FWHM values as the N_2 percentage in chamber ambient was increased from 0% to 25% indicates either increased crystallinity or formation of nanorods or nanowires along the *c*-axis. No significant N concentrations (at.%) were found for the ZnO thin films as measured by XPS.

AFM images revealed that the significantly increased (002) peak in the XRD curve, obtained for ZnO thin films, is largely due to the formation of nanorods aligned along the *c*-axis. Figure 2 shows AFM surface morphology (5 μm × 5 μm) of ZnO

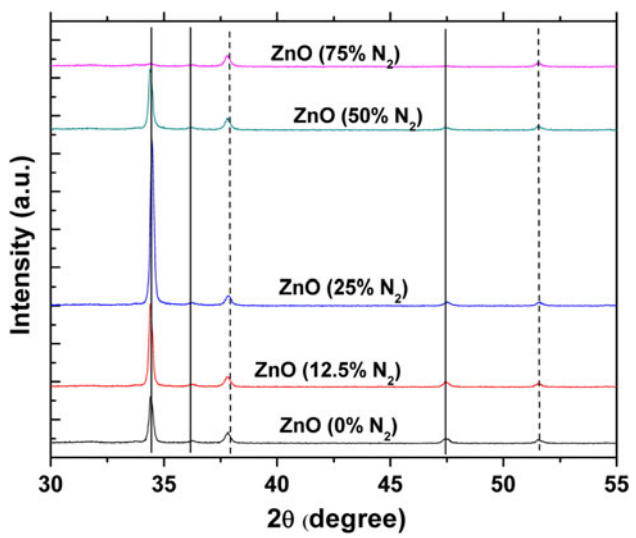

Fig. 1. XRD curves for ZnO thin films deposited at different nitrogen-to-argon ratios (color online).

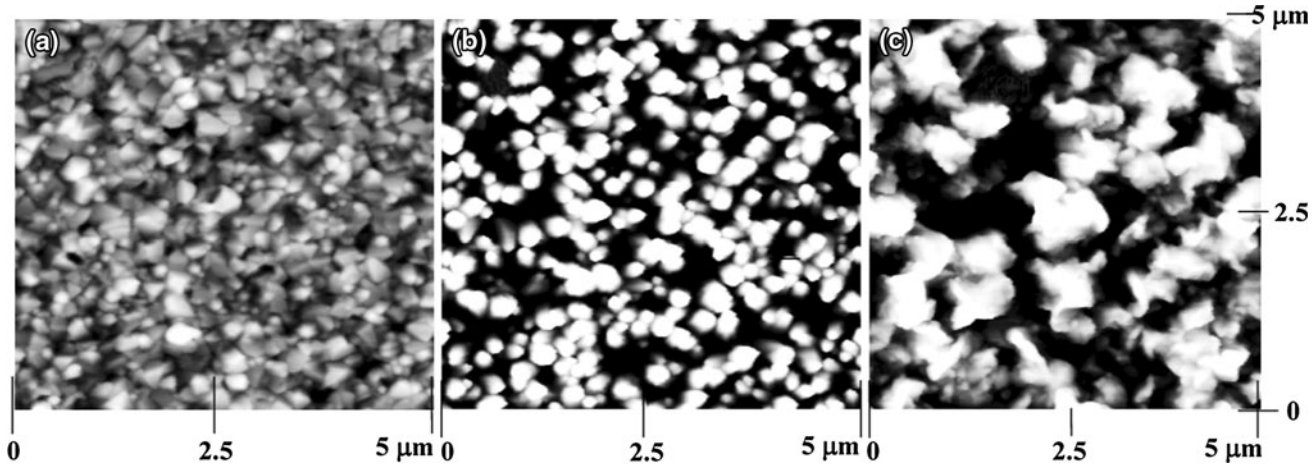

Fig. 2. AFM surface morphology (5 μm $\times$ 5 μm) of (a)–(c) ZnO thin films deposited at nitrogen to argon ratio of 0%, 25%, and 75%, respectively.

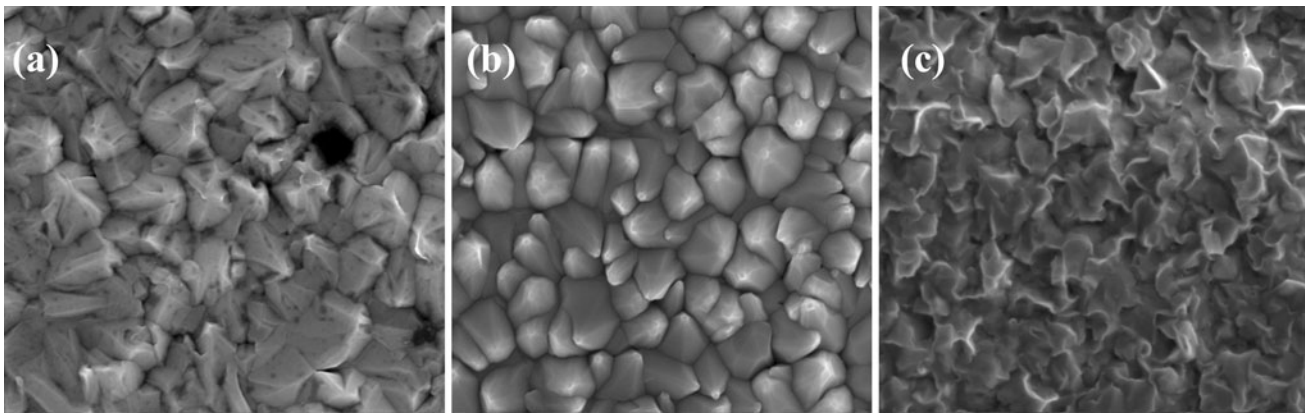

Fig. 3. FE-SEM top views of (a)–(c) ZnO thin films deposited at nitrogen-to-argon ratio of 0%, 25%, and 75%, respectively.

thin films deposited in ambient with 0%, 25%, and 75% nitrogen, respectively. It clearly shows that the ZnO thin film deposited at 0% N_2 has random orientation. ZnO thin film grown at chamber ambient with 25% N_2 reveals growth of hexagonal-like nanorods. It should be noted that the diameter of the nanorods is smaller than that of the grains in the polycrystalline ZnO thin film. The smaller FWHM value for the ZnO thin film is attributed to the nanorod feature.[10,11,26] ZnO thin film grown at 75% nitrogen chamber ambient is polycrystalline.

Figure 3 shows FE-SEM top views of the ZnO thin films deposited at 0%, 25%, and 75% nitrogen, respectively. It clearly shows that the nanorod structure was not present in the ZnO thin film grown at 0% and 75% N_2 chamber ambient, whereas ZnO(25%N_2) film exhibited vertically aligned, single-crystal hexagonal-like nanorods. No metal clusters were found at the end of the nanorods, indicating that the growth mechanism is not catalyst-assisted vapor–liquid–solid (VLS) growth.[10–12] Recently, catalyst-free ZnO nanorods/nanowires have been synthesized by various chemical and physical techniques such as MOVPE, PECVD, PLD, etc.[10–13] The nanorod structures provide high surface area and superior carrier transport (or conductivity) along the *c*-axis, which may lead to increased interfacial reaction sites and reduced recombination rate.[9,27] Therefore, the aligned nanorod films should lead to enhanced PEC response.

Figure 4 shows absorption coefficients of ZnO thin films deposited at different N_2-to-Ar gas flow rate ratios in the chamber ambient. The direct optical bandgaps of the films were determined by extrapolating the linear portion of each curve in Fig. 4 to $\alpha h\nu^2 = 0$. The measured optical bandgaps for ZnO thin films deposited at different N_2-to-Ar ratios were almost same (about 3.25 eV).[14–22,28] It should be noted that the films were deposited at substrate temperature of 500°C. No significant amount of nitrogen is incorporated into the film, as confirmed by XPS. However, ZnO thin film deposited with 25% nitrogen in the chamber ambient showed a slight reduction in bandgap. Since there is no detectable N incorporated into the ZnO(25%N_2)

nanorod film, bandgap reduction may be caused by intrinsic defects such as oxygen vacancies,[29] which are responsible for the absorption tail below 3 eV.

Figure 5a, b shows photocurrent–voltage curves for ZnO(0%N_2) and ZnO(25%N_2) thin films deposited at 500°C, respectively, under dark condition (black curve) and continuous illumination (red curve), with a UV/IR filter. A very small dark current up to a corresponding potential of 1.2 V is exhibited by both films. ZnO(25%N_2) thin film exhibited much higher photocurrent than the ZnO(0%N_2) film due to the aligned nanorods formed along the *c*-axis.

Figure 6 shows the measured photocurrents as a function of the nitrogen-to-argon gas flow rate ratio in the chamber ambient for ZnO thin films. To observe the effects of the percentage of N in the chamber ambient on the PEC response, we measured the photocurrent at 1.2 V potential for ZnO thin films under continuous illumination with the UV/IR filter. For 0% nitrogen, the photocurrent of ZnO thin film is lower than that for the films deposited at 12.5% nitrogen chamber ambient. Low crystallinity could be responsible for this reduced photocurrent. However, the photocurrent increases for ZnO thin films as the nitrogen percent in the chamber ambient increased up to 25%, and again starts decreasing as the nitrogen percent increased further above 25%. The ZnO thin film deposited at 25% nitrogen exhibited the best PEC response. This enhancement can be attributed to the aligned nanorod structure along the *c*-axis. The decrease in photocurrent above 25% nitrogen in the chamber ambient is because of the absence of nanorod structure in the films; instead, random orientation of grains is observed. Our results show that there is an optimum chamber ambient for formation of nanorods along the *c*-axis in sputter-deposited ZnO thin films which leads to greatly enhanced PEC response.

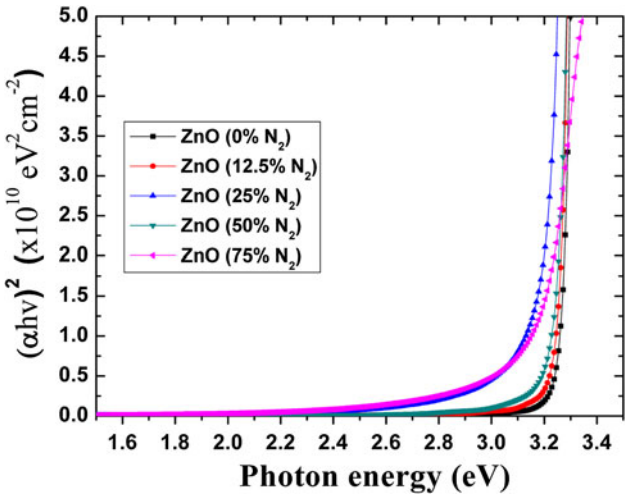

Fig. 4. Absorption coefficients for ZnO thin films deposited at different nitrogen-to-argon ratios (color online).

CONCLUSIONS

ZnO thin films were synthesized on FTO substrates by reactive RF magnetron sputtering at substrate temperature of 500°C with different ratios of nitrogen to argon gas flow rates. We investigated the structural properties and PEC responses of the deposited ZnO thin films. We found that use of a 25% N_2-to-Ar gas flow rate ratio helps to promote formation of aligned ZnO nanorods, whereas 75% N_2-to-Ar gas flow rate ratio results in polycrystalline films. ZnO thin films with aligned nanorods exhibited significantly enhanced PEC response compared with films grown at other nitrogen-to-argon flow rate ratios. Our results suggest that there must be an optimum nitrogen gas flow rate in

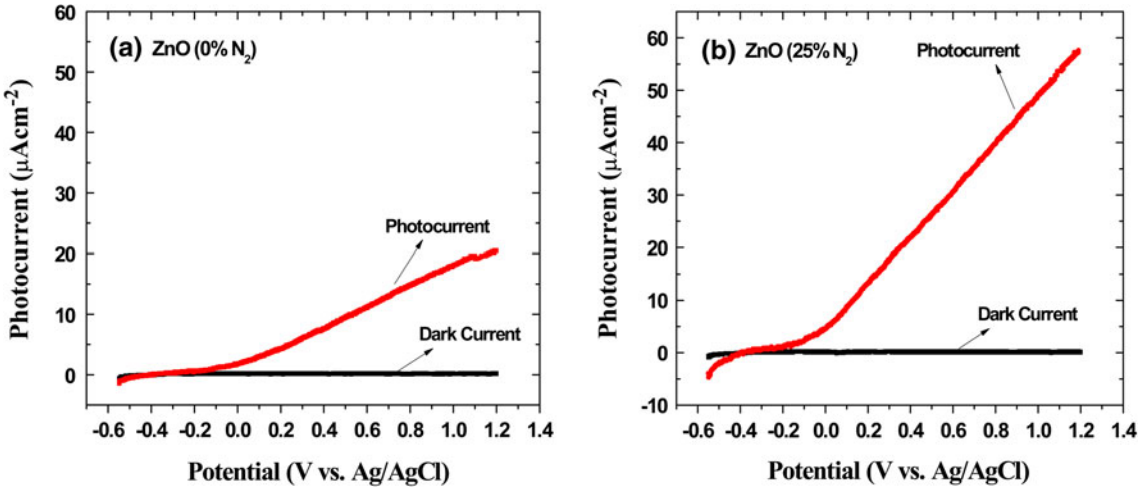

Fig. 5. Photocurrent–voltage curves of (a) ZnO(0%N_2) and (b) ZnO(25%N_2) films, deposited at 500°C under (red curve) continuous illumination and (black curve) dark condition, with a UV/IR filter. Electrolyte and scan rates were 0.5 M Na_2SO_4 mild aqueous solution and 5 mV/s, respectively (color online).

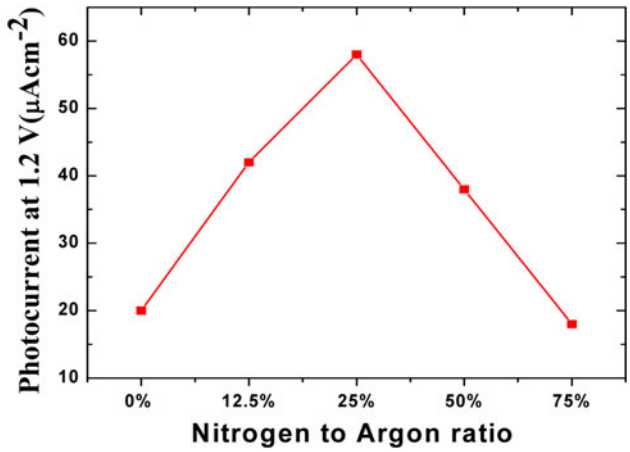

Fig. 6. Photocurrents measured at 1.2 V as a function of nitrogen-to-argon ratio for ZnO thin films deposited at substrate temperature of 500°C (color online).

the ambient to promote formation of well-aligned nanorod structure in the film, resulting in significantly enhanced PEC response.

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