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Broadband anti-reflective properties of grown ZnO nanopyramidal structure on Si substrate via low-temperature electrochemical deposition

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Abstract

Anti-reflection coatings (ARCs) are widely used in various optical and optoelectronic devices to minimize the reflection of light. In this study, we demonstrated the fabrication of ZnO nanopyramidal structures on Si substrate via low-temperature electrochemical deposition. We also investigated the anti-reflection (AR) properties of these nanostructures compared with nanorods and planar ZnO texture on Si substrates. We changed the growth conditions, namely, growth temperature and applied current density, to modify the shape of the ZnO nanorod tips. Nanopyramidal structures with continuously varying refractive index profiles in a single layer were obtained. Reflectance spectra show that the nanopyramid-based texture reduced the reflection of light in a broad spectral range from 380 nm to 1000 nm and is much more effective than nanorod and planar textures. For nanopyramid arrays (NPAs) with average tip diameter of 20 nm, we achieved a 6.5% reflectance over a wide range of wavelengths, which is superior to an optimized single-layer ARC such as SiO_2 or TiO_2. These textured ZnO ARCs may be applied to a wide variety of photovoltaic devices and other anti-reflection applications with large areas because of their low temperature, fast growth, and simple fabrication.

Keywords: E. Electrode; Anti-reflection; ZnO nanopyramid; Nanorods; Si substrate

1. Introduction

Anti-reflection coating (ARC) is a type of optical coating widely applied on the surface of lenses and many optoelectronic devices to minimize the reflection of light [1–5]. ARCs are used to increase light transmittance through interfaces that would otherwise reflect some of the incident light. A portion of light is reflected, and a portion is transmitted when light travels from one medium to another. Reflection occurs when light propagates through two media with different refractive indices. For air and Si media, approximately 35% of incident light is reflected back to the Si surface because of the difference in the refractive indices of air (1.0) and Si (3.8). Therefore, ARCs fabricated by depositing a thin planar layer with low refractive index between air and Si are widely used to enhance absorption by minimizing the abrupt change in the refractive index at the interface.

Conventional single-layer ARCs [6] consist of a single quarter-wavelength layer of transparent material, such as SiO_2 or TiO_2. These coatings depend significantly on the wavelength and angle of incident light because the anti-reflection (AR) process is realized by destructive interference.

Double-layer ARCs have been extensively investigated because single-layer ARCs cannot cover a broad range of light spectrum [7,8]. However, fabrication of multilayer ARCs is expensive because of the stringent requirement of high vacuum, material selection, and layer thickness control. Additionally, thermal mismatch-induced lamination and material diffusion of multilayer ARCs limit the device performance at high power densities.

Sub-wavelength structured surface with dimensions smaller than the wavelength of light is an alternative to multilayer ARCs [9]. Few studies have reported about sub-wavelength structured surface ARCs fabricated by photolithography [10],

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e-beam lithography [11], pulsed laser irradiation [12], and patterning by mask [13] or template [14–15]. However, these top–down techniques require expensive and complex manufacturing processes.

Lee et al. [16] recently reported that transparent well-aligned ZnO nanorod arrays (NRAs) are promising ARC structures to suppress spectral reflection because of the sub-wavelength structure and wide band gap of ZnO.

In the present work, we focused on the fabrication of ZnO nanopyramidal structures with sub-wavelength structures and broadband anti-reflective properties by using low-temperature electrochemical method. We also investigated the effects of highly tapered ZnO NRAs on ARC performance. We changed the growth conditions to modify the shape of the ZnO nanorod tips, thereby continuously varying the refractive index profiles in a single layer. Subtle changes in the nanorod tip shape resulted in significantly improved AR properties. The superior AR of the nanopyramid array (NPA) provides great potential for application in photovoltaic and electro-optical devices.

The electrochemical method is a promising approach among various ZnO nanostructure synthesis methods because of its simplicity, rapid process, and low cost.

2. Materials and methods

Si substrates were cleaned using a standard cleaning method (Radio Corporation of America). A ZnO thin film measuring ~100 nm was deposited on n-type Si (100) by using radio-frequency magnetron sputtering at room temperature. The samples were then heat treated in air at 500 °C for 15 min to obtain ZnO seeds for electrochemical growth. The ZnO-seeded samples were placed on an external wall of screw-capped Teflon cell, as shown in Fig.1.

Pyramid-shaped and rod-shaped ZnO nanostructures were synthesized using analytical-grade zinc nitrate hexahydrate [$Zn(NO_3)_2$●$6H_2O$] (Sigma Aldrich) and hexamethylenetetramine [HMT; $C_6H_{12}N_4$] (Sigma Aldrich) without any additives or metal catalysts via electrochemical deposition. In a typical reaction process, the mixture of 25 mM aqueous solution of [$Zn(NO_3)_2$●$6H_2O$] and HMT were stirred for 10 min in a beaker and then transferred to a screw-capped Teflon cell. A simple thermometer was inserted into the solution, allowing temperature control and measurements. A Pt wire (99.99%) was used as the counter electrode, and the ZnO-seeded Si was used as the working electrode. The growth of pyramid-shaped ZnO nanostructure was carried out for 1 h at a constant current density of 450 μA cm−2 at reaction temperature of 85 °C, and the rod-shaped ZnO nanostructure was grown at reaction temperature of 95 °C with an applied current density of 100 μA cm−2 for 1 h. After the ZnO nanostructures were synthesized, the samples were rinsed with deionized water and dried under nitrogen gas flow.

Morphologies of the ZnO nanostructures were observed under a field emission scanning electron microscope (FE-SEM; FEI Nova NanoSEM 450). The phase and crystallinity of the nanostructures were determined using an X-ray diffractometer (PANalytical, X'Pert PRO). Reflectance spectra of the samples were measured on a spectrophotometer (Cary 500, Varian) with the wavelength ranging from 200 nm to 1000 nm.

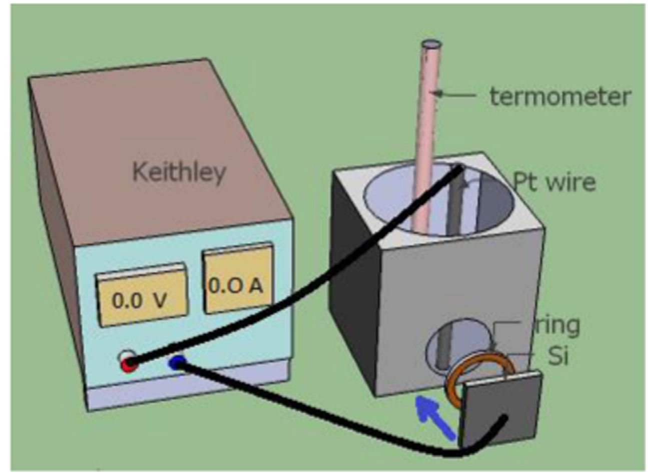

Fig. 1. Schematic diagram of the teflon cell used for, electrochemical deposition of ZnO nanostructures.

3. Results and discussion

Variations in the nanorod growth conditions strongly influenced the morphology of the textured ZnO ARCs. Fig. 2 shows the FE-SEM images of the top and side views of the ZnO nanorods synthesized under different conditions. Fig. 2(a) and (e) show a narrow (~50 nm) distribution of nanorods grown electrochemically at 85 °C under an applied current density of 100 μA cm^{-2}. By contrast, nanorods grown at higher temperature and current density display broader diameter distribution, hexagonal, and flat top structure. Fig. 2 (c) and (g) show high compact of thick nanorods grown at 95 °C under a current density of 450 μA cm^{-2}.

Interestingly, fixing the reaction temperature at 85 °C under an applied current density of 450 μA cm^{-2} resulted in NPA-like morphology over the whole substrate [Fig. 2(d), (h), and (s)]. Each ZnO NPA consists of a hexagonal stem with a tapering tip. The average diameters of the base and tip of the NPAs are in the range of 110 ± 20 and 20 ± 5 nm, respectively. The typical length of the NPAs is ~1.5 μm. Moreover, these NPAs are grown almost aligned to the substrate, which is not vertical in direction but slightly tilted.

X-ray diffraction (XRD) patterns of the ZnO nanorods with different growth conditions are illustrated in Fig. 3. Four pronounced wurtzite ZnO diffraction peaks, namely, (100), (002), (101), and (004), appear at 2θ=31.75°, 34.43°, 36.26°, and 72.61°, correspondingly [17]. The XRD spectra of all ZnO nanorods revealed a strong (002) peak, indicating that the nanorods demonstrate high orientation with c-axis vertical to the substrate surface.

The optical properties of the four different substrates, namely, bare Si (sample 1), ZnO thin film (sample 2), ZnO NRAs (sample 3), and ZnO NPAs (sample 4), were quantitatively compared to investigate how efficiently the newly fabricated ARCs improved the anti-reflectance.