Nano-structured optical hetero-coatings for ultraviolet protection

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ABSTRACT

A new nano-structured optical hetero-coating, i.e., combination of absorptive Ge and transparent conductive oxide Ga-doped zinc oxide (GZO) film has been developed for ultraviolet (UV) protection. GZO (3% Ga) film spin-coated by metal organic deposition (MOD) acts as a UV light absorber because of its large band gap, while Ge film deposited by electron-beam evaporation is used as visible light absorber. Modulating the nanometer-level Ge thickness causes the prominent variations of transmittance and reflectivity, therefore coloring Ge/GZO system, ascribed to strong interference effect and therefore absorption resonance.

1. Introduction

Ultraviolet (UV) radiation is severely harmful to human skin, eyes and immune system. Even long time exposition in UV radiation will cause skin cancer and damage cornea and retina [1,2]. It is essential to protect us from exposure to hazardous UV radiation.

Transparent conducting oxide (TCO) thin films, which possess good electrical conductivity and optical transparency at visible region, are of considerable interest in applications such as touch screens, flat-panel displays [3,4], light emitting diode (LED) [5,6], solar cells [7–9]. Ga-doped zinc oxide (GZO) is one of the most attractive candidates with the advantages of low cost, high performance and stability. The applications of GZO films were mainly in transparent electrode [10–16], electromagnetic interference (EMI) shield to our knowledge [17]. As one kind of wide band gap materials, strongly depending on the Ga doping concentrations, the theoretical band gap of GZO varies from 3.3 to 4.9 eV, and the corresponding absorption edge fluctuates from 253 nm to 376 nm, which contributes to a good choice for ultraviolet (UV) protective materials. Recent work [18] shows coloring effect by depositing ultrathin Ge films on Au reflective layer, ascribing to the variation of reflectivity by modulating the Ge thickness. The novel structure provides a simple way for spectra modification, nevertheless, its applications are only limited to coloring fields such as labeling and visual art. In this work, we firstly proposed a new nano-structured optical hetero-coatings for UV protection, i.e., combination of absorptive Ge and transparent conductive oxide GZO film, in which GZO film acts as UV light absorber, while Ge film acts as visible light absorber. The interference effect between Ge and GZO heterostructure is strongly expected.

2. Experimental details

The UV protective hetero-coatings consisted of GZO (3% Ga) and Ge films were successively deposited on quartz substrates by metal organic deposition (MOD) [19,20] and electron-beam evaporation, respectively. Gallium acetylacetonate and zinc acetylacetonate were used as the starting materials, and ethanol was selected as the solvent. Stoichiometric Ga and Zn sources were dissolved in enhanol at room temperature with the total metal concentration of 0.2 M. The precursor films were spin-coated on the substrates with the spin speed of 2500 rpm for 40 s, and baked at 100 °C in air for 5 min to evaporate the solvent. The samples were then heat treated at 300 °C for 10 min to decompose organic component in films. By repeating this process, desired thickness can be obtained. The decomposed amorphous films were crystallized at 500 °C in air for 1 h, and finally annealed at 500 °C in Ar-4% H2 atmosphere for 30 min in order to reduce the resistivity. 250 nm-GZO samples were obtained and the resistivity was 5.42 × 10−2 Ω cm. The Ge films were subsequently deposited on GZO films at a rate of 1 nm/min under a pressure of 5 × 10−4 Pa without substrate heating. The thickness was controlled for required optical properties.

The crystal structure of the GZO films was characterized by X-ray diffraction using a Bede D1 X-ray diffractometer. The surface morphology was examined by Atomic Force Microscopy (AFM, CSPM 5500). The thickness of Ge and GZO was evaluated by X-ray reflectivity using the X-ray diffractometer and cross-sectional
scanning electron microscopy (SEM, JSM-5900). The optical properties were evaluated using an ultraviolet–visible spectrometer (Lamda 750, PerkinElmer).

3. Results and discussion

Fig. 1 shows the typical XRD pattern of MOD-derived GZO films. A strong and dominating peak at about 34.4° was found, corresponding to (002) diffraction peak of wurtzite phase of GZO, indicating preferred c-axis orientation growth. Compared with undoped ZnO film, the intensity of (002) peak decreased significantly with 3% Ga incorporation. The deteriorated crystallinity of GZO film might be attributed to the stresses induced by the difference of ionic radii of Zn and Ga dopant [21]. It should be pointed out that there are several weak peaks in Fig. 1 which can be attributed to GZO (100), (101), (102), (110), confirming polycrystalline phase. The grain size of GZO film estimated by the Scherrer formula [22] was 16.7 nm from the XRD θ–2θ spectra.

The surface morphology and the surface roughness of GZO film were investigated by AFM. The film surface in Fig. 2 is dense and smooth with no detectable microcracks. The root-mean-square (rms) surface roughness, measured from a 2 μm × 2 μm area, is 1.6 nm, which provides a good template for evaporated Ge films.

The optical properties of GZO film were assessed, as shown in Fig. 3. The transmittance at the wavelength beyond 400 nm was more than 85%, and dropped rapidly to nearly zero at wavelength below 400 nm (Fig. 3(a)), indicating GZO film allowed visible and infrared light to pass while absorbing UV light. As a kind of direct band gap materials, the optical band gap of 3.35 eV was calculated by an extrapolation of linearly part of (αhν)² vs hν plots (Fig. 3(b)), which responds to UV region (200–400 nm). These results demonstrate that GZO is a good candidate for UV light protection.

Nano-structured Ge/GZO hetero-coatings were assembled by modulating the nanometer-level thickness of Ge absorptive layers. Fig. 4 shows the reflectance and transmittance spectra of Ge/GZO films with 7, 14 and 21 nm Ge. The transmittance in Fig. 4(a) was near zero at the wavelength below 300 nm, which could meet the requirement of the standard of UV protection. Thicker Ge films would result in lower transmittance, which was consistent with the characteristics of Ge. Fig. 4(b) shows the reflectivity spectra of Ge/GZO films. The minimum of reflectivity spectrum indicates the destructive interference and strong absorption resonance [23–25], which is typical phenomenon of interference effect. The wavelength corresponding to lowest reflectivity of Ge/GZO system moved to long wavelength as Ge thickness increase, as shown in Fig. 4(b). Different part of visible region reflectance of Ge/GZO system as Ge thickness varied, as a result, different colors appeared on Ge/GZO coatings (inset of picture in Fig. 4(b)). Despite large difference between highly reflective Au and transparent GZO, the phenomenon of strong absorption resonance and coloring effect still existed. The same interference phenomenon of Au and GZO may be caused by good conductivity of GZO films. These interesting results explore the conception of Fabry–Perot type Ge–Au system [18] to half-transparent Ge–GZO system, and expand applications from decoration function to UV protection.
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Reference


4. Conclusions

The UV protective hetero-coatings consisted of GZO (3% Ga) and Ge films were successively deposited on quartz substrates by MOD and electron-beam evaporation, respectively. Modulating the reflectivity of Ge/GZO system by changing Ge thickness resulted in coloring effect due to strong interference effects. The combination of visible light absorptive Ge and transparent conductive GZO film provides a new way for UV protection.

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