Materials Letters 152 (2015) 290–292

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Nano-structured optical hetero-coatings for ultraviolet protection

Pei Guo, Jie Xiong*, Xiaohui Zhao, Bowan Tao, Xingzhao Liu*

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

ARTICLE INFO

Article history:
Received 2 February 2015
Accepted 26 March 2015
Available online 3 April 2015

Keywords:
Structural
Optical materials and properties
Metal organic deposition
Ultraviolet protection
Coloring effect

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 exposion 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 enthanol was selected as the solvent. Stoichiometric Ga and Zn sources were dissolved in enthanol 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% H_2 atmosphere for 30 min in order to reduce the resistivity. 250 nm-GZO samples were obtained and the resistivity was $5.42 \times 10^{-3}\ \Omega$ 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

---

* Corresponding authors. Tel.: +86 2883201232; fax: +86 2883202569.
E-mail addresses: jiexiong@uestc.edu.cn (J. Xiong), xzliu@uestc.edu.cn (X. Liu).

http://dx.doi.org/10.1016/j.matlet.2015.03.129
0167-577X/© 2015 Elsevier B.V. All rights reserved.

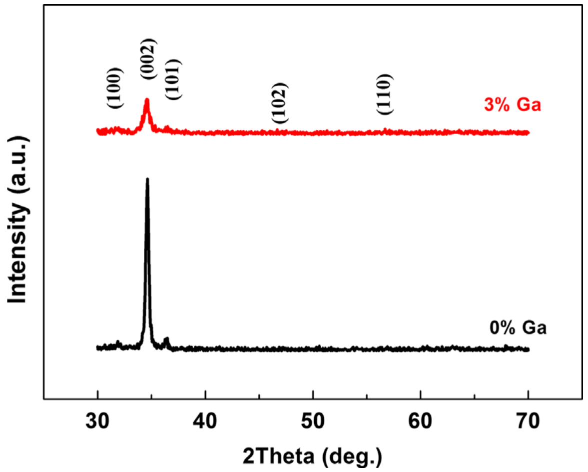

Fig. 1. Typical θ–2θ scan of 250 nm-thick GZO film grown on quartz substrate.

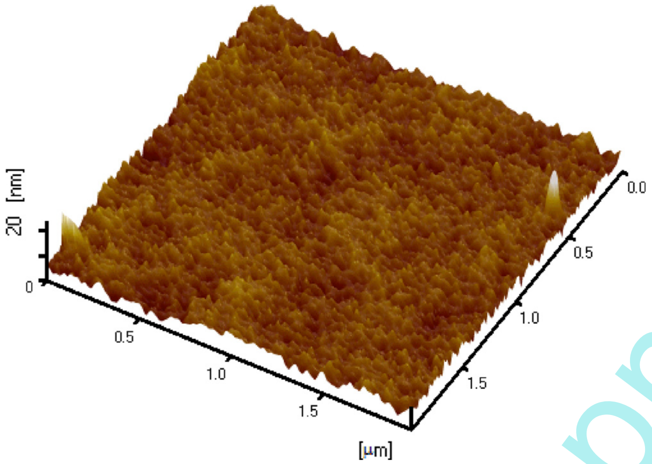

Fig. 2. Typical AFM image of GZO thin films (RMS = 1.6 nm).

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.

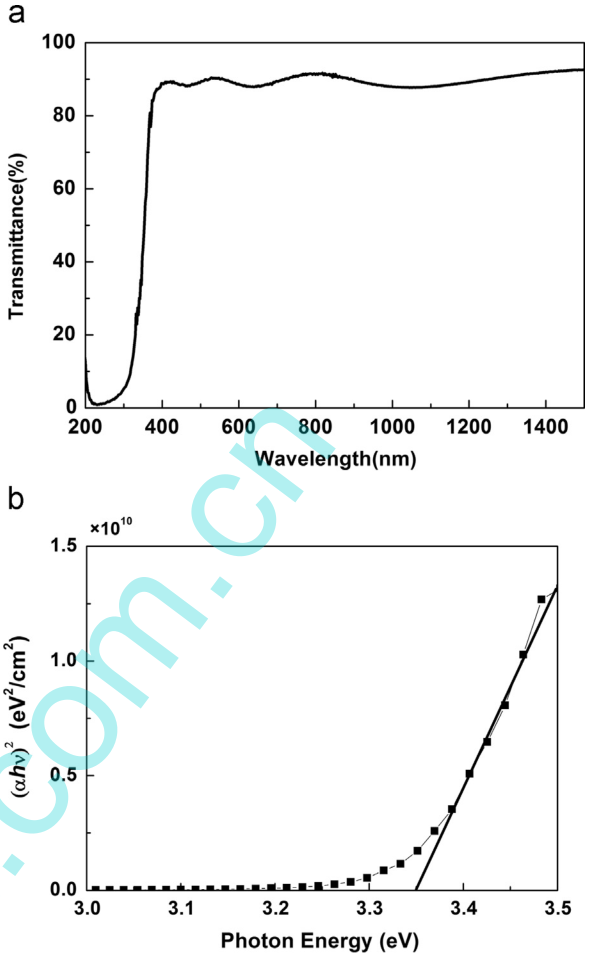

Fig. 3. (a) Transmission spectra for the GZO films and (b) square of absorption coefficient as a function of photon energy for GZO films.

The optical properties of GZO film were assessed, as shown in Fig. 3. The transmittace 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 $(\alpha h\nu)^2$ vs $h\nu$ 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 charactericisics of Ge. Fig. 4(b) shows the reflectivity spectra of Ge/GZO films. The minimum of reflective 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 wavelengh 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.

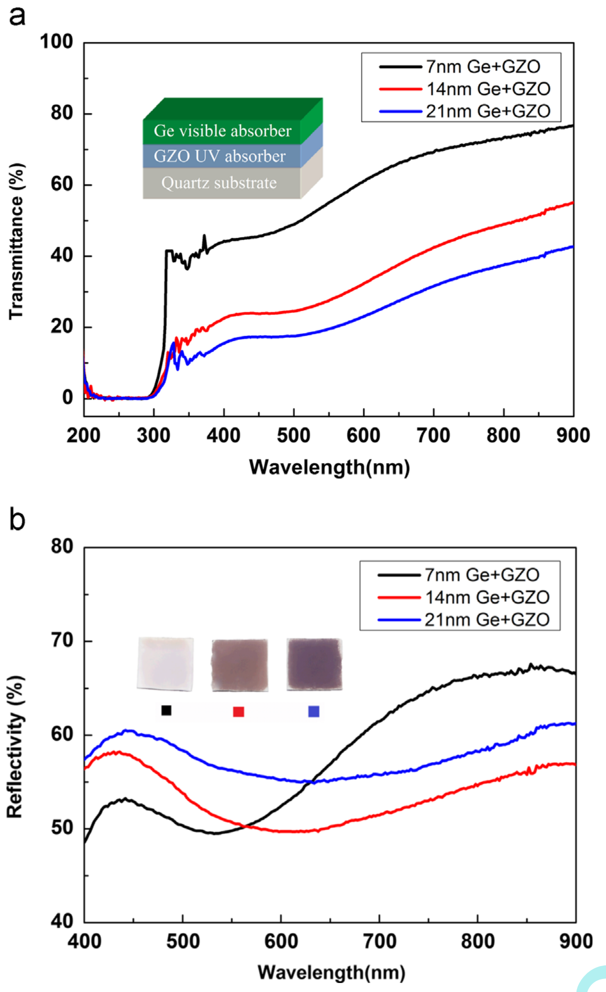

Fig. 4. (a) Transmittance and (b) reflectance spectra of Ge/GZO films with 7, 14 and 21 nm Ge.

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.

Acknowledgements

We gratefully acknowledge the support of the National Natural Science Foundation of China under Grant no. 91421110, National Basic Research Program (973) of China through Grant no. 2015CB358600, Sichuan Youth Science and Technology Innovation Research Team Funding (No. 2011JTD0006), and Sichuan Provincial Fund for Distinguished Young Academic and Technology Leaders (No. 2014JQ0011) for this work.

Reference

[1] Armstrong BK, Kricker A. The epidemiology of UV induced skin cancer. J Photochem Photobiol B-Biol 2001;63:8–18.
[2] Ringvold A. Corneal epithelium and UV-protection of the eye. Acta Ophthalmol Scand 1998;76:149–53.
[3] Kawazoe H, Yasukawa M, Hyodo H, Kurita M, Yanagi H, Hosono H. P-type electrical conduction in transparent thin films of $CuAlO_2$. Nature 1997;389(6654):939–42.
[4] Fortunato E, Barquinha P, Martins R. Oxide semiconductor thin-film transistors: a review of recent advances. Advan Mater 2012;24(22):2945–86.
[5] Kim H, Horwitz JS, Kim WH, Makinen AJ, Kafafi ZH, Chrisey DB. Doped ZnO thin films as anode materials for organic light-emitting diodes. Thin Solid Films 2002;420:539–43.
[6] Liu H, Avrutin Ve N, Ozgur U, Morkoc H. Transparent conducting oxides for electrode applications in light emitting and absorbing devices. Superlattices Microstruct 2010;48(5):458–84.
[7] Muller J, Rech B, Springer J, Vanecek M. TCO and light trapping in silicon thin film solar cells. Sol Energy 2004;77:917–30.
[8] Guillen C, Herrero J. TCO/metal/TCO structures for energy and flexible electronics. Thin Solid Films 2011;520:1–17.
[9] Zang ZG, Nakamura A, Temmyo J. Single cuprous oxide films synthesized by radical oxidation at low temperature for PV application. Opt Express 2013;21:11448–56.
[10] Minami T. Transparent conducting oxide semiconductors for transparent electrodes. Semicond Sci Technol 2005;20:S35–44.
[11] Fortunato E, Ginley D, Hosono H, Paine DC. Transparent conducting oxides for photovoltaics. MRS Bull 2007;32:242–7.
[12] Tak YH, Kim KB, Park HG, Lee KH, Lee JR. Criteria for ITO (indium-tin-oxide) an organic light thin film as the bottom electrode of emitting diode. Thin Solid Films 2002;411:12–6.
[13] Calnan S, Tiwari AN. High mobility transparent conducting oxides for thin film solar cells. Thin Solid Films 2010;518:1839–49.
[14] Armstrong NR, Veneman PA, Ratcliff E, Placencia D, Brumbach M. Oxide contacts in organic photovoltaics: characterization and control of near-surface composition in indium-tin oxide (ITO) electrodes. Acc Chem Res 2009;42:1748–57.
[15] Lee S, Noh JH, Han HS, Yim DK, Kim DH, Lee JK, et al. Nb-Doped TiO_2: a new compact layer material for TiO_2 dye-sensitized solar cells. J Phys Chem C 2009;113:6878–82.
[16] Harvey SP, Mason TO, Gassenbauer Y, Schafranek R, Klein A. Surface versus bulk electronic/defect structures of transparent conducting oxides: I. Indium oxide and ITO. J Phys D-Appl Phys 2006;39:3959–68.
[17] Yamada T, Morizane T, Arimitsu T, Miyake A, Makino H, Yamamoto N, et al. Application of low resistivity Ga-doped ZnO films to transparent electromagnetic interference shielding material. Thin Solid Films 2008;517:1027–31.
[18] Kats MA, Blanchard R, Genevet P, Capasso F. Nanometre optical coatings based on strong interference effects in highly absorbing media. Nature Mater 2013;12:20–4.
[19] Bhuiyan M, Paranthaman M, Salama K. Solution-derived textured oxide thin films – a review. Supercond Sci Technol 2006;19:R1–21.
[20] Xiong J, Xu WL, Feng XH, Guo P, Zhao XH, Tao BW. Chemical solution route to epitaxial gallium nitride thin films. Chem Lett 2014;43:447–9.
[21] Nishino J, Ohshio S, Kamata K. Preparation of aluminum-doped zinc oxide films by a normal-pressure CVD method. J Am Ceram Soc 1992;75:3469–72.
[22] Xie YB, Yuan CW. Visible-light responsive cerium ion modified titania sol and nanocrystallites for X-3B dye photodegradation. Appl Catal B: Environ 2003;46:251–9.
[23] Panjan M, Gunde MK, Panjan P, Cekada M. Designing the color of AlTiN hard coating through interference effect. Surf Coat Technol 2014;254:65–72.
[24] Sheng CC, Cai YY, Dai EM, Liang CH. Tunable structural color of anodic tantalum oxide films. Chin Phys B 2012;21:088101.
[25] Chiu TL, Hsiao YP, Chuang YT, Lai CM, Ho HC. Colored reflective organic light-emitting device without bias. Org Electron 2014;15:785–91.