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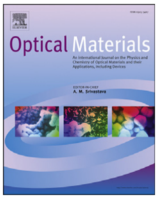

Characterization of hexagonal ε-$Ga_{1.8}Sn_{0.2}O_3$ thin films for solar-blind ultraviolet applications

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ABSTRACT

$Ga_{1.8}Sn_{0.2}O_3$ thin films were deposited on *c*-plane Al_2O_3 (0001) substrates by laser molecular beam epitaxy technology. Well crystallized (002) oriented ε-phase $Ga_{1.8}Sn_{0.2}O_3$ thin films were obtained at the substrate temperature above 750 °C and the oxygen partial pressure more than 5×10^{-3} Pa. The band-gap slightly shrinks with Sn^{4+} ions incorporated into Ga^{3+} sites, showing an excellent solar-blind ultraviolet (UV) characteristic. The conductivity of hexagonal ε-$Ga_{1.8}Sn_{0.2}O_3$ films is very low in the dark, and permitting the design and fabrication of solar-blind photodetector. The photodetector exhibits obvious photo-response under 254 nm UV light irradiation, and it increases in photocurrent with both the rise of applied bias and optical input power. The results suggest that ε-$Ga_{1.8}Sn_{0.2}O_3$ thin film is a promising candidate for using in solar-blind photodetectors.

1. Introduction

With the improvement of the epitaxial growth and the process techniques, the wide band-gap semiconductors attracted increasing interest for upcoming novel device applications. Recently, gallium oxide (Ga_2O_3) as a unique ultraviolet (UV) transparency with the band-gap of 4.9 eV–5.3 eV, is fascinating attention as a promising new candidate for application to solar-blind UV photodetectors [1–4]. Ga_2O_3 occurs in five polymorphous structures depending on ambient conditions, like α-, β-, γ-, δ-, and ε-phase [5–7]. The solar-blind photodetectors based on pure α- and β-phase Ga_2O_3 have been demonstrated in our previous studies [3,4]. Although the device performance could improve by changing the interface of metal-electrode/semiconductor [8] and doping technology [9,10], the resistivity is also upsurge in the dark resulting in a decrease in photocurrent sensitivity.

With the exception of the α- and β-phase, researchers have not paid much attention to the other phases of Ga_2O_3. The crystal structure of ε-Ga_2O_3 maintain unclear for more than a half century although the powder *x*-ray diffraction intensities were reported in 1952 [5]. In recently years, it is confirmed that the crystal structure of ε-Ga_2O_3 belonged to the high symmetry hexagonal system with space group $P6_3mc$ (PDF# 01-082-3196) [11]. The lattice parameters of ε-Ga_2O_3 are a = b = 2.90 Å, c = 9.26 Å, respectively, and the band-gap is 4.9 eV. The growth of pure ε-Ga_2O_3 thin films was proved by Oshima et al. for the first time in 2015 on GaN, AlN, and β-Ga_2O_3 substrates [12]. The ε-Ga_2O_3 is metastable structure which have a tendency to transform to β-Ga_2O_3 depending on growth conditions [11,13]. Sn-doped ε-Ga_2O_3 films was obtained from β-Ga_2O_3 through increasing the growth temperature by Orita et al. on *c*-plane sapphire substrates [13]. The conductivity of Sn-doped ε-Ga_2O_3 films is two orders of magnitude than β-Ga_2O_3 may be due to the formation of deep donor energy level with the phase transition. Meanwhile, *C*-plane (0001) sapphire substrates could provide distortion force in order to the phase transition from β-Ga_2O_3 to ε-Ga_2O_3 [13]. In this paper, we explored the growth of ε-$Ga_{1.8}Sn_{0.2}O_3$ epitaxial thin films on *c*-plane sapphire substrates under different temperature and oxygen pressure by laser molecular beam epitaxy (L-MBE) technology. Meanwhile, in consideration of the particularly suitable dark resistance and band-gap of ε-$Ga_{1.8}Sn_{0.2}O_3$ thin film for solar-blind photodetector, we fabricated

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a prototype device with metal-semiconductor-metal (MSM) structure using ε-$Ga_{1.8}Sn_{0.2}O_3$ epitaxial film and studied the UV photo-response characteristic.

2. Experimental details

A substrate of *c*-plane Al_2O_3 (0001) single crystal was put in the deposition chamber and the base pressure in chamber was 1×10^{-6} Pa. The Ga_2O_3 and 10 mol % of SnO_2 powders were thoroughly mixed according to the composition ratio, pressed into a disk, and then sintered. The laser ablation was carried out at a laser fluence of ~5 J/cm^2 using a KrF excimer laser with a wavelength of 248 nm. The target-substrate distance was 50 mm and *in-situ* reflection high energy electron diffraction (RHEED). The total number of pulse laser is fixed at 3000 and the laser frequency is 1 Hz. The thickness of the films was estimated to be 80 nm by scanning electron microscope (SEM). The crystallinity and orientation of the thin films were investigated by X-ray diffraction (XRD) at θ-2θ scan using a PANalytical X'pert PRO diffractometer with Cu K_a ($\lambda = 1.5405$ Å) radiation. Ultraviolet–visible (UV–vis) absorption spectrum was recorded using a Hitachi U-3900 UV–visible spectrophotometer. The chemical compositions and valences of elements were analyzed by X-ray photoelectron spectroscopy (XPS). For the fabrication of solar-blind photodetector, the interdigital Au/Ti electrode was deposited on the thin film surface using a shadow mask and radio frequency magnetron sputtering system. The size of an interdigitated electrode was 2.8 mm long, 0.2 mm wide, and the finger spacing was 0.2 mm (Fig. 3(a)). Thus the effective irradiated area was 0.045 cm^2. The current-voltage (I-V) and time-dependent photo-response of photodetectors were measured by a Keithley 2450. An UV-lamp was served as the light source with the wavelength of 254 nm.

3. Results and discussion

Fig. 1(a) (up) shows the representative XRD pattern of $Ga_{1.8}Sn_{0.2}O_3$ thin film deposited on Al_2O_3 (0001) substrate with the growth condition of ~800 °C & 5×10^{-1} Pa. It is observed that the diffraction peaks are located at around 19.09°, 38.79° and 59.75° except for the diffraction peaks of Al_2O_3 substrates. All of them belong to $Ga_{2-x}Sn_xO_3$ and no peaks derive from Sn metal clusters, Sn oxide, or Sn_xGa_y phases. On the basis of the powder diffraction file, the peaks position is identified as ε-Ga_2O_3 (PDF# 6-509). The peaks position are corresponding to (002) and higher order peaks of hexagonal ε-Ga_2O_3. The ε-$Ga_{1.8}Sn_{0.2}O_3$ thin films could achieve with the temperature above 750 °C and the oxygen pressure exceed 5×10^{-3} Pa through our tests. Compared to a (-201) oriented β-$Ga_{1.8}Sn_{0.2}O_3$, is reported in Fig. 2(a) (low). The high 2θ about 59° could highlight the difference of the XRD peak positions, which becomes negligible at low angle because of the small difference between the inter-planar spacing of β- and ε-phase. The high crystallographic quality of the epitaxial film is demonstrated by the value of FWHM = 0.104° of the (002) diffraction peak, which is smaller than the reports by others [14]. The UV–vis absorbance measurements are important in evaluating the optical parameters, for example, the absorption coefficient and band-gap, and so on. Fig. 1(b) shows that the UV–vis absorbance spectrum of $Ga_{1.8}Sn_{0.2}O_3$ thin film deposited on Al_2O_3 (0001) with the growth condition of ~800 °C & 5×10^{-1} Pa. It is evident that ε-$Ga_{1.8}Sn_{0.2}O_3$ thin film has a significant absorption at wavelengths less than 280 nm, located at the lower edge of the solar-blind region. A further analysis of the optical spectrum is completed to calculate the band-gap (E_g). The E_g can be derived according to the energy exponential relation [15]:

$$\alpha h\nu = B\left(h\nu - E_g\right)^{1/2} \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the energy of the incident photon, B is the constant, respectively. The optical absorption coefficient (α) is evaluated using the following relation:

$$\alpha = [1/d]\ln\left(10^A\right) \tag{2}$$

where A is the absorbance, and d is the film thickness, 80 nm in our case. The E_g of the thin film is obtained through fitting the linear region of the $(\alpha h\nu)^2$ versus $h\nu$ plot, and shown by the inset to Fig. 2(b). The E_g is 4.88 eV, which is smaller than that of ε-Ga_2O_3

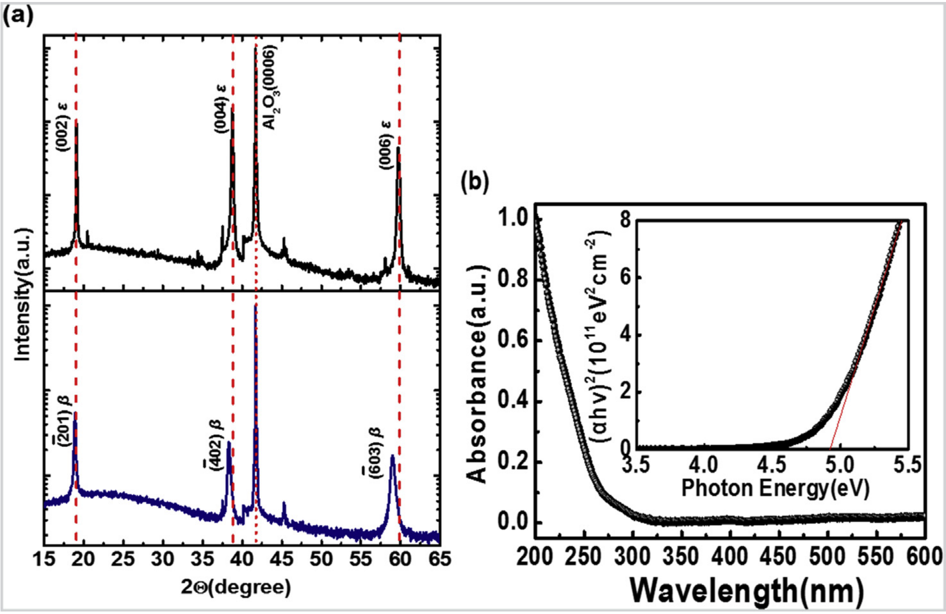

Fig. 1. (a) XRD pattern of $Ga_{1.8}Sn_{0.2}O_3$ thin film with the growth condition of ~800 °C & 5×10^{-1} Pa, a (-201) oriented β-$Ga_{1.8}Sn_{0.2}O_3$ film as a comparison. (b) Absorption spectrum of ε-$Ga_{1.8}Sn_{0.2}O_3$ thin film, the E_g is shown by the inset.

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