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Effects of substrate temperature on the properties of Ga-doped ZnO by pulsed laser deposition

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Abstract

High-quality transparent conductive gallium-doped ZnO (GZO) thin films were deposited on quartz glass substrates using pulsed laser deposition. The structure and electrical and optical properties of the as-grown GZO films were mainly investigated. In X-ray diffraction, (002) and (004) peaks were detected, indicating that Ga doping did not cause structural degradation of wurtzite ZnO. The chemical state of GZO films was investigated by X-ray photoelectron spectroscopy. The GZO films formed at a substrate temperature of 300°C showed a low electrical resistivity of 8.12×10^{-5} Ω cm, a carrier concentration of 1.46×10^{22} cm^{-3} and a carrier mobility of 30.96 cm^2/Vs at an oxygen pressure of 0.67 Pa. A visible transmittance of above 90% was obtained.

Keywords: Ga-doped ZnO (GZO); Pulse laser deposition (PLD); X-ray photoelectron spectroscopy (XPS); Electrical properties and measurements; Structure properties; Optical properties

1. Introduction

ZnO is an inexpensive optical material that has attracted much attention recently [1,2]. Undoped ZnO thin films generally typically exhibit *n*-type conduction with a background electron concentration as high as 10^{21} cm^{-3} [3]. When doped with group-III elements, such as Al and Ga, its resistivity can be reduced to $1.2–1.3\times10^{-4}$ Ω cm [4]. This is a II–VI semiconductor, highly transparent in the visible region with a wide and direct band gap of about 3.37 eV at room temperature and a high exciton binding energy of 60 meV. This material is very attractive because it has many applications such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers and thin-films transistors [5–9]. Various techniques, including chemical vapor deposition, sputtering, pulsed laser deposition (PLD) and atomic layer epitaxy, have been used to deposit crystalline ZnO thin films. Among the several fabrication techniques, PLD has attracted much attention because the fabrication process is quite suitable for optoelectronic devices using the ZnO thin films. The composition of films grown by PLD is quite close to that of the target, even for a multi component target. PLD films may be crystallized at deposition temperatures lower than those of other physical vapor deposition techniques due to the high kinetic energies of the ionized and ejected species in the laser plumes [10]. However, it is difficult to make the transparent layer on the optoelectronic devices because the electrical and optical properties of ZnO films vary markedly depending on the PLD conditions. A comprehensive report of our results on fabrication of Ga-doped ZnO (GZO) films by PLD with different deposition temperatures, and their effects on the structural, electrical and optical properties of the GZO films are given in the paper.

2. Experimental details

Fig. 1 shows a schematic diagram of the PLD system. Transparent conductive GZO films were prepared by pulsed laser deposition on quartz glass substrates. The pulsed laser was a KrF excimer laser (Lambda Physik, LPX305icc, $\lambda=248$ nm, 25 ns pulse width) with an energy fluence of 2 J/cm^2. The GZO

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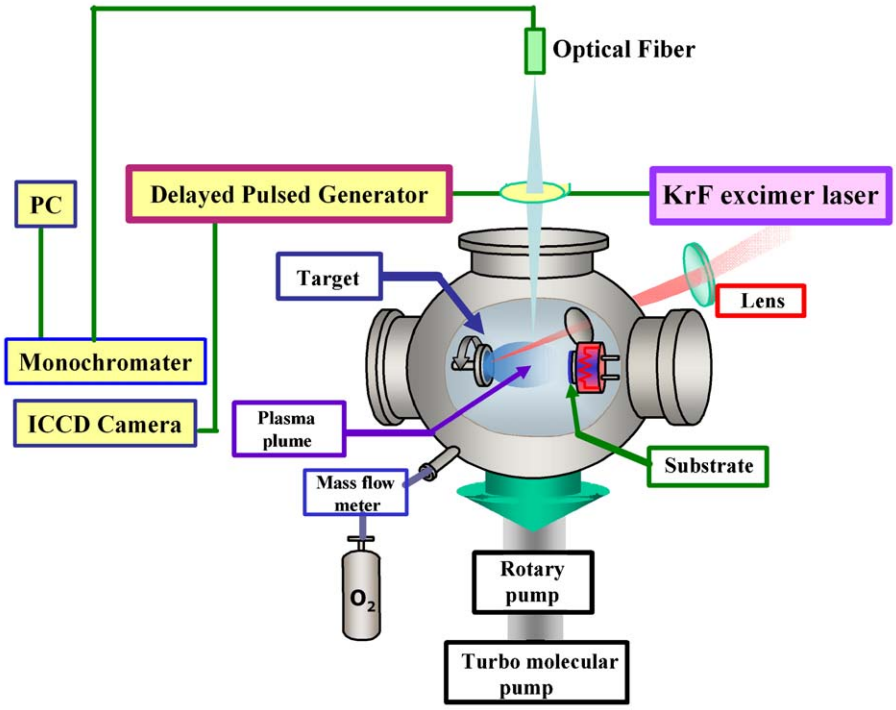

Fig. 1. Schematic diagram of the KrF excimer laser ablation system.

films were prepared by ablating a ZnO target containing 5 wt.% Ga_2O_3. A substrate was placed 40 mm away from the target and could be heated up to 1000 °C. The typical growth run consisted of 9000 laser shots with a repetition rate of 10 Hz. All of the films were also deposited on quartz glass cleaned in an ultrasonic bath using acetone and then ethanol for 5 min. The deposition chamber was initially evacuated to 5×10^{-3} Pa and, during deposition, oxygen gas was introduced into the growth chamber and the pressure was 0.67 Pa using a conductance valve and a turbo molecular pump. The as-grown GZO films were characterized by X-ray diffraction (XRD, Rigaku, RINT 2100/PC) with a CuKα (λ=1.5406 Å) source. Surface atomic composition analyses were performed by X-ray photoelectron spectrometer (XPS, VG Scientific, Sigma Probe) with an AlKá (1486.6 eV). The surface morphology of the deposited films was observed by atomic force microscopy (Seiko Instrument, SPI 3800N). The growth rate and the thickness of the sample were determined by cross-sectional scanning electron microscopy (JEOL JSM-T200), using an acceleration voltage in the 5–20 kV range. Then the resulting GZO films revealed thickness of about 200 nm. Transmission through the films was measured using a UV–visible spectrophotometer in the wavelength range from 200 to 800 nm. The electrical properties of the GZO films were measured by the van der Pauw method in a magnetic field (B=0.3 T) at room temperature.

3. Results and discussion

3.1. Structure characterization

A series of films grown in 0.67 Pa of O_2 were investigated by varying the substrate temperature. The XRD spectra of the GZO films deposited are shown in Fig. 2. Two diffraction peaks corresponding to (002) and (004) reflections are predominant and indicate that the film has a *c*-axis direction with an out-of-plane lattice parameter of around 5.2 Å. They show the characteristic of the hexagonal ZnO wurtzite, the *c*-axis being perpendicular to the substrate plane [11]. At higher substrate temperatures, the intensity of (002) peaks increased. Fig. 3 shows that the full width a half maximum (FWHM) of the XRD

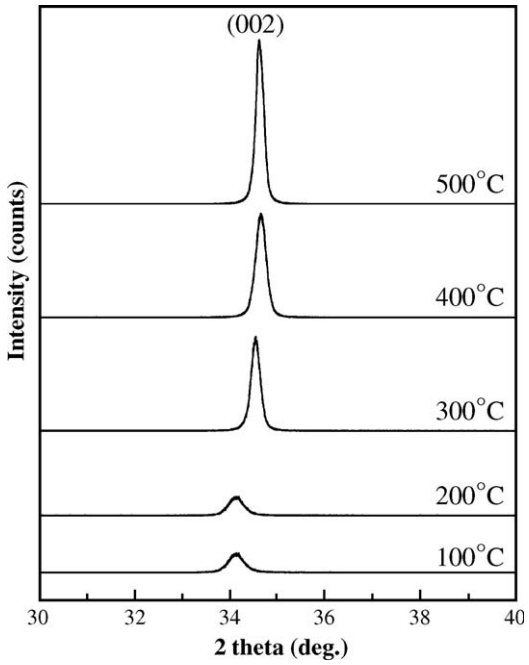

Fig. 2. XRD peaks for different GZO films grown under 0.67 Pa of O_2 at various substrate temperatures.

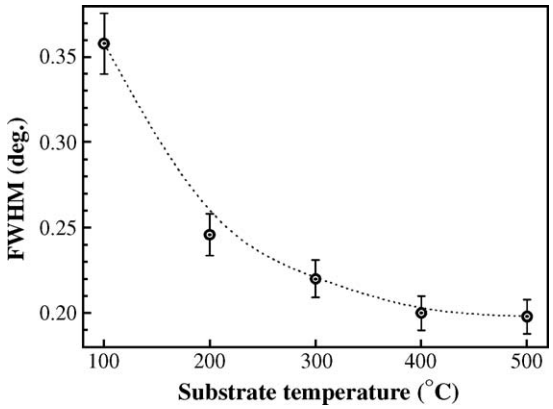

Fig. 3. FWHM of 2θ scan plotted as a function of deposition temperature (for oxygen pressure of 0.67 Pa).

(002) peaks are plotted by calculation. The FWHM values decreased from 0.360° to 0.198° as growth temperature increased from 100 to 500 °C. These results indicate that the high growth temperature can improve the crystallinity of the GZO film due to small crystallites coalesce together to make larger crystallites in the GZO films [12]. XRD measurements do not detect any trace of Ga elements in 5 wt.% doped sample due to the solubility of the Ga in ZnO crystals.

After the measurement of crystallographic structure of GZO films by XRD, XPS was applied to identify the change of chemical structure caused by substrate temperature and in order to find the Ga elements in the GZO films. XPS spectrum

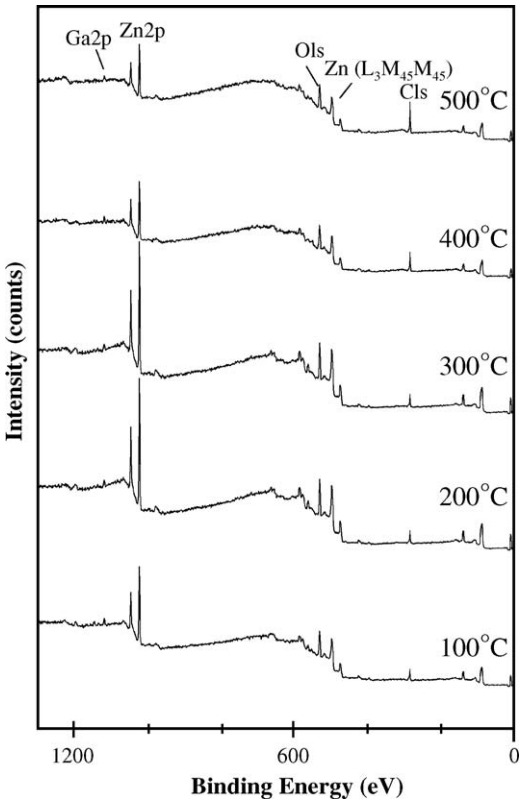

Fig. 4. GZO peaks by XPS as a function of substrate temperature: XPS was applied to identify the change of chemical structure caused by substrate temperature.

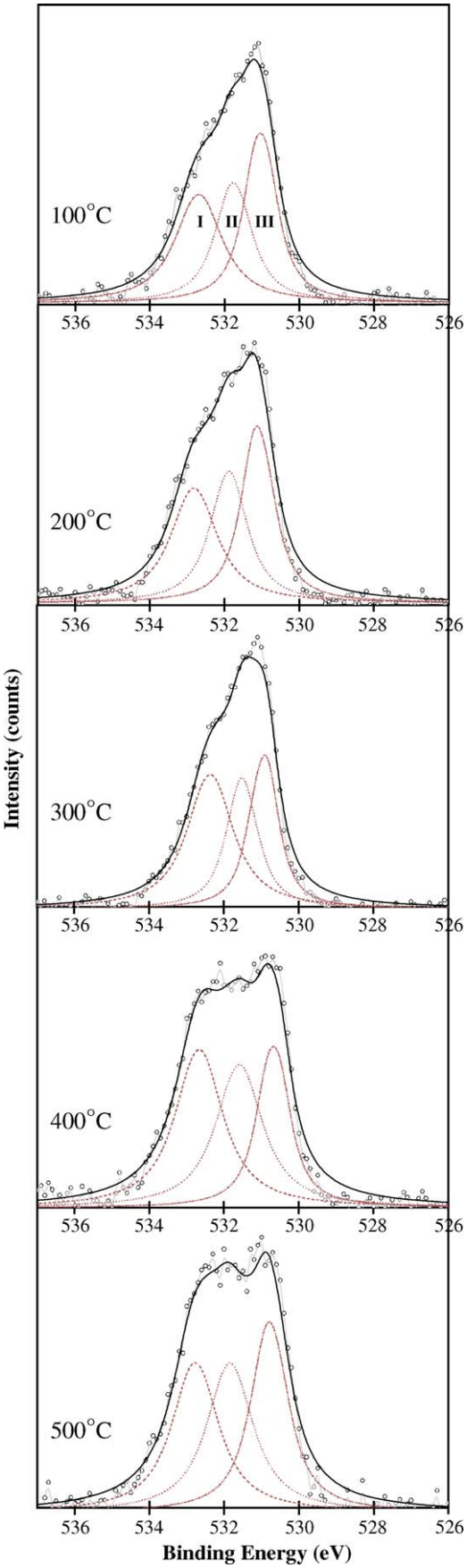

Fig. 5. The change of O 1s as function of substrate temperature.

showed the peaks at 1117.72, 1022.23, 530.9 and 285.43 eV from the photo-ionization gallium 2s (Ga 2s), zinc 2s (Zn 2s), oxygen 1s (O1s) and carbon 1s (C 1s), respectively (Fig. 4). The C contaminants were found to be increased with increasing growth temperature maybe due to the remainder on quartz glass substrate after cleaning process. The typical O 1s peak in the surface can be consistently fitted by three nearly Gaussian, centered at 532.30±0.30, 531.51±0.03 and 530.93±0.03 eV, respectively (Fig. 5). The high binding energy component located at 532.30±0.30 eV is usually attributed to the presence of loosely bound oxygen on the surface on ZnO film. The peak (O I) at 532.30±0.30 eV was reported that the chemisorbed oxygen impurities could be considered as $-CO_3$, adsorbed H_2O or adsorbed O_2^- [13]. It was also observed that this component slight increased as growth temperature increased from 300 to 500 °C. The slight increase of this component in films grow at higher substrate temperature from 300 to 500 °C may be contamination of the alkali ions from quartz glass substrates [14]. The component on the low binding energy side of O 1s spectrum at 530.93±0.03 eV is attributed to O^{2-} ions in wurtzite structure of hexagonal Zn^{2+} ion array. The medium binding energy component centered at 531.51±0.03 eV is associated with O^{2-} ions in the oxygen deficient regions with the matrix of ZnO [15]. Therefore, changes in the intensity of this component may be connected in part to the variations in the concentration of oxygen vacancies. The peak (O II) at 530.93±0.03 eV may be due to the oxygen in the $ZnGa_2O_4$ and the peak (O III) at 530.51±0.03 eV due to the oxygen in the ZnO structure [13,16].

3.2. Optical and electrical properties

Fig. 6 shows the optical transmittance for GZO films grown under 0.67 Pa of O_2 at various substrate temperatures. As our goal is to prepare a transparent electrode with a high conductivity for optical applications, a film with a high transmittance in the visible range is very important. The optical transmittance measurements between 200 and 800 nm show that the films are highly transparent in the visible region and present a steep decline at around 380 nm. The transmittance of GZO films reaches up to 90% in the visible range (400–800 nm). A conventional ITO electrode has transmittance of about 80% [17]. This indicates that GZO films could transmit more light and, therefore, the GZO film would be a better transparent electrode for display applications. This optical transmittance can be used to determine the value of the optical band gap. The optical band gap was calculated from the transmittance data by using Tauc's plot ($ahv \approx (hv - E_g)^{1/2}$) [18]. With increasing substrate temperature, the optical band gap is gradually increased from 3.38 to 3.51 eV as growth temperature increased from 100 to 500 °C.

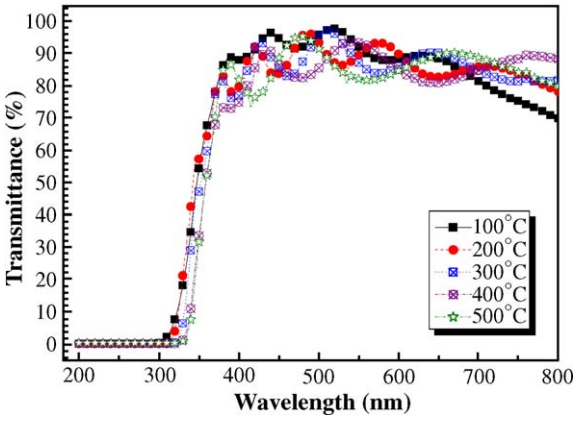

Fig. 6. Optical transmittance for GZO films grown under 0.67 Pa of O_2 at various substrate temperatures.

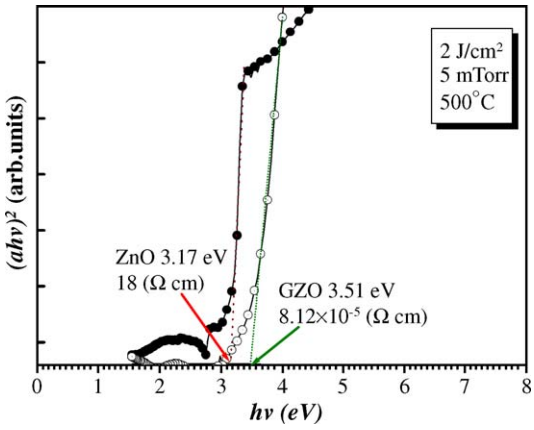

Fig. 7. Tauc's plot of transparencies in optical properties of ZnO and GZO thin films prepared at substrate temperature of 500 °C and at oxygen pressure of 0.67 Pa. The electrical resistivity of the films was measured by the Van der Pauw method at room temperature.

Fig. 7 shows the shift of the optical band gaps of ZnO and GZO films. The high-energy shift of the optical band gap of the GZO films compared with that of the ZnO films is due to the much higher carrier concentration and the filling of electronic states of the conduction band in the GZO films [19]. This is the well-known Burstein-Moss effect. According to the Burstein-Moss effect, the broadening of the optical band gap is

$$\Delta E_g = \left(\frac{\hbar^2}{2m_{cv}^*}\right)\left(3\pi^2 n\right)^{2/3}, \quad (1)$$

where ΔE_g is the shift of the doped semiconductor with respect to the undoped semiconductor, m_{cv}^* is the reduced effective mass

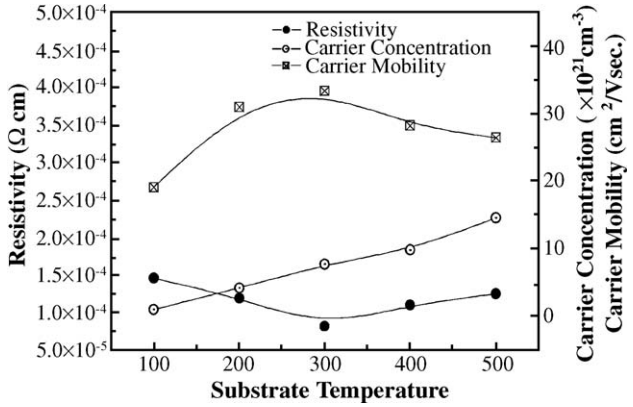

Fig. 8. Variations in resistivity, carrier concentration and carrier mobility as functions of substrate temperature for GZO films deposited under oxygen pressure of 0.67 Pa.

($1/m^*_{cv} = 1/m^*_c + 1/m^*_v$: $m^*_c = 0.38m_0$ and $m^*_v = 1.8m_0$), $\hbar$ is Plank's constant and n is the carrier concentration [20].

Fig. 8 shows the variations in resistivity, carrier concentration and carrier mobility as functions of substrate temperature for the GZO films grown at an oxygen pressure of 0.67 Pa. As substrate temperature increases from 100 to 300 °C, resistivity decreases from 1.46×10^{-4} to 8.12×10^{-5} Ω cm and then increases again. The decrease in resistivity is due to the increase in both carrier concentration and carrier mobility [21]. As substrate temperature increases to 500 °C, the corresponding resistivity becomes 1.25×10^{-4} Ω cm. The slight increase in resistivity of the films grown at higher substrate temperatures from 300 to 500 °C may be due to contamination of the alkali ions from quartz glass substrates and increase of C contamination with increasing substrate temperature. Carrier concentration in the GZO films was observed to gradually increase as deposition temperature was increased. This increase in carrier concentration may be due to an increase in diffusion of Ga atoms from interstitial locations and grain boundaries into the Zn cation sites [22]. Carrier mobility increases from 19.12 cm^2/Vs at to 30.96 cm^2/Vs at substrate temperature of 100 °C to 300 °C, then decreases to 26.42 cm^2/Vs.

4. Conclusions

High-quality transparent conductive GZO thin films were grown using by PLD on quartz glass substrates starting from a ZnO target containing 5 wt.% Ga_2O_3. The GZO films formed at a substrate temperature of 300 °C showed a low electrical resistivity of 8.12×10^{-5} Ω cm, a carrier concentration of 1.46×10^{22} cm^{-3} and a carrier mobility of 30.96 cm^2/Vs at an oxygen pressure of 0.67 Pa. A visible transmittance of above 90% was obtained. The optical band gap of the films increased from 3.38 to 3.51 eV with the increase in substrate temperature from 100 to 500 °C. It has been confirmed that pulsed laser deposited n-type transparent ZnO can be applied to electrode as a potential good challenger to ITO films.

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