Thin Solid Films 519 (2011) 8166–8172

Contents lists available at ScienceDirect

Thin Solid Films

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

Structural, electronic, and optical properties of nanocrystalline As-doped ZnO films on quartz substrates determined by Raman scattering and infrared to ultraviolet spectra

W.W. Li [a], W.L. Yu [a], J.D. Wu [b], J. Gan [b], M. Zhu [c], Z.G. Hu [a,*], J.H. Chu [a]

[a] Key Laboratory of Polar Materials and Devices, Ministry of Education, Department of Electronic Engineering, East China Normal University, Shanghai 200241, People's Republic of China
[b] Key Laboratory for Advanced Photonic Materials and Devices, Ministry of Education, Department of Optical Science and Engineering, Fudan University, Shanghai 200433, People's Republic of China
[c] Department of Physics, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

ARTICLE INFO

Article history:
Received 19 January 2010
Received in revised form 14 March 2011
Accepted 18 May 2011
Available online 27 May 2011

Keywords:
Arsenic doped Zinc Oxide
Nanocrystalline Films
Pulsed Laser Deposition
Optical Spectroscopy
Raman Spectroscopy
X-ray Diffraction

ABSTRACT

Nanocrystalline As-doped ZnO films with different laser power energy (40 mJ and 55 mJ) and As doping concentrations (C_{As} from 1% to 3%) have been grown on quartz substrates by pulsed laser deposition. The average grain size of the films was calculated from the (002) peak of x-ray diffraction patterns and is estimated to vary from 9 to 13 nm. Electronic transitions and optical properties of the films have been investigated by Raman scattering, far-infrared reflectance, and infrared-ultraviolet spectral transmittance technique. With increasing doping concentration, the A_1 longitudinal optical phonon mode shifts towards the lower energy side and can be described by $(564\text{-}75C_{As})\,\mathrm{cm}^{-1}$ owing to the increment of free carrier concentration. The E_1 transverse optical phonon frequency is located at about 415 cm^{-1} and does not show an obvious decreasing trend with the C_{As}. The optical constants in the photon energy range of 0.5–6.5 eV have been extracted by fitting the experimental data with the Adachi's model. The refractive index dispersion in the transparent region can be well expressed by a Sellmeier's single oscillator function. Due to different doping concentration and hexagonal crystalline structure, the optical band gap of the films grown at 40 mJ linearly decreases with increasing As concentration. The phenomena agree well with the results from the theoretical calculations.

1. Introduction

For several decades, much effort has been made on the studies of zinc oxide (ZnO) materials with regard to its excellent electronic, optical, and magnetic properties, such as wide band gap and large exciton binding energy at room temperature (RT) [1–5]. Moreover, ZnO has attracted more attention as a promising semiconductor material owing to the potential applications in spintronic and ultraviolet (UV) optoelectronic devices [6–9]. As known, a critical step for optoelectronic devices is the realization of *pn* junction and/or heterostructures. Recently, some interests have been focused on arsenic (As) element doped ZnO (ZnO:As) materials for the fabrications of *p*-type ZnO materials [10–12]. This is because As was predicted to be a good *p*-type dopant source. Under oxygen rich (O-rich) growth conditions, a complex involving an As atom and two Zn vacancies (V_{Zn}) would have a low formation energy and behave as a shallow acceptor with an ionization energy of 150–160 meV [12–14]. In addition, it is easy to realize the high solubility of As by some appropriate doping methods. However, only a few experimental and theoretical investigations were performed on ZnO:As materials, especially for the As dopant effects on its optical properties, which are still not completely understood and need further investigations. Therefore, a detailed study on the structural, electronic, and optical properties of ZnO:As films is required.

There has been an increased interest in ZnO-based diluted magnetic semiconductors (DMS), which was amplified by theoretical predictions suggesting that ferromagnetism (FM) of diluted magnetic compounds with Curie temperatures above RT could be obtained [15–17]. For ZnO, the FM properties can be realized by the substitution with *3d* transition metals, such as Mn, Fe, Cr, and Co, etc. Therefore, it is intriguing and prerequisite to study the physical properties of *p*-type ZnO-based DMS for spin electronic devices [6,18]. The spin properties are strongly related to the carrier concentration and conductivity type of ZnO-based DMS because the electronic structure of the substituted *3d* transition-metal impurities in semiconductors is influenced by strong *3d* hybridization and strong Coulomb interactions between *3d*–*3d* electrons [19]. Some deposition techniques have been used to explore the growth of ZnO films on various substrates, such as sapphire, quartz, and silicon. The growth techniques include pulsed laser deposition (PLD) [20,21], molecular beam epitaxy [22,23], magnetron sputtering [24], and metalorganic chemical vapor deposition [25]. Among them, the PLD is the most suitable technology and widely acceptable for the ZnO film deposition because of its ability to create high-energy source particles,

---

* Corresponding author. Tel.: +86 21 54345150; fax: +86 21 54345119.
E-mail address: zghu@ee.ecnu.edu.cn (Z.G. Hu).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.05.049

which can permit high quality film growth at low substrate temperatures [8,11]. It was reported that the laser pulse power and ambient pressure are main factors for the film quality in the PLD. The physical properties of oxide film can show different variation trend from various growth methods [26]. For example, the "*A*" exciton energy gap at RT is estimated to 3.416 eV [24] and 3.4 eV [27] for the ZnO films grown by magnetron sputtering and PLD, respectively. Note that the discrepancy cannot be neglected as compared with the exciton binding energy of bulk single crystal. Moreover, there are different exciton characteristics observed from the above fabrication technology [24,27,28]. It indicates that growth condition dependence of optical properties in the ZnO-based materials still needs further clarifications.

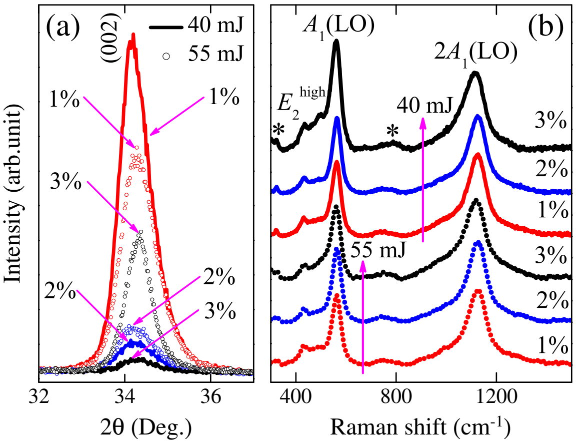

Fig. 1. (a) The XRD patterns of the ZnO:As films with different As concentration grown at the laser pulse power of 40 mJ (solid lines) and 55 mJ (dotted lines), respectively. (b) Raman scattering of the ZnO:As films grown on quartz substrates at different laser energies with the excitation line of 325 nm. The symbol "*" indicates the "additional vibration modes".

On the other hand, electronic and optical properties could be directly correlated with the electronic band structure due to the density-of-states (DOS). For ZnO materials, the physical properties have been mainly investigated by photoluminescence (PL) or cathodoluminescence (CL) characterizations [8,29,30]. Although PL and CL can underestimate the optical band gap (OBG) value due to several band tailing effects and excitonic absorption [4,5], the optical constants cannot be derived from the above spectral measurements. As known, the optical constants (i.e., dielectric function), are directly related to the electronic band structure of material, play a critical role in design, optimization, and evaluation of optoelectronic and spin-electronic devices [31,32]. Teng et al. reported the refractive index of PLD deposited $Mg_xZn_{1-x}O$ alloy films in the transparent region using transmittance spectroscopy [33]. At present, there are only few reports on the dielectric functions of the ZnO:As films and its low-dimensional structures. Fortunately, optical transmittance spectroscopy can determine the absorption edge and optical constants and is a preferential spectral technique [5,8]. By fitting transmittance spectra with an appropriate dielectric function model, one can obtain the optical constants and OBG value simultaneously [34,35]. It is desirable to carry out a delicate study regarding these essential properties of high quality *p*-type ZnO:As films for device applications.

In this paper, the structural, electronic, and optical properties of wurtzite ZnO:As layers with different As doping concentration and deposited with various laser pulse power are investigated. The phonon modes, optical constants, the OBG energy, and the effects from deposition parameter of laser energy and As doping on the electronic structure have been discussed in detail.

2. Experimental details

The ZnO:As films were grown on double-side polished quartz wafers by the PLD in an O-rich ambient. The substrates were cleaned in pure ethanol with an ultrasonic bath. Then the substrates were rinsed several times by de-ionized water. Finally the quartz wafers were dried in a pure nitrogen stream before the deposition. The As_2O_3-mixed ZnO targets were prepared using a conventional process for ceramic power. The ZnO:As films were deposited at an O_2 pressure of 5 Pa and a substrate temperature of 450 °C. A pulsed Nd:YAG laser was used as the ablation source, which operated with an energy of 40 mJ and 55 mJ, respectively. The deposition time was usually 30 min, and then the films were annealed at 900 °C in an oxygen ambience for 10 min by a rapid thermal annealing process. The As atom concentration (C_{As}) of the ZnO:As films, which were determined by X-ray photoelectron spectroscopy (XPS) and the error is located in about ±0.1%, is kept at 1%, 2% and 3%, respectively. The detailed growth process and concentration evaluation can be found in Refs. [3,11,36].

The crystalline structure of the ZnO:As films was analyzed by X-ray diffraction (XRD) using Cu $K\alpha$ radiation (D/MAX-2550 V, Rigaku Co.). The XRD patterns of the ZnO:As films with C_{As} of 1%, 2%, and 3% grown at different laser pulse power are shown in Fig. 1(a). As can be seen, the samples exhibit a single phase with the hexagonal wurtzite structure. The diffraction peak that appears near 34° is from the ZnO (002) plane. Note that these results are slightly different to the single crystalline films on sapphire substrate [37]. It indicates that the As atom has been incorporated into the ZnO matrix lattice. For the 40 mJ samples, the intensity is highest for 1% As and lowest for 3% As doping. However, the XRD intensity of the 2% As sample grown at 55 mJ is less than that for 3% As doping, which could be ascribed to the different crystalline quality and/or thickness of the sample. The full width at half maximum (FWHM) of the (002) peak for the ZnO:As layers varies from 0.712° to 0.989° by the Gauss line shape analysis and is listed in Table 1, which confirms the reasonable good crystalline quality. It should be emphasized that the (002) peak FWHM differs in the layers due to the variation of As doping concentration. One can conclude that the crystallinity decreases with increasing As atom incorporation. Moreover, the FWHM values increase from 1% to 2% and then decrease for 3% As doping for both 40 mJ and 55 mJ depositions. The calculated *c*-axis lattice constant from the (002) plane for all samples is about 5.23 Å. The result shows that lattice is slight larger than that from pure ZnO and transition-metal (Cr, Mn, and Ni) doped ZnO films [17]. Note that the diffraction peaks shift to the large angle and the lattice constants decrease with increasing laser power. This is because the film crystallinity changes with the laser energy. The grain size *r* can be calculated from the (002) peak according to Scherrer equation: $r = K\lambda/\beta cos\theta$, here $K \approx 1$ is the shape factor, $\lambda = 1.540$ Å is the average wavelength of Cu $K\alpha$ radiation, β is the FWHM, and θ is the diffraction angle. The average grain size of the ZnO:As films is estimated from 9 to 13 nm, which suggests that the films have the nanocrystalline formation. For comparison, the *c*-axis lattice constants and grain sizes are also listed in Table 1.

Raman spectra were recorded under unpolarized mode using a Jobin-Yvon LabRAM HR 800 UV micro-Raman spectrometer and a resonant Raman spectral method with a He-Cd laser as the excited source operating at the wavelength of 325 nm (3.82 eV) [34]. The laser power was 30 mW and the on-sample laser power for the Raman measurements was 3.2 mW. Far-infrared (FIR) reflectance spectra were measured over the wavenumbers range of 200–700 cm^{-1} with a spectral resolution of 2 cm^{-1} using a Bruker VERTEX 80V Fourier transform infrared (FTIR) spectrometer. The reflectance experiments were carried out at near-normal incident configuration (the angle of incidence is about 11° by spectral reflectance accessory A510 Q/T). A TGS/POLY detector and a 6 μm-thick mylar beamsplitter were employed for the measurements. Aluminum (Al) mirror, whose absolute reflectance was directly measured, was used as reference for the FIR spectra. The UV-near-infrared (NIR) optical transmittance was recorded with a double beam UV–IR spectrophotometer (PerkinElmer