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Optical and structural investigation of ZnO thin films prepared by chemical vapor deposition (CVD)

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Abstract

Transparent and conductive ZnO thin films have been prepared by a method derived from chemical vapor deposition using Zn $(C_5H_7O_2)_2$ as Zn source. The deposited thin ZnO layers of $\sim$0.1 μm thickness on Si and InP semiconductor substrates, have been investigated with respect to the crystalline phase by X-ray diffraction (XRD), and surface morphology by atomic force microscopy (AFM). Spectrophotometric measurements in the ultraviolet-visible-near infrared spectral range and optoelectrical measurements of ZnO/semiconductor heterostructures have been performed.

Keywords: ZnO films; X-Ray diffraction (XRD) spectra; Opto-electrical measurements; Photovoltaic applications

1. Introduction

In the last decade, there has been a resurgence in the development of thin films for use in optoelectronic devices, thin-film gas sensors, surface acoustic wave devices, thin-film piezoelectric transducers and other devices [1–3]. The applications of ZnO films in various devices require different physical properties of films, which means different deposition techniques and conditions. ZnO is an II–VI semiconductor with a wide band-gap (3.2 eV) and a crystal structure which involves a polycrystalline structure when obtained as thin layers. The deposition techniques for ZnO thin films preparation used in the published reports are: activated reactive- or electron-beam evaporation; magnetron-, reactive- or ion beam sputtering; spray pyrolysis; chemical vapor deposition (CVD) with many variants; and recently, solution deposition techniques and pulsed laser deposition methods. The structure and properties of ZnO films such as crystallite orientation, grain sizes, layer resistivity, carrier mobility or optical transparency are influenced by fabrication techniques and processing variables. For example, ZnO films obtained by reactive or magnetron sputtering technique exhibit preferred *c*-axis grain orientation normal to the substrate surface. The grain size and lattice strain in these films can be modified by post-deposition annealing [4]. The magnetron deposition method has been shown to be effective for preparing doped ZnO films with high electrical conductivity. For ZnO films deposited by plasma-enhanced chemical vapor deposition (PECVD), the growth rate and crystallite orientation was observed to depend on substrate temperature and r.f. power density [4]. Work reported here concerns the characterization of ZnO films deposited by a method derived from chemical vapor deposition (CVD) from a metal–organic precursor. The crystal orientation and surface morphology were studied by X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) technique. Hall measurements, sheet resistance measurements with the four-point d.c. method and spectroscopic measurements have been used to characterize electrical and optical properties of the prepared films. The availability of these transparent conductive oxide (TCO) films for optoelectronic device applications were demonstrated by photoresponse measurements on ZnO/Si and ZnO/InP heterostructures.

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2. Film deposition procedure

ZnO thin films were prepared by a single source chemical vapor deposition (SSCVD) technique using zinc acethylacetonate [$Zn(C_5H_7O_2)_2$] as source materials. Some aspects of our SSCVD and experimental setup have been described by Rusu et al. [5]. A major advantage of the SSCVD process is that the precursor molecules from low kinetic energy vapor ($3kT/2=50$ meV, $T=393$ K) precipitate evenly on all exposed surfaces. This leads to uniform films. The process consists of two steps: thermal decomposition of the metal–organic compound [$Zn(C_5H_7O_2)_2$] followed by oxidation. The deposition takes place in a quartz reactor in a mixture of gases (argon and oxygen), and the process conditions were optimized to improve the film stoichiometry. The argon flux of 200 cm^3/min passes through the Zn-acetylacetonate source, which is maintained at a temperature of 80–120°C. During the deposition process, the substrate was maintained at ~360°C. In these conditions, ZnO films were deposited on (111) oriented p-Si, (100) oriented p-InP and glass substrates. The thickness of the thin layers was in the range of 0.1–0.12 μm.

3. ZnO films characterization

3.1. XRD spectra

The X-ray diffraction measurements of the deposited films were performed to identify the resident phase of the films, to verify crystallite orientation and to evaluate crystallite grain size. To obtain XRD spectra a DRON 3 type diffractometer equipped with a scintillation detector based on the double crystal method was used. X-Ray spectra are shown in Fig. 1 for ZnO film on a (111) oriented Si substrate, and in Fig. 2 for ZnO on InP substrate with (100) orientation. In Tables 1 and 2 the calculated distances between crystalline planes, which lead to Bragg reflections in Figs. 1 and 2 are given. The obtained spectra, compared to the spectra of a ZnO powder where crystallites are randomly oriented, show for the prepared films, a polycrystalline structure having a preferred orientation depending on the substrate orientation. In both X-ray patterns the (002) crystal plane line characteristic of the wurtzite phase (*c*-axis orientation perpendicular to the substrate) can be detected.

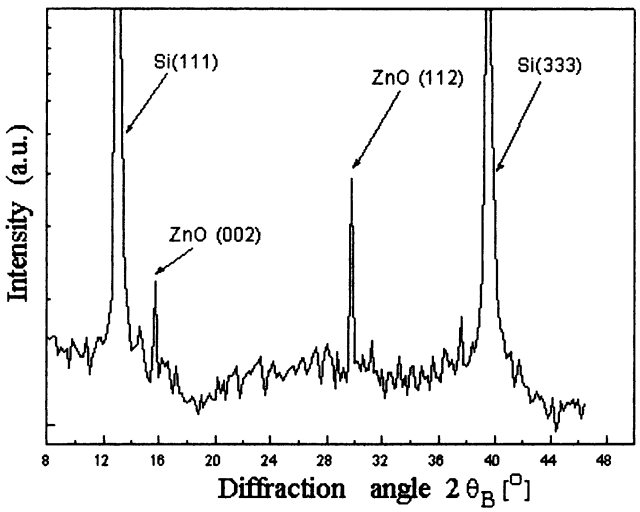

Fig. 1. X-Ray diffraction spectra of ZnO on (111) oriented Si substrate.

Table 1

$2\theta_B$ (°)	*d* (Å)	Crystal	(*hkl*)
12.98	3.14	Si	(111)
15.68	2.6	ZnO	(002)
29.8	1.379	ZnO	(112)
39.6	1.04	Si	(333)

The main observation was that the preferred orientation of the crystallites was (112) for (111) Si and (002) for (100) InP substrate. An explanation for the differences in crystallite orientation would be due to modes of same symmetry — the wurtzite structure of ZnO has a six-fold symmetry in the direction perpendicular to the *c*-axis [6]. The relatively small values of the line intensity attest the presence of a polycrystalline phase

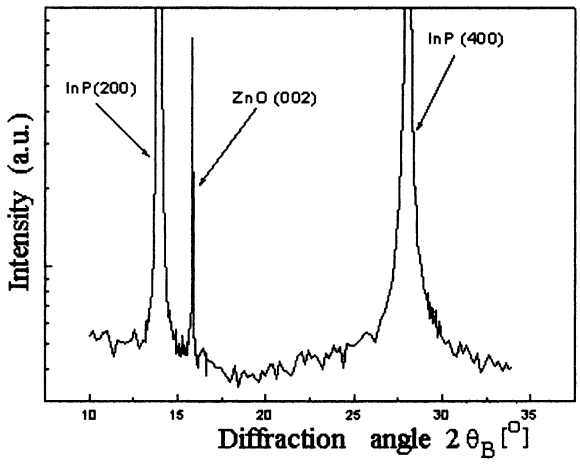

Fig. 2. X-Ray diffraction spectra of ZnO on (100) oriented InP substrate.

Table 2

$2\theta_B$ (°)	*d* (Å)	Crystal	(*hkl*)
13.85	2.94	InP	(200)
15.74	2.59	ZnO	(002)
27.97	1.467	InP	(400)

Table 3

d (Å)	Film orientation	Substrate
265	ZnO (002)	InP
250	ZnO (002)	Si
181	ZnO (112)	Si

of ZnO and the relatively large value of full width at half maximum (FWHM) are correlated with a small grain size ($\lambda_{X\text{-}Ray} \ll D$). The grain size dimensions were evaluated using the Debye–Scherrer relation:

$$D = \frac{0.9\lambda}{\beta\cos\theta_o}$$

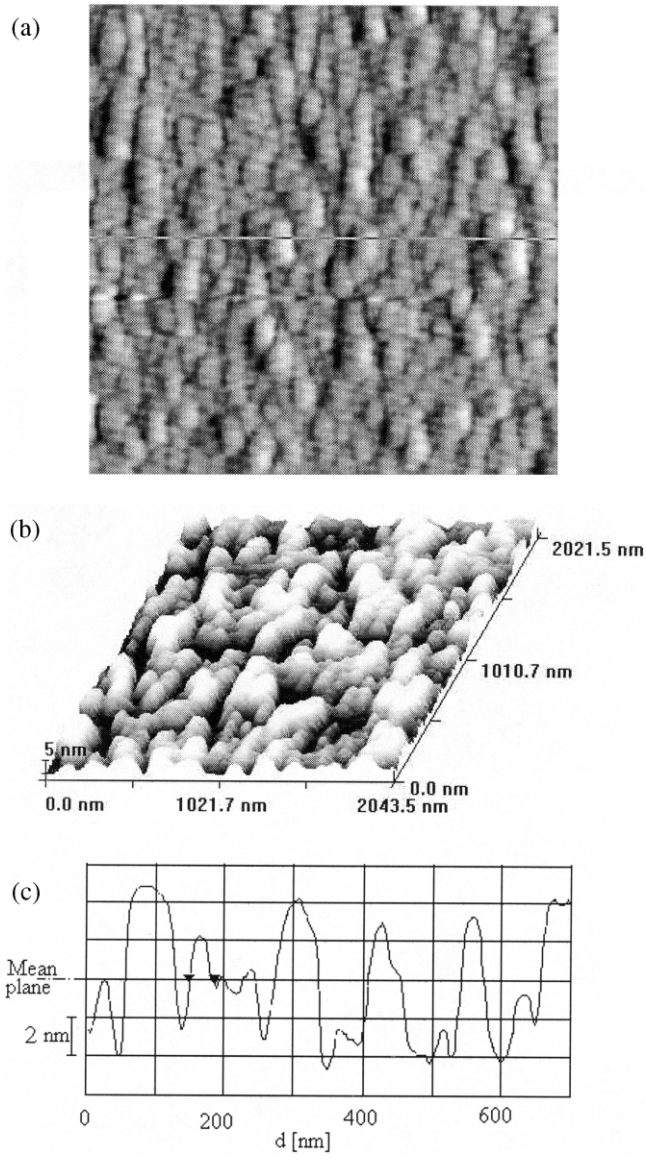

Fig. 3. AFM image of ZnO film on InP substrate: (a) 2D-image for a scanning area of 2043.5×2021.5 nm²; (b) 3D-image; and (c) line profile.

where D is the grain size dimension, λ equals X-ray radiation wavelength, β = FWHM, and θ_0 is the Bragg angle. The calculated values are listed in Table 3.

The dimensions of grain size in the range of 18–27 nm evaluated by X-ray diffraction analyses, show the nanocrystalline nature of the prepared films.

3.2. Surface morphology

Surface morphologies of ZnO thin films deposited on Si and InP were investigated by the AFM technique. The AFM 2D- and 3D-images of ZnO thin films deposited on InP substrates are presented in Fig. 3. For a scanning area of 2043.5×2021.5 nm², the maximum value of roughness is 5.40 nm and the average value is 1.31 nm. Fig. 3a,b suggests a polycrystalline structure with a grain size of less than 40 nm. The width and the highness of the marked peak in the line profile, Fig. 3c, are 39.57 and 1.96 nm, respectively. One can see from the figures that the grain size of the observed surface structures is less than 10% of the wavelength of visible light, which accounts for the high optical quality.

3.3. Optical and electrical characterization

The optical properties were investigated by spectrophotometric measurements. Transmission spectra of films deposited on glass substrate were recorded in the wavelength range from 200 to 900 nm using a SPECORD-M42 double beam spectrophotometer. A typical transmission curve for the obtained film is shown in Fig. 4.

The deposited films showed high transmission (over 80%) in the near-infrared and visible region with a steep fall-off in transmission at approximately >400 nm. The flat aspect of transmission spectra without interference fringes emphasizes the surface uniformity due to the small crystallite size. The transmission data have been used for the determination of the band-gap energy of ZnO films. The inset from Fig. 4 shows a plot of $(\alpha h\nu)^2$ vs. $(h\nu)$, and the extrapolation of this curve to zero absorption coefficient in the range where band–band absorption of the radiation begin. An E_g of 3.47 eV for deposited films compared to an E_g of 3.2 eV for ZnO bulk semiconductor can be determined from the figure. The significant shift to large values of E_g is caused by a thin film structure and suggests the presence of a polycrystalline phase of different grain sizes [6]. The ZnO thin films deposited from Zn acetylacetonate on the heated semiconductor substrate (Si, InP) at 360°C have been obtained with low resistivity of $\sim 3\times10^{-4}$ Ωcm, and a high carrier concentration in the range of $0.5\text{–}6\times10^{20}$ cm^{-3}, with Hall mobilities of 30–40 cm²/V s.

High optical transparency and conductivity of the obtained films demonstrate the applicability of these

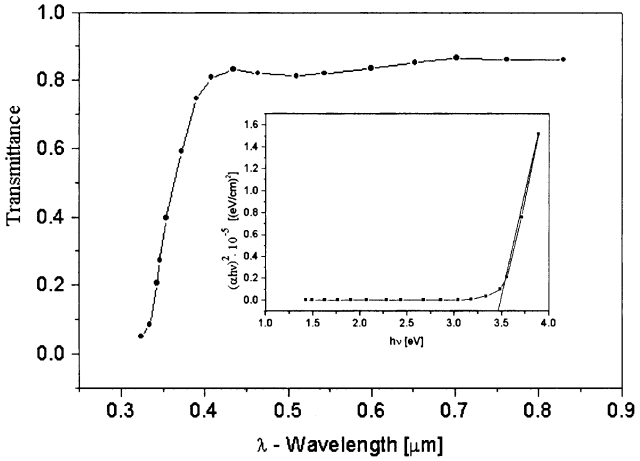

Fig. 4. Transmittance of the ZnO films.

transparent conductive oxide (TCO) layers for optoelectronic device fabrication. ZnO with a large bandgap of 3.47 eV is a window material for visible and infrared radiation and thus, optoelectronic characteristics of ZnO/semiconductor heterojunctions will be determined by the absorption characteristics of the substrate.

The *I–V* characteristic of the n-ZnO/p-InP heterostructures at dark and static illumination conditions is shown in Fig. 5. The V_{OC} is approximately 0.52 V and I_{SC} is approximately 120 μA at illumination level, where $E_V = 1$ klux. The heterojunction presents a good reverse

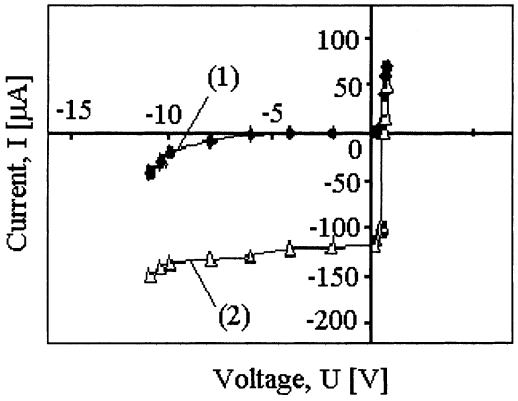

Fig. 5. *I–V* characteristics of ZnO/InP heterostructure at dark conditions (curve 1) and static illumination conditions (curve 2).

characteristic with a 10-V breakdown voltage and a forward voltage, $V_F = 0.7$ V at 60 μA.

The measured spectral characteristic of the ZnO/InP heterostructure is nearly flat over the visible region and presents a maximum in the near infrared at ~0.85 μm. The quantum efficiency (η) determined from photoresponse measurements [$R(A/W) = \eta\lambda(\text{nm})/1240$] presents high values >70% over a large region of wavelength from 500 to 900 nm.

4. Conclusion

Highly transparent ($T > 80\%$) and conductive ($\rho < 3\times10^{-4}$ Ωcm) ZnO films have been prepared by a SSCVD technique using Zn acetylacetonate as source. The XRD and AFM investigations show:

1. the preferential orientation of the crystallites for prepared ZnO films were (112) on (111)-Si substrate and (002)-wurtzite *c*-axis orientation perpendicular to the surface of (100)-oriented InP substrate;
2. the dimensions of grain sizes are in the range of 18–40 nm and reveal the nanocrystalline nature of the prepared films; and
3. the AFM 2D- and 3D images for a scanning area of 2043.5×2021.5 nm^2 show a maximum value of roughness of 5.4 nm and average value of 1.31 nm.

The measured photoresponse of 120 μA/klux and a quantum efficiency of over 70% demonstrate that the heterostructures based on ZnO films on Si and InP substrate can be used for optoelectronic device applications.

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