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Effect of substrate on ZnO thin films synthesized by sol-gel method

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ZnO thin films have attracted significant attention because of their applications in surface acoustic wave (SAW) devices, gas sensors, solar cells etc. based on their multifunctional piezoelectric, thermal, electrical, and optical properties. The stoichiometric ZnO films with highly insulating and piezoelectric characteristics are very effective for ultrasonic oscillator devices. For example, in SAW applications, ZnO thin films must have a smooth surface be highly insulating and have a high packing density. In this investigation, sol-gel synthesis technique is adopted to prepare effective ZnO thin films on single crystalline silicon and amorphous glass substrates to study the influence of the substrate on ZnO films. Highly c-axis oriented ZnO thin films have been produced by the sol-gel method on various substrates. The morphologies and microstructures of the ZnO films were observed by scanning electron microscopy (SEM). The surface roughness was determined using atomic force microscopy (AFM). The crystallization and orientation of the ZnO films were identified from X-ray diffraction (XRD) patterns. The dependence of the crystallization and preferred orientation of the ZnO films on various substrates is characterized.

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1. Introduction

ZnO is an extensively adopted oxide semiconductor material, which has attracted considerable interest because of its unique and multifunctional properties. ZnO has been employed in surface acoustic wave devices [1,2], transparent conductive electrode [3], gas sensor devices [4], and low-voltage varistors [5]. In particular, under ambient conditions, ZnO thin films crystallize with a wurtzite structure, which is a tetrahedrally coordinated structure with a hexagonal lattice. In c-axis orientation (002-direction), ZnO films exhibit piezoelectric properties, which can be exploited in integrated piezoelectric thin film devices. Furthermore, since the degree of (002) plane orientation of the ZnO films is directly related to the piezoelectric property, control of the preferred (002) orientation is an important issue in SAW-related devices. With very strong c-axis orientation, the use of SAW requires that the ZnO thin films have low residual stress, small grain, low roughness, and high electrical resistivity.

Several methods for preparing ZnO thin films with a preferential c-axis texture and high electrical resistivity have been investigated. They include sputtering [6,7], chemical vapor deposition (CVD) [8], molecular beam epitaxy (MBE) [9], spray pyrolysis [10], and pulsed laser deposition (PLD) [11,12]. More recently, interest in the production of ZnO thin films by sol-gel technology has been increasing. Among all approaches for preparing ZnO thin films, the sol-gel reaction is simple and inexpensive and enables large-area films to be produced. Most related studies have focused on the preparation by the sol-gel process of ZnO films with high electrical conductivity, good optical transmittance, or gas sensing characteristics [13,14]. However, ZnO thin films have seldom been grown using the sol-gel approach with various substrates. In this work, ZnO films were fabricated on single crystalline silicon and amorphous glass substrates to study the dependence of crystallization and preferred orientation in ZnO films on the substrate.

2. Experimental

ZnO thin films were deposited on silicon (Si) and commercial "Soda" glass substrates using the sol-gel method. The ZnO thin films were deposited on Si and glass substrates with a sol concentration of 1M. The substrates were coated with the spin-coating with 1M zinc acetate in ethanol and ethanolamine at a rotational speed of 3000 rpm for 20s. Between each coating process, the substrates were dried at 300°C for 10 min in air over a hot plate to evaporate the solvent and remove organic residue. The process from coating to drying was performed six times to ensure complete coverage of the ZnO films. The numbers of coating on Si and the glass substrates were equal. Finally, the ZnO films were inserted into a quartz furnace and heated in air to 500°C for 2h. The surface roughness of the deposited ZnO films was observed by an atomic force microscopy (AFM). The crystalline phase of the ZnO films was determined from X-ray diffraction (XRD) patterns obtained using Cu Kα radiation with a wavelength of 1.5418Å. The morphology and microstructure were characterized by field-emission scanning electron microscopy (FE-SEM).

3. Results and discussion

Fig. 1 presents 3D AFM images obtained in contact mode over a scanned area of 1.0μm×1.0μm to determine the surface roughness of the bare substrates and the ZnO thin films. Fig. 1 (a) and (c) are of bare Si substrate and of bare glass substrate. The AFM measurements yield the root mean square (rms) surface roughness of the substrates [15]. As shown in Figs. 1 (a) and (c), the bare Si and glass substrates have quite smooth surface with an rms roughness of 0.11 and 0.15 nm, respectively. The smooth surface of dielectric films reduces the leakage current [16]. Therefore, less rough ZnO thin films grown on the proper substrate are expected to be associated with a lower leakage current.

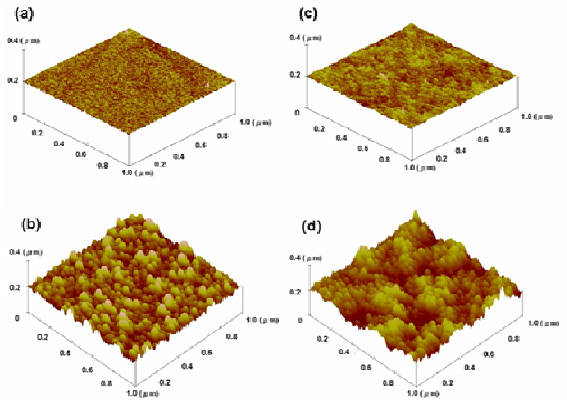

Fig. 1. 3D AFM images of (a) bare silicon substrate, (b) ZnO films deposited on silicon substrate, (c) bare glass substrate, (d) ZnO films deposited on glass substrate.

Figs. 1 (b) and (d) show the typical 3D AFM images of ZnO thin films deposited on Si and glass substrates by the sol-gel technique. The roughness of ZnO films grown on Si substrate is less than that of those prepared on glass substrate. The rms roughness values of ZnO films grown on Si and glass substrates are 3.4 and 4.9 nm, respectively. The surface roughness of the ZnO films apparently depends on the substrates.

The AFM images indicate that the ZnO thin films comprise densely packed columns perpendicular to the substrates. Comparing Figs. 1 (b) and (d) with Figs. 1 (a) and (c) reveal a significant change in the surface morphology of the substrates upon the sol-gel fabrication procedure. From Figs. 1 (b) and (d), the ZnO films are clearly to be made up of near-spherical nanoparticles that are uniformly dispersed throughout the ZnO thin films.

Fig. 2 shows the grazing incidence XRD patterns of the ZnO films prepared on Si and glass substrates. Three ZnO diffraction peaks, (100), (002) and (101) appear at 2θ = 31.76, 34.40 and 36.28°, respectively. These peaks agree closely with the JCPDS standard (card No. 36-1451) data of pure ZnO with a hexagonal wurtzite structure. The XRD pattern reveals no other impurity. This result indicates that the sol-gel process yields wurtzite hexagonal ZnO. Furthermore, the intensity of the (002) plane markedly exceeds those of the (100) and (101) plane in the ZnO thin films, suggesting that the preferred orientation of the films is along the c-axis perpendicular to the substrate surface. In spite of the use of Si and glass as the substrates for the growth of ZnO films, the films do exhibit a preferential orientation. The c-axis orientation of the ZnO films may follow from the fact that the surface free energy of the (002) orientation is the lowest for the ZnO crystal [17] or it may be related to a preferred growth since the atomic density is highest in the (002) plane [18]. The ZnO films will be self-textured along the c-axis when grown on single crystalline Si or amorphous glass substrates.

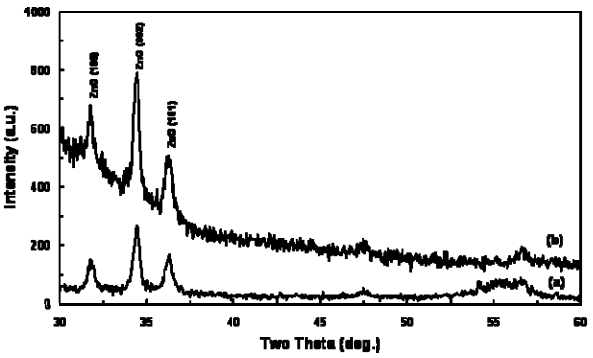

Fig. 2. XRD spectra of ZnO films deposited on different substrates: (a) silicon, (b) glass.

Table 1. Characteristics of ZnO thin films obtained from XRD pattern.

Substrate	Θ (deg.)	d-spacing (nm)	F-WHM (deg.)	Peak intensity (a.u.)	Lattice constant (nm)
Si	17.20	0.2605	0.50	266	0.5210
glass	17.22	0.2602	0.37	791	0.5204

Table 1 presents additional information on the (002) diffraction peak from ZnO thin films deposited on Si and glass substrates. The position of (002) diffraction peak of the ZnO films grown on Si substrates is shifted towards a slightly lower angle, suggesting that the inner strain exceeds higher than that of the films deposited on glass substrate. The full-width at half-maximum (FWHM), determined from the XRD spectra of ZnO films prepared on Si and glass substrates, are 0.50 and 0.37, respectively. The smaller FWHM value indicates that the ZnO films are

more textured along the c-axis. The peak intensity of ZnO films deposited on glass substrates is higher than that of those prepared on Si substrates and the FWHM is lower. Based on above discussion, the ZnO films deposited on glass substrate should have better crystalline properties than those prepared on Si substrate.

Fig. 3 displays the FE-SEM images of ZnO thin films deposited on Si and glass substrates at low and high magnification. The high-magnification image in Figs. 3 (b) and (d) reveal that the ZnO films prepared on Si and glass substrates have many nanograins with diameters of about 20 and 27 nm, respectively. The ZnO films prepared on glass substrates contained the larger grains. Additionally, all ZnO films on both Si and glass substrates were composed of closely packed nanograins.

4. Conclusions

Highly oriented and smooth ZnO thin films have been grown on Si and glass substrates using the sol-gel technique. The influence of the substrate on the crystalline and oriented properties of ZnO films was investigated. AFM, XRD, and SEM experimental results indicated that the substrate is one of the most important factors in obtaining highly crystalline ZnO thin films with a preferred c-axis orientation. ZnO films deposited on amorphous glass substrates have better crystalline properties than those prepared on single crystalline Si substrates, since the inner strain of the ZnO films is higher when they are prepared on crystalline Si substrate.

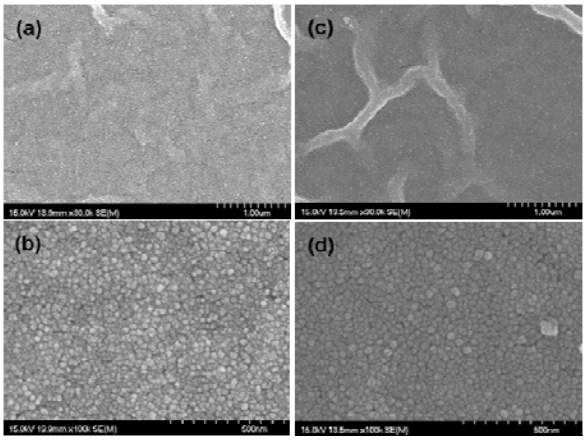

Fig. 3. FE-SEM images of ZnO thin films on different substrates: (a) silicon (low magnification), (b) silicon (high magnification), (c) glass (low magnification), (d) glass (high magnification).

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