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Influence of annealing on optical properties and surface structure of ZnO thin films

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Abstract

Thermal annealing effects on optical properties and surface structure of zinc oxide (ZnO) thin films prepared by filtered cathodic vacuum arc technique were investigated by spectroscopic ellipsometry (SE) and atomic force microscopy (AFM). In the SE study, Cauchy model was used to extract the optical constants of ZnO thin films for photon energies below the band gap while point-by-point fitting was used to determine the optical constants of the films for photon energies above the band gap. The influence of annealing on the optical properties, in the photon energy ranging from 1.1 to 5 eV, has been demonstrated. It was found that the values of the refractive index, the reflectance and the real part of the complex dielectric function decrease with increasing annealing time. On the other hand, tapping mode AFM was used to study the surface structure and topography of ZnO thin films. AFM study revealed that annealing roughened the surface of the films and increased the size of grains on the surface. It was observed that the changes in the optical properties were correlated to the changes in the surface structure as a result of annealing.

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Keywords: A1. Annealing; A1. Optical properties; A1. Surface structure; B1. Zinc oxide

1. Introduction

Zinc oxide (ZnO) is a versatile II–VI semiconductor material that can be used for a variety of applications such as varistors, phosphors, gas sensors, surface acoustic wave devices, solar cells windows or transparent contacts. With its direct band gap of about 3.3 eV at room temperature, ZnO is a promising material for short-wavelength light-emitting devices and daylight-blind UV detectors [1,2]. Since ZnO has high transmittance in the visible region and low electrical resistivity, it is an ideal window material for solar cell and flat panel displays [3]. Moreover, the binding energy of the exciton of ZnO (60 meV) is large [4], which allows efficient excitonic emission at high temperature. Recently, optically pumped ultraviolet (UV) laser emission in ZnO thin films grown by molecular beam epitaxy has been demonstrated at room temperature [1,5]. As a result, ZnO-related materials have received considerable attention. More recently, extensive research studies on ZnO for the application of photoluminescence have been carried out [6–12]. It is believed that ZnO is one of the most promising materials for the fabrication of the next generation of optoelectronic devices in the UV region and optical or display devices.

There have been extensive studies on the crystalline structure, optical transmittance and photoluminescence of ZnO thin films prepared by various techniques [6–10,13,14]. There are, however, few studies on the optical constants, dielectric function, reflectance, and absorption coefficient of ZnO thin films in the photon energy ranging from 1.1 to 5 eV. It is known that the precise knowledge of the above optical properties of the material is important for designing optoelectronic and optical devices. The surface structure of the material is also one of the key factors affecting the optical properties of the material and the performance of the optical devices prepared by this material [15]. In this work, atomic force microscopy

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(AFM) and spectroscopic ellipsometry (SE) are used to study the surface structure and optical properties of ZnO thin films and the influence of annealing on its structural and optical properties.

2. Experimental details

Filtered cathodic vacuum arc technique was employed to prepare high-quality ZnO thin films. Before deposition, n-type (1 0 0) silicon substrate was cleaned ultrasonically using acetone, methanol and de-ionized water. The substrate was subsequently dried by blowing it with nitrogen gas. The cathode was a 99.99% purity zinc target with a diameter of 60 mm mounted onto a water-cooled copper plate. An off-plane double-bend filter was inserted between the plasma source and the main chamber to remove effectively macro-particles produced in the cathodic arc plasma. An arc current of approximately 15 mA was used and the oxygen partial pressure during the deposition was about 2×10^{-4} Torr. The temperature of the substrate was controlled at 230 °C and a bias of 0 V was applied to the substrate. The thickness of the films was controlled approximately from 200 to 400 nm. After deposition of the ZnO thin films, samples were annealed to investigate the effects of annealing on the optical and structural properties. During the annealing process, the samples inside the furnace were firstly heated from room temperature to 900 °C within 20 min, annealed for a given period of time (t_a) at 900 °C and subsequently left to cool to room temperature inside the furnace. This annealing process was used in order to minimize the build-up of thermal strain and stress at the interface of ZnO/Si.

The crystalline phase and crystal orientation of the thin films were analyzed by an X-ray diffractometer. A copper target was used. The high tension and current used were 40 kV and 30 mA, respectively. A dominant diffraction peak at 34.4° was observed. It suggested that the ZnO thin film was of (0 0 2) hexagonal structure.

Spectroscopic ellipsometry (SE) measurements were made with a rotating analyzer ellipsometer. A xenon arc lamp was used as the light source. An optical fiber coupled the light beam from the output of light source to the input of polarizer. The polarizer converted the light with random polarization state into linearly polarized light oriented along the transmitting axis. The linearly polarized light illuminated the sample and was subsequently reflected from it. The polarization state of the reflected beam was measured by the combination of rotating analyzer and silicon photodiode detector. The incident angles of the beam were 70° and 75°. The wavelength range of the spectrum was from 250 to 1100 nm (i.e., from 1.1 to 5 eV) with a step of 5 nm. The system recorded the spectra of psi (ψ) and delta (Δ) as functions of wavelength (λ). ψ and Δ are measures of the changes in the amplitude and phase of the incident light upon reflection, respectively. The spectra of ψ and Δ for the as-deposited sample, in which the incident angle is 70°, are illustrated in Fig. 1. Interference oscillations below the band gap (3.3 eV) or in the wavelengths longer than 375 nm are observed. This is due to the multiple internal reflections between the film and substrate. For wavelengths less than 375 nm, i.e., photon energy above band gap, no interference oscillation is seen because of the occurrence of light absorption resulting from the interband transition in ZnO film. The spectra are therefore, for this work, separated into two spectral ranges, i.e., photon energies below and above the band gap, for the purpose of simplifying the fitting of the ellipsometric data. As there might be a thin interface layer with unknown properties existing between ZnO and Si substrate and voids might also exist in or on the surface of ZnO film, the ZnO film in this study was treated as an effective layer composed of ZnO, the interface layer and the voids for simplifying the fitting of the ellipsometric data. A three-phase (i.e., air/effective ZnO film/Si substrate) was therefore used to model the layered structure in the ellipsometric analysis. The determination of the film thickness and the complex refractive index below the fundamental energy band gap was done by fitting the ellipsometric data with a three-phase Cauchy dispersion model [16] given as

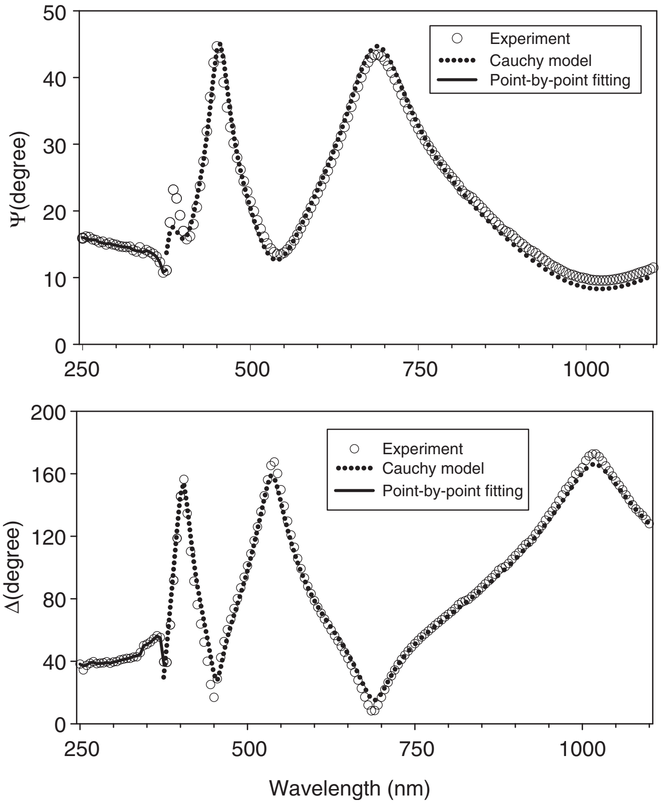

Fig. 1. The ellipsometric spectra of the as-deposited sample. A three-phase Cauchy dispersion model is used to fit the spectra in the wavelength range from 375 to 1100 nm, while point-by-point fit is used to fit the spectra in the wavelength range from 250 to 375 nm.

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4, \tag{1}$$

$$k(\lambda) = \sigma \exp\{\beta[12\,400(1/\lambda - 1/\gamma)]\}, \tag{2}$$