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Multiple oscillator models for the optical constants of polycrystalline zinc oxide thin films over a wide wavelength range

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ABSTRACT

Zinc oxide (ZnO) films were prepared on Si(1 1 1) and quartz substrates using RF-magnetron sputtering in N_2 plasma at room temperature. From the X-ray diffraction observations, it was found that all films are polycrystalline with a preferred orientation of (1 0 1). X ray photoelectron spectroscopy was used to analyze the chemical composition of the films by observing the behavior of the Zn2p3, O1s, N1s, and C1s lines. The thicknesses and optical constants of the ZnO thin films were determined using variable angle spectroscopic ellipsometry through the Genosc™ Herzinger–Johs parameterized semiconductor oscillator functions and multiple Gaussian oscillator models. Combining multiple oscillator types provided a very flexible approach to fitting optical constants over a wavelength range 190–1400 nm while simultaneously enforcing Kramers–Kronig consistency in the fitted ellipsometric parameters. Refractive indices of the films were determined to be in the range 1.68–1.93 and extinction coefficients in the range 4.56×10^{-6}–0.23. A direct bandgap of 3.38 ± 0.03 eV was calculated from the extinction coefficient. Low temperature photoluminescence studies of the films exhibited one prominent peak at 3.41 eV. The equality of the ZnO thin films was obtained through the depolarization measurements.

1. Introduction

Recently, an extraordinary effort has been directed toward group II–VI semiconductors such as zinc oxide (ZnO) material. ZnO is an attractive II–VI group compound because of its potential applications in the fields of electronic and optoelectronics such as surface acoustic wave (SAW) devices, film bulk acoustic resonator (FBAR) filters [1–5], transparent electrodes in solar cells [6], gas sensors [7], and a material in renewable energy storage processes [8,9], which are correlated with technology fabricating reliable p-type ZnO material. This has been achieved by thermal oxidation of Zn_3N_2 at temperatures higher than 400 °C [10,11]. p-Type ZnO:N was first proposed by Kobayashi et al. [12] in 1983, but experimental work has proven that it is difficult to produce. Challenges arise from an asymmetric doping limitation that strongly favors n-type conductivity [13,14]. Theoretical calculations suggest that nitrogen solubility in ZnO is strongly affected by the nitrogen source [15]. However, it is still very challenging to prepare high quality ZnO:N thin films. In addition, reproducibility, low hole mobility, low hole concentrations, and poor film stability are some of the problems with ZnO:N materials [16,17].

Although ZnO thin films have been intensively studied and fabricated by various techniques [18–23], relatively little experimental work has been done to study the optical constants (index of refraction (n) and extinction coefficient (κ)) of ZnO thin film over a wide wavelength range (i.e., vacuum ultraviolet (VUV) to near infrared (NIR)) and thus obtained its bandgap energy using n and κ data. Depending on either the preparation methods [18–23] or techniques for characterization [24–35], the reported direct optical bandgap energy of ZnO was estimated to be around 3.37 eV. Most of the optical techniques for obtaining the optical properties including the bandgaps of ZnO thin films were photoluminescence (PL) measurements either at room or low temperatures, UV–vis spectrophotometer, and transmission spectra [24–29]. Whereas little work was down on the optical constants of ZnO thin films by variable angle spectroscopic ellipsometry

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(VASE) [30–39]. The optical functions of uniaxial ZnO have been determined using two-modulator generalized ellipsometry above the direct bandgap of about 3.3 eV by Jellison and Boatner [30]. Based on the electronic energy band structure with excitonic interaction of three-dimensional critical point, the optical constants near the band edge were fitted to modified model dielectric function by Holden et al. [31]. The complex dielectric functions, $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$, of single crystalline ZnO have been measured by spectroscopic ellipsometry (SE) in the photon-energy range between 1.5 (830 nm) and 5.0 eV (250 nm) at room temperature based on a simplified model of the interband transitions [32]. The adapted model was the first-order Sellmeier equation for the refractive index in the region below and near the fundamental absorption edge. Whereas Sun and Kwok [33] have used the second-order Sellmeier equation for the refractive index of epitaxially ZnO thin films on sapphire substrate in the wavelength range of 375–900 nm by the VASE. Postava et al. [34] have improved the model dielectric function by including Lorentz approximation of line broadening and high-energy absorption term to account for Kramers–Kronig (KK) relations of epitaxial ZnO layer on sapphire substrate in the spectral region from 1.5 eV (827 nm) to 5.4 eV (230 nm). A layer model-based regression analysis using an error function weighted to the experimental error was performed by Rebien et al. [35] to deduce the complex refractive index, film thickness, and surface roughness of ZnO thin films in the UV–vis-near infrared range. The pseudo-dielectric functions, $\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$, of the ZnO thin films on crystalline Si(1 0 0) have been studied using the SE in the spectra region (191–827 nm) by Logothetidis et al. [36]. They modeled that functions by the Tauc–Lorentz (TL) dispersion model with the Bruggeman effective medium approximation layer (BEMAL). The Cauchy dispersion relations have been used for model the optical constants of single crystalline Al-doped ZnO thin films on Si(1 0 0) substrates [37] in the wavelength range 300–900 nm. Cho et al. [38] have been reported the optical constants of DC sputtered ZnO films on thermally oxidized SiO_2/p-type Si(1 0 0) substrates by the Cauchy relations in the spectral range 400–730 nm. Three dispersion models, namely, Sellmeier dispersion model, Cauchy model and Forouhi–Bloomer model, were evaluated for determining the optical constants of ZnO thin films below the energy band gap by Liu et al. [39]. They found that the Cauchy model provides the best spectral fittings among these three models. However, the parameters of the Cauchy–Urbach and Sellmeier's dispersion models were systematically allowed to vary until the generated ellipsometric curves, $\Psi(\lambda)$ and $\Delta(\lambda)$, have best fitted to the measured curves without involving Kramers–Kronig analysis. In our previous work, the optical constants and the band edge of amorphous zinc oxide (a-ZnO) thin films have been investigated in the spectral range 340–1300 nm by the Cauchy–Urbach dispersion model [40].

Therefore, most of the previous studies [24–40] were concentrated on the value of bandgap energy while the optical constants have been studied experimentally only over a short wavelength range and most of those constants have not been recognized, or not fully understood over a wide spectral range. Accurate knowledge of the optical constants of ZnO films is indispensable for understanding its electronic structure and hence for the design and analysis of various optoelectronic devices such as transparent electrodes in solar cells, UV and blue light emitters, and antireflection coatings.

In this paper, ZnO thin films were obtained by reactive sputtering of Zn in pure N_2 plasma at room temperature. The optical constants and the thicknesses of the films were mainly investigated, for the first time, by means of variable angle spectroscopic ellipsometry (VASE) over a wide wavelength range (190–1400 nm) through the Genosc™ parameterized semiconductor oscillator functions and Gaussian oscillator models. X-ray diffraction (XRD) was employed to examine the structure properties of the films while X ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the studied samples. The value of the bandgap energy of the films was investigated by the analysis of the ellipsometric data, photometric spectra, and low temperature photoluminescence (PL) spectrum.

2. Experimental details

ZnO thin films of (90 nm to 0.6 μm) thick were grown on cleaned crystalline Si(1 1 1) and quartz substrates by RF sputtering system of a metallic Zn target (99.999% purity) in reactive nitrogen (99.999% purity) plasma gas. The substrates were clamped to a thick copper block that limited the temperature during deposition to be at room temperature. The deposition system had a base pressure in the range $6–8 \times 10^{-7}$ torr ($8–10.7 \times 10^{-5}$ Pa), while the sputtering pressure was kept at 11 mtorr (1.29 Pa). The films were deposited at a rate of 0.1–0.4 Å/s which correspond to the RF power of 120 W with zero average back power. The deposition rate and the film thickness were monitored with a vibrating quartz crystal thickness monitor. The as-deposited ZnO thin films in a pure N_2 atmosphere showed light to dark blue colors which are corresponding to the sputtered film thickness.

The crystal structure and crystal orientation of the films studied were verified using X-ray diffraction (XRD) measurement with Cu Kα (1.5405 Å) as the incident radiation (Rigaku Geigerflex, 2000 W, X-ray diffractometer). The XRD measurements of θ–2θ scan were performed on ZnO/Si(1 1 1) and ZnO/quartz films over a wide range of diffraction angles (i.e., 10–80°).

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific Escalab 250 X-ray photoelectron spectrometer using monochromatic Al Ka radiation. The wide scanning spectral range was between 10 and 1400 eV, with steps of 0.5 eV and the step for narrow spectra was 0.1. To produce depth profiles, the ZnO thin films were bombarded using argon ions with energy 1 keV. The depth profiles were completed into the silicon substrate in about 2200 s of etching. The XPS has been widely used to determine the chemical composition and stoichiometry, because it offers excellent elements selectivity, quantitative character and high surface sensitivity.

For the optical analyses, spectroscopic ellipsometry measurements of ZnO films on c-Si(1 1 1) were made using a Variable Angle Spectroscopic Ellipsometry (VASE™ J.A. Woollam Co.) of the rotating analyzer type with an autoretarder. A distinct advantage of the VASE over more traditional intensity-related optical measurements, such as reflectance and transmittance, is that ellipsometry deals with the complex reflectance ratio (ρ), which is defined in terms of the standard ellipsometric parameters $\Psi(\lambda)$, the relative amplitude change, and $\Delta(\lambda)$, the relative phase change [41]. Moreover, both of these parameters relate to a rapidly modulating intensity ratio which makes ellipsometric measurements insensitive to fluctuating light intensity, electronic drift, etc. [41]. Thus, the VASE provides more information from a single measurement than reflectance and transmittance, eliminates the need for Kramers–Kronig analysis, and its measurements can be accurate and highly reproducible. Furthermore, it is useful in measuring the depolarization caused by the surface roughness, quartz back side reflection, and thickness non-uniformity. In this work, the ellipsometric measurements $\Psi(\lambda)$ and $\Delta(\lambda)$ were acquired in reflection mode on all samples over the spectral range of 190–1400 nm with 10 nm steps in air at room temperature. For the SE analyses, the angles of incidence of the light beam on the sample surfaces were chosen to be 65°, 70° and 75°. These angles were carefully chosen to maximize the sensitivity of the VASE near the Brewster angle that varies with wavelength due to index dispersion of the silicon substrate. Further details about VASE measurements and

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