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Investigations on zinc oxide thin films grown on Si (1 0 0) by thermal oxidation

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Abstract

Thin films of ZnO were grown on p-type Si (1 0 0) substrates by thermal oxidation. The *in situ* growth of the metallic Zn films were thermally oxidized at different temperatures ranging from 300 to 500 °C to yield ZnO thin films. The structural characterization of the thin films was carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The X-ray diffraction measurements show that the films deposited at 500 °C had better crystalline quality than the rest. The electrical transport properties of the ZnO/Si heterojunction were investigated by current–voltage (*I*–*V*) and capacitance–voltage (*C*–*V*) measurements. The heterojunction exhibited a barrier height, which is consistent with the energy difference between the work functions of Si and ZnO. Complex impedance spectroscopy measurements at temperatures ranging from 50 to 125 °C were performed on these heterojunctions.

Keywords: Thermal oxidation; Heterojunction; Complex impedance spectroscopy

1. Introduction

Zinc oxide (ZnO), which is a functional oxide material, has been studied over several decades due its immense applications in variety of fields. They are used as coatings in thin film photovoltaic cells [1], antireflective coatings in conventional silicon solar cells [2], light emitting diodes [3], thin film transistors [4], etc. Due to its unique conduction mechanism based on oxygen vacancies, it is widely used in oxygen gas sensors [5]. ZnO has a unique combination of piezoelectric, conductive and optical properties [6]. In recent years, it has been considered as an alternative to GaN due to its superior properties, namely: (i) a large exciton binding energy (~60 meV), (ii) low power thresholds for optical pumping at room temperature, and (iii) tunable band gap energy from 2.8 to 3.3 eV and 3.3 to 4 eV by doping with CdO [7] and MgO [8], respectively. The large exciton binding energy (~60 meV) of ZnO makes it well suited for developing UV light sources and transparent electronics. It is also possible to achieve ZnO p–n diode using excimer laser doping [9]. Growth techniques such as sol–gel process [10], electrochemical growth [11], chemical vapor deposition, dc [12] and rf [13] reactive magnetron sputtering have been used to deposit high-quality ZnO films, but deposition by sputtering proved advantageous because highly oriented films can be obtained [14]. ZnO films on Si substrate attracted great attention due to the advantages of Si substrate in integrated photo electronic devices. Recently, Kim et al. [15] reported the fabrication of a single ZnO nano dot through thermal oxidation route. However there are no reports on the transport properties of the films grown by this method. The objective of the present work is to investigate the structural properties of ZnO thin films on Si substrate grown by thermal oxidation and also to study their heterojunction properties such as current–voltage, capacitance voltage and the impedance studies. A simplified equivalent circuit model with a series resistance is used for the investigation.

2. Experimentation

Metallic Zn thin films were grown on single crystalline p-type Si substrates by dc magnetron sputtering. The substrates were polished one side and oriented along (1 0 0) direction. Its resistivity was around 0.8–1.2 Ω cm, and doping density is about (4–6) × 10^{15} cm^{-3}. The native oxide on Si was chemically etched in diluted hydro fluoric acid (HF) solution for 3 min

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to remove SiO_2 followed by a thorough rinse in de-ionized water. The cleaned Si wafers were immediately transferred to the vacuum chamber and placed on the substrate heater. The base vacuum was maintained at 2×10^{-5} Torr. The films were deposited from a Zn metal target (50 mm diameter) placed at a distance of about 100 mm from the substrate. The target was supplied by a dc power supply. The dc power to the target was fixed at 25 W. Argon gas was used as a sputter gas. The deposition was carried out at a substrate temperature of 200 °C and the deposition pressure was maintained at 100 mTorr. The thickness of the films was about 500 Å. The as deposited Zn metallic films were oxidized in a tube furnace under O_2 flow at different temperatures ranging from 300 to 500 °C at an interval of 100 °C. The duration of oxidation was 120 min. The thickness of the film was measured using a Dektak thickness profilometer. Structural phase determination was carried out using X-ray diffractometer with a Cu Kα radiation (λ = 1.54 Å). The morphology of the films was studied through scanning electron microscopy. Aluminum electrodes were realized on ZnO thin films through a shadow mask, which served as an ohmic contact. The rear side of Si was also coated with Al to realize an ohmic contact [16]. Post metallization annealing was performed at 200 °C in air for 30 min. The *C–V* and *I–V* characteristics were measured by a Keithley LCZ meter and SMU 236, respectively. The temperature dependent *C–V* and the impedance measurement were performed at different frequencies ranging from 1 to 100 kHz. Double beam spectrophotometer was used to measure the transmission spectra of the samples at room temperature.

3. Results and discussion

The structural, optical and transport properties of the thermally oxidized ZnO thin films on Si substrates are discussed in this section.

3.1. X-ray diffraction and scanning electron microscopy

The X-ray diffraction spectrum (Fig. 1) of the thermally oxidized ZnO thin films at different temperatures present intense peak of (0 0 2) orientation of the wurtzite structure. The dominant peak in the XRD spectrum is located at $2\theta = 34.4°$. Indeed, no diffraction peak of metallic Zn was detected by XRD for the samples oxidized at different temperatures ranging from 300 to 500 °C. Even though metallic Zn(1 0 1) are present in the films oxidized at 300 °C, oxidizing at higher temperatures indicated that the metallic Zn films are completely transformed into crystalline ZnO at the specified temperature range 400–500 °C. The peak at $2\theta = 69.5°$ is attributed to the (0 0 4) reflection from Si. The XRD pattern depicts highly oriented crystallographic growth of ZnO films with *c*-axis perpendicular to the substrate. The diffraction peaks become more intense when the growth temperature is increased. As Fujimura et al. [17] reported, the surface free energy is the smallest on the (0 0 2) surface of ZnO and hence the thin films tend to grow along it. Fig. 2 shows the SEM pictures the ZnO films oxidized in the temperature range 300–500 °C. The grains tend to grow larger when the growth temperature is increased. The pictures also reveal pellet structure with dense grains.

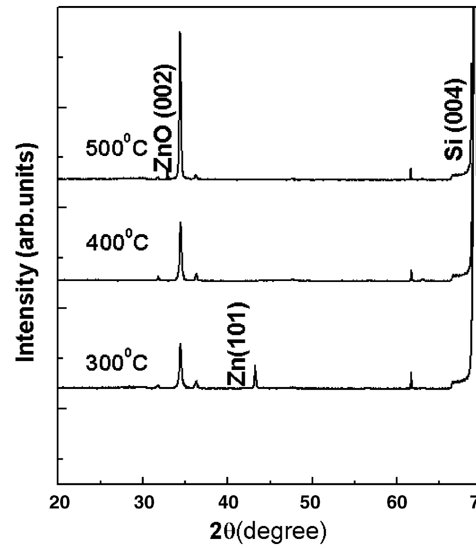

Fig. 1. XRD pattern of ZnO thin films grown at 300, 400 and 500 °C.

3.2. Transmission spectra

Optical transmission spectra are measured by an UV–vis spectrophotometer at room temperature. For the transmission measurements, the films were grown on corning glass and irradiated at a perpendicular angle of incidence with corning glass as the reference. For all the films the average transmission for the visible wavelength region (400–900 nm) is more than 70%. Fig. 3(a) shows the transmission spectra of ZnO thin films grown on corning glass at different temperatures (300–500 °C). The absorption coefficient α of the films is calculated using

$$\alpha = \frac{1}{t} \ln\left(\frac{T}{1-R}\right) \quad (1)$$

where T and R were transmittance and reflectance and t is the thickness measured by the surface profilometer. It is observed that the transmittance in the visible region increases with growth temperature. Fig. 3(b) shows $(\alpha h\nu)^2$ versus energy plot of the films. From the sharp absorption edge, the band gap is estimated. A blue shift in the optical band gap is observed and this could be attributed to the Burstein–Moss effect [18]. A slightly low value of overall transmittance observed in the films grown at 300 °C is due to the lower oxygen incorporation and the associated high density of absorption centers generated within the gap oxygen vacancies and with the morphological effects.

3.3. Current–voltage characteristics

Fig. 4 depicts the *I–V* characteristics of a n-ZnO/p-Si heterojunction thin film diode. Several features of these *I–V* characteristics are noteworthy. The heterojunction demonstrates rectifying behavior with a typical forward-to-reverse current ratio of 8 in the voltage range of −2 to 2 V. It is also evident that forward threshold voltage occurs at ∼1.5 V. This forward