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Characterization of electron beam evaporated ZnO thin films and stacking ZnO fabricated by e-beam evaporation and rf magnetron sputtering for the realization of resonators

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Abstract

High quality Zinc oxide thin films have been fabricated by reactive e-beam evaporation in an oxygen environment. The effect of air annealing on the optical and structural properties of the e-beam evaporated ZnO is investigated. Raman spectroscopy has been found to be an efficient tool to evaluate the residual stress in the as-grown ZnO films from the position of the E_2 (high) mode. Photoluminescence and transmittance measurements showed that the best optical and structural quality of the e-beam evaporated ZnO occurred at 300 °C. Finally, thin films of ZnO evaporated by e-beam technique have served to eliminate the compressive stress due to the sputtered piezoelectric ZnO and therefore to improve the quality of the fabricated resonators by stacking these ZnO layers fabricated by electron beam technique and rf magnetron sputtering, respectively.

Keywords: Zinc oxide; Electron beam evaporation; Annealing treatment; Structural properties; Optical measurements; Resonator

1. Introduction

Zinc oxide normally forms in the hexagonal (wurtzite) crystal structure with $a = 3.25$ Å and $c = 5.12$ Å and is a wide bandgap material, with a high chemical stability, and good photoelectric and piezoelectric properties [1–4]. It is used in various technological domains such as transparent electrodes, solar cells, gas sensors and surface acoustic wave devices [5,6]. Its low price compared with other material makes it a good candidate for industrial applications [7]. Many techniques, such as laser ablation [8], spray pyrolysis [9], sputtering [10,11], electron beam evaporation [12,13] and metal–organic chemical vapour deposition [14] have been developed and used to grow ZnO on a variety of substrates.

Optical and structural characteristics of ZnO thin films evaporated by reactive electron beam technique in an oxygen environment have been studied in this work. Raman spectroscopy, photoluminescence and transmittance have been done in order to observe the effect of the temperature growth variation and the post annealing process on the e-beam evaporated ZnO thin films.

Once the evaporation of ZnO by e-beam technique has been optimized, thin layers of piezoelectric ZnO have been sputtered by rf magnetron on the e-beam evaporated films trying to reduce the compressive stress due to the sputtered ZnO and to improve the quality of the formed resonator

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because the rf magnetron sputtered ZnO was found to be in compressive stress [10,11].

2. Experimental procedure

The target used to fabricate zinc oxide films on (1 0 0)-oriented silicon substrate and on glass corning by reactive electron beam technique was a high-purity (99.99%) polycrystalline ZnO source. The vacuum chamber was evacuated, using a primary and a turbomolecular pump, to a pressure below 10^{-6} Torr. The substrate temperature was varied from 100 to 500 °C by Joule effect. A thermo-couple (K-type chromel–Alumel) placed in contact with the substrate was used to monitor the substrate temperature. The substrate to target distance was 12 cm and the high voltage was about 5 kV. Before the deposition, the substrates were cleaned successively with degreaser in an ultrasonic cleaner, and then rinsed in distilled water and alcohol. A metal foil covered the borders of each substrate to provide a sharp edge on the film for metric thickness measurements with a Dektak profilometer after the thin layer deposition. The required oxygen gas can be introduced in the deposition chamber through a variable leak valve and is maintained at a pressure of 8×10^{-5} Torr in the evaporation chamber. The collisions of O_2 molecules with both high-energy electrons and particles evaporated out from ZnO source partly ionize the O_2 molecules and improve the film stoichiometry. The film growth rate has ranged from 3 to 5 Å s^{-1}, depending on the substrate temperature, the oxygen pressure and the filament current of the electron beam. After the deposition, the films were annealed for one hour in air at 750 °C, to investigate the effect of annealing on the structural and optical properties of the evaporated ZnO thin films.

Micro-Raman spectra were measured in a large frequency range, 50–730 cm^{-1}, using the 514.5 nm excitation lines from a mixed Ar/Kr ion laser (Spectra physics 2017) in the back scattering geometry on a Jobin–Yvon T64000 spectrometer equipped with a liquid nitrogen cooled CCD detector. In order to avoid the heating of the sample, the incident power was limited at 20 mW. Photoluminescence measurements were controlled at room temperature using the 244 nm wavelength of a doubled Ar^+ ion laser as the excitation source with an output power of 10 mW. A Triax 550 spectrometer from Jobin–Yvon and a cooled CCD camera from Hamamastu completed the setup. Optical transmittance measurements were carried out in the wavelength range from 280 to 1000 nm by using a CARY UV–Vis spectrophotometer.

In previous studies, ZnO deposition by magnetron sputtering has been investigated and an optimum temperature growth of 100 °C has been found [10,11]. The target was metallic zinc with 99.95% purity. The residual pressure was about 10^{-4} Pa. Magnetron sputtering was carried out in an oxygen and argon mixed gas atmosphere by supplying rf power at a frequency of 13.56 MHz. High-purity mixed oxygen–argon introduced during deposition raised the pressure in the chamber to 0.44 Pa, the oxygen concentration was 20%, the sputtering power was 50 W and the target to substrate distance was 70 mm. Prior to the deposition, the target was pre-sputtered for a few minutes to remove any contamination on its surface.

The structural properties of the ZnO thin films were analysed by X-ray diffraction (XRD) using Cu Kα radiation. The morphology of the stacked ZnO layers was observed by scanning electron microscopy (SEM). The piezoelectric activity was characterized by using a network analyzer whose band-width varies from 200 kHz to 1.3 GHz.

3. Experimental results and discussion

3.1. Raman spectra

ZnO crystallizes in the hexagonal wurtzite structure, which belongs to the space group C^4_{6V}. The group theory predicts that the phonon modes belong to the $2E_2$, $2E_1$, $2A_1$ and $2B_1$ symmetries. The two B_1 symmetry modes are not Raman active [14].

In Fig. 1 are compared the Raman spectra measured on e-beam evaporated ZnO films grown on Si(1 0 0) at 300 °C as grown (Fig. 1(a)), and after annealing (Fig. 1(b)). The intensity of both Raman spectra is strong compared to that of Raman spectrum recorded on other e-beam ZnO samples [12]. This results from the relatively large grain size in our sample. The shift of the E_2 phonon frequency gives information on stress. Previous investigations have shown the relation between the stress and the E_2 (high) mode frequency: under a compressive stress the E_2 (high) upshifts, whereas a tensile stress leads to a downshift of the E_2 (high) mode [15]. In Fig. 1(a) the position of the E_2 (high) mode of the ZnO thin films is observed at 434.5 cm^{-1}. With respect to the frequency of the E_2 (high) mode in ZnO standard sample (437 cm^{-1}) [15], a Raman shift of 2.5 cm^{-1} is

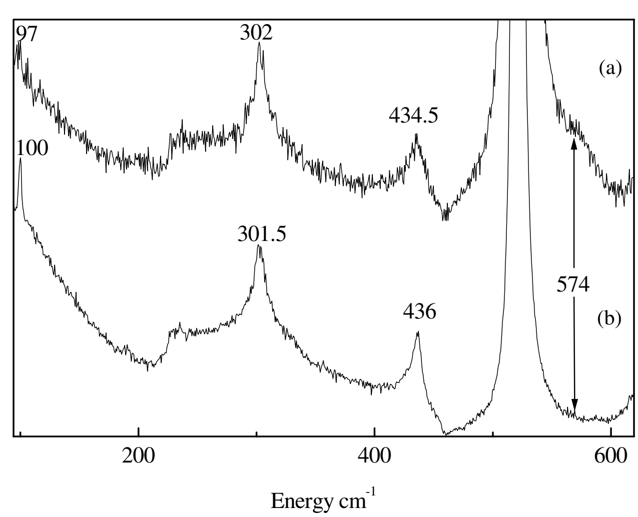

Fig. 1. Raman spectra of e-beam evaporated ZnO films grown on Si(1 0 0) at 300 °C, as grown (a) and after annealing process (b).