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COMMUNICATIONS

Optical properties of the plasma hydrogenated ZnO thin films

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We have optimized the deposition of the highly electrically resistive undoped (intrinsic) polycrystalline ZnO thin layers on fused silica substrates by the DC reactive magnetron sputtering of metallic zinc target in argonne/oxide atmosphere and we introduced the post-deposition hydrogen plasma doping. The thickness of thin film was evaluated by reflectance interferometry using the metallographic optical microscope fiber coupled to the CCD spectrometer operating in 400-1000 nm spectral range. The optical absorption was measured by photothermal deflection spectroscopy operating in 300-1600 nm spectral range. The change of the optical absorption edge and the increase of the infrared optical absorption was detected in hydrogenated ZnO. The increase of the infrared optical absorption goes with the increase of the electrical conductivity. We conclude that the plasma hydrogenation of the intrinsic ZnO thin films is related to increase of the free carrier concentration.

K e y w o r d s: metal oxide, magnetron sputtering, thin films, reflectance interferometry, photothermal deflection spectroscopy

1 Introduction

The intrinsic (undoped) zinc oxide (ZnO) is an electrically resistive wide band gap semiconductor optically transparent for the visible light with the large exciton binding energy, high electron mobility, high refractive index and diversity of nanostructure shapes which makes it suitable for many applications in the optoelectronic devices, optical sensors, and biosensors [1]. The resistivity of ZnO film can be significantly reduced by the addition of H_2 in Ar during RF sputtering, likely due to the hydrogen donor of ZnO [2]. First-principles calculations of the optical and electronic properties of H-doped ZnO system show that there is a strong band formation between H and O, while H intersects the ZnO bond and increases charge of jointed oxygen, due to decrement of volume of supercell. The energy band gap and the optical absorption edge shift to higher energy due to the Burstain Moss effect[3].

In magnetron sputtering the Ar^+ bombardment process causes the sputtering of Zn, which then react with oxygen and condensate in the form of the thin ZnO lm on substrate. Secondary electrons emitted from the target surface as a result of the ion bombardment play an important role in maintaining the cold plasma [4]. Recently, we have optimized the deposition of the intrinsic ZnO thin films by the reactive magnetron sputtering of metallic Zn target in a DC capacitive coupled glow discharge plasma of the reactive mixture of argon and oxygen [5]. We have studied the effect of hydrogen plasma treatment on the intrinsic ZnO thin films and we confirmed by 4-point resistivity measurements that the electrical conductivity increases after hydrogen plasma treatment [6]. We observed the increase of the infrared optical absorption in hydrogenated ZnO films correlated with the increase of the electrical conductivity. Therefore, we concluded that the increase of the electrical conductivity in hydrogen plasma treated ZnO layers is related to the increase of the free carrier concentration indicating the post-deposition hydrogen plasma doping.

In this paper, we introduce the reflectance interferometry microscope for fast evaluation of the thin film thickness with the high spatial resolution. We also discuss the differences in the optical absorption coefficient spectra of the oxidized and plasma hydrogenated ZnO thin films.

2 Experimental procedures

Thin ZnO films were grown by the reactive magnetron sputtering [7] in the stainless steel vacuum chamber using Zn target with purity 99.9%, diameter 60 mm, sputtered zone diameter 45 mm, distance between target and sample holder 75 mm. The residual pressure in vacuum chamber prior deposition was 0.01 Pa. The magnetic field was induced electromagnetically by current 4.5 A. The Zn target was sputtered in a dc capacitively couple glow discharge plasma (grounded substrate holder, constant +400 V on target, dc current 0.13 A) of the reactive mixture of argon (purity 99.999%) and oxygen (purity 99.95%) under flow rate 2.0 and 0.5 sccm and the pressure 1 Pa. The temperature of the resistively heated substrate holder stage was regulated from 100 to 450 °C.

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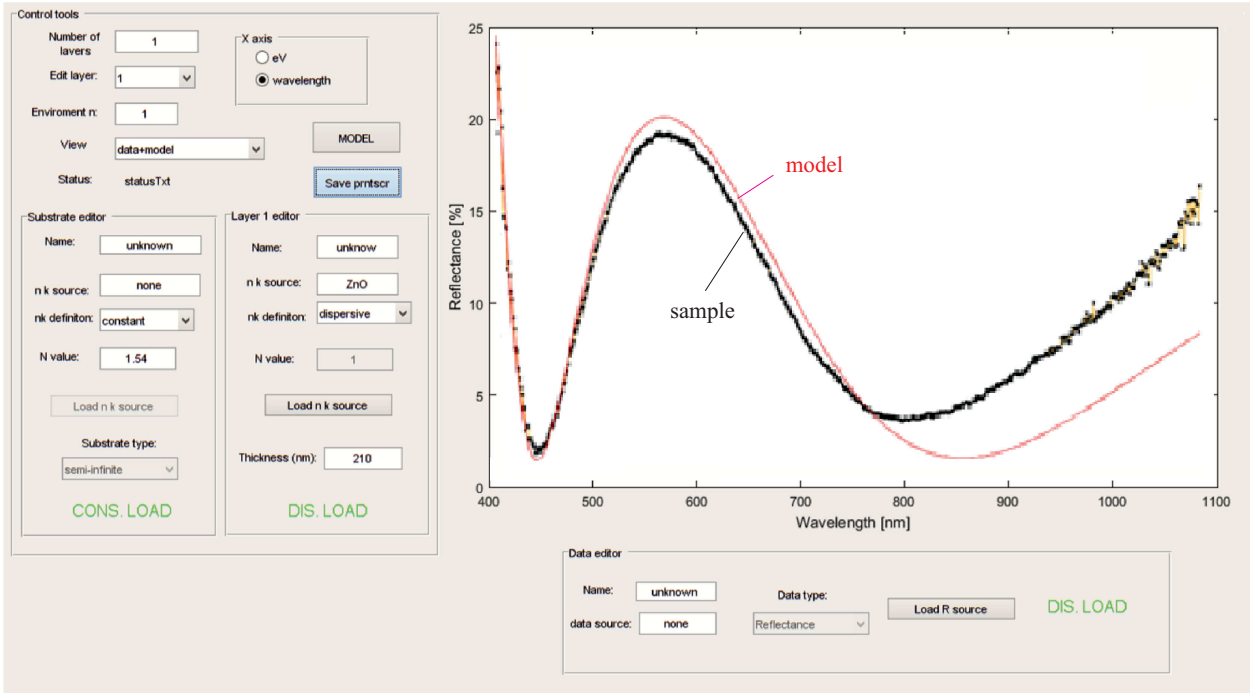

Fig. 1. The thin layer inspector GUI interface of the thin film model reflectance spectra

The post-deposition hydrogenation was performed in capacitively coupled plasma (CCP) reactor operating at room temperature at radio frequency (RF) of 13.56 MHz at the working pressure of 70 Pa. The ion energy was controlled by the applied RF power. During plasma treatment, the density of RF power was kept about 0.01 W/cm^2 for 10 min. Prior the hydrogen plasma treatment, the chamber was evacuated to a base pressure of 1 mPa.

Here we introduce for the first time the fast and simple optical setup to evaluate the thickness of thin film by the optical reflectance interferometry using the metallographic trinocular optical microscope MTM409 (INTRACO MICRO, Ltd.). The microscope is equipped with 10 W halogen lamp as a light source, the external power supply and the fiber coupled TE cooled 16 Bit CCD spectrometer operating in the wavelength range of 400 to 1000 nm with 0.5 nm resolution. The optical fiber is coupled to camera eyepiece on top of the microscope. The spatial resolution varies from about 0.1 mm (objective 50$\times$ to 1 mm (objective 5$\times$.

To evaluate the thickness we developed the user-friendly software that reads directly the ASCII data exported from CCD spectrometer [8]. Our program works in the semi-infinity substrate approximation to speed the calculations. The optical parameters of the thin film and substrate are either constants or the tabulated values of the complex index of refraction loaded from the extendable database files in simple ASCII format of three columns (wavelength in nm, n and k, where $n + ik$ is the complex index of refraction).

The program calculates the reflectance spectrum for selected thin film thickness and compares the calculated and measured spectra, see Fig. 1. The user finds the correct thin film thickness by changing manually the model thickness. The manual approach has an advantage that it can be applied also for partly scattering samples where the reflectance spectra are suppressed.

We measured the optical absorption of thin films directly using the photothermal deflection spectroscopy (PDS) with high sensitivity of four orders of magnitude [9]. The heat absorbed in the sample immersed in transparent liquid in quartz cuvette generates the periodical thermal waves in the medium surrounding the sample causing the periodical deflection of the laser beam parallel to the sample surface. The amplitude of the deflection normalized on the black sample spectra gives the optical absorption of thin film. The laser beam deflection is detected by the position detector. For details see [10].

The surface morphology was observed using Scanning Electron Microscopy (SEM) MAIA3-TESCAN. at the accelerating voltage of 10 keV using In-lens detector. The Agilent 34410 a digital multimeter and the 4-point method was employed to measure the electrical resistance of the ZnO films using and the van der Pauw contact configuration based on four 150 nm thick Al electrodes evaporated in each corner of the sample. The consecutive measurements were performed with the voltage source applied to two adjacent electrodes and the current being measured at the opposite side electrodes, [11].

3 Experimental results and discussion

Figure 2 and 3 represent SEM images of the top and cross section view of ZnO layer deposited on glass sub-

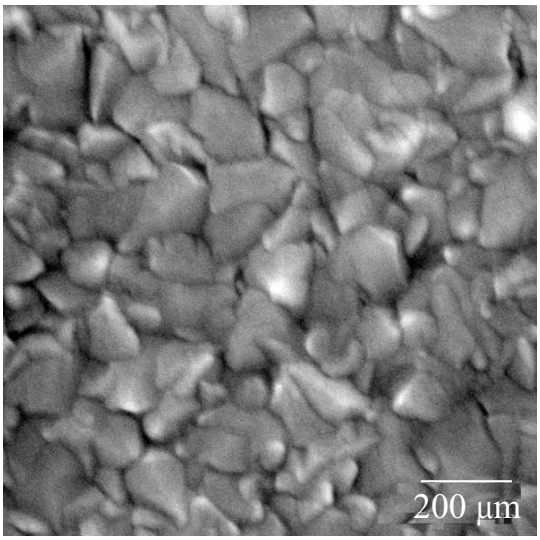

Fig. 2. The SEM image of the top view of nanocrystaline ZnO layer

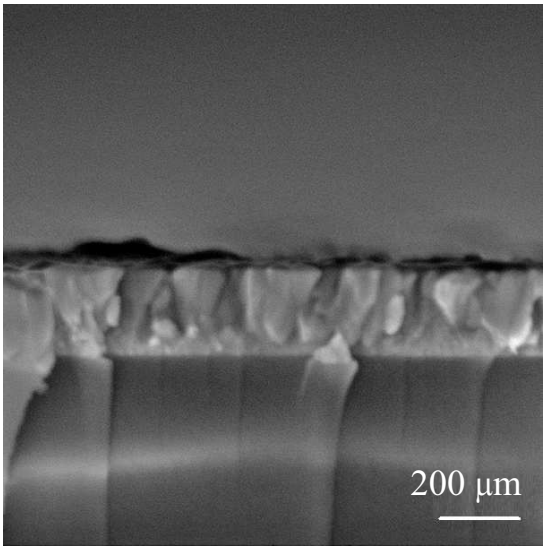

Fig. 3. The SEM image of the cross section view of the 210 nm thick ZnO layer

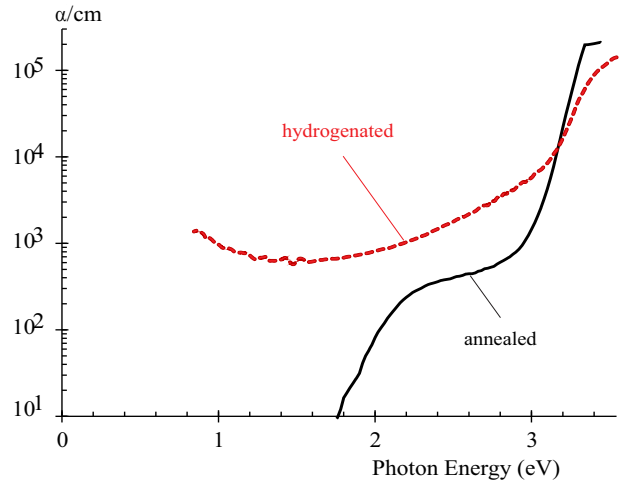

Fig. 4. Dispersion of the optical absorption coefficient α of the annealed and hydrogenated ZnO thin films

strate. Figure 2 shows the average grain size about 130 nm. The thin film thickness can be directly evaluated from the cross section SEM image in Fig. 3 to be about 210 nm.

There is a need of the contactless, fast and user-friendly method for the thin film thickness evaluation, such as the spectrally resolved reflectance interferometry[12]. Using the spectrometer attached to optical microscope, the reflectance $R = (S - D)/(B - D)$ of thin film is a ratio of the signal S reflected from the sample and the reference spectrum B after subtracting both spectra by dark signal D. The reference and sample reflectance is measured using image focused on the sample or mirror surface. Prior the measurements, the intensity of the reference spectrum is adjusted using blue color glass filter and two partly crossed polarizing filters. The dark scan is measured as a reflectance of the black sample holder using defocused objective. It takes about 100 ms to measure one spectrum and when repeated 10 $\times$ to reduce noise, the total time is about 1 s. This allows manually monitoring the homogeneity of the thin thickness by moving the sample using microscope XY stage.

The thin film thickness 210 nm evaluated from the reflectance spectra correlates with thickness shown by the cross section scanning electron microscopy image, see Fig. 1 and Fig. 3.

Figure 4 shows the optical absorption coefficient spectra of the annealed and hydrogenated nanocrystalline ZnO thin films. The hydrogenated ZnO absorbs the near infrared light and is electrically conductive with the specific resistivity about $10^{-2}\Omega$cm. After thermal annealing in air at 400 °C, the optical absorption was significantly reduced in the infrared region and the electrical resistivity increased by 4 orders of magnitude to $10^{2}\Omega$cm. Thus, we conclude that the near infrared optical absorption in the hydrogenated sample is related to the increase of the free carrier concentration.

4 Conclusions

We applied the reflectance interferometry for fast and economical evaluation of the thin film thickness from the optical interference fringes. The reflectance was measured in the 400 to 1000 nm spectral range using the metallographic optical microscope fiber coupled to the CCD spectrometer. We have developed the software to simulate the interference fringes of thin film on semi-infinite substrate for simple evaluation of the film thickness and we have shown that it correlates very well with thickness evaluated from the cross section scanning electron microscopy image. We studied the effect of hydrogen plasma

treatment and thermal annealing of the nominally undoped ZnO thin film deposited by DC reactive magnetron sputtering of Zn target in the gas mixture of argon and oxygen plasma. After oxidation due to thermal annealing in air, the optical absorption was significantly reduced in the infrared region and the electrical resistivity increased. After hydrogen plasma treatment, the increase of the infrared optical absorption, related to free carrier concentration, was detected below the optical absorption edge. The increase of the optical absorption goes with the increase of the electrical conductivity related to the increase of the free carrier concentration.

Acknowledgements

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