HYDROGEN PLASMA TREATMENT OF ZNO THIN FILMS

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Abstract

ZnO is an attractive wide band gap semiconductor with large exciton binding energy, high refractive index, high biocompatibility and diversety of nanostructure shapes which makes it suitable for many applications in the optoelectronic devices, optical sensors, and biosensors. We study the effect of hydrogen plasma treatment 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. The SEM images show that the crystal size increases with film thickness. We confirm, that the electrical conductivity significantly increases after hydrogen plasma treatment by 4 orders of magnitude. Moreover, the increase of the infrared optical absorption, related to free carrier concentration, was detected below the optical absorption edge by the photothermal deflection spectroscopy.

Keywords: ZnO, reactive magnetron sputtering, hydrogen plasma treatment

1. INTRODUCTION

ZnO is an attractive II-VI semiconductor material with a wide direct band gap about 3.3 eV, large exciton binding energy (60 meV), high refractive index, high biocompatibility, and diversety of nanostructure shapes which could lead to great applications in the optoelectronic devices, optical sensors, and biosensors [1-3]. Some of the possible optoelectronic devices applications of ZnO films are for visible and ultraviolet light emitters, for emission displays and UV light emitting diodes [3]. ZnO is naturally an n-type semiconductor because of the self-compensation from defects, such as the oxygen vacancy and the zinc interstitial [1]. Doping changes the electrical properties of ZnO films. For example, the conductivity of ZnO films have been improved using aluminum (Al) doping of the ZnO film. The Al doping generates a free electrons and results in increasing the electrical conductivity [4, 5]. Hydrogen doping in ZnO is also a likely source of the n-type conductivity. Hydrogen has many states in a ZnO such as located at the bond-centered or the antibonding, trapped at an oxygen vacancy or zinc vacancy, and occurs in the ZnO interstitial hydrogen molecule (H_2) [6].

Many techniques have been used for the fabrication of ZnO thin fIlm, such as molecular beam epitaxy, pulsed laser deposition, chemical vapor deposition, magnetron sputtering [7-10]. AC magnetron sputering of the insulating (undoped) ZnO target and the DC reactive magnetron sputtering of metalic Zn target in the gas mixture of argon and oxygen are both techniques for deposition of intrinsic ZnO films. By variation of gas composition and substrate temperature we can influence the structures and optical properties of the deposited ZnO films [11-13]. In this article, we describe the DC reactive magnetron sputtering of metalic Zn target in the gas mixture of argon and oxygen and we show the effect of the post-deposition hydrogen treatment on the electrical resistivity and optical absorption.

2. EXPERIMENTAL

2.1. Reactive magnetron sputtering and plasma treatment

ZnO films were deposited on fused silica substrates (10 × 10 mm^2) by direct current (DC) reactive magnetron sputtering of metallic zinc target. Before placing into the deposition chamber, the substrates were sequentially

cleaned in ultrasonic baths of acetone and alcohol for 5 min, and rinsed in de-ionized water. Finally, they were blown dry with nitrogen and introduced into the chamber. The distance from the substrate to the target was 75 mm. The sputtering chamber was evacuated to the base pressure of 1 mPa at a constant substrate temperature of 400°C. High purity argon (99.999 %) and oxygen (99.95 %) gases were introduced to a pressure of 1 Pa through the mass flow controller at flow rate of 2.0 and 0.5 sccm. The zinc target was first sputtered for 10 min to remove the target surface oxide layer followed by deposition performed with a direct current of 0.1 A for 10 and for 60 min.

The post-deposition hydrogenation was performed in capacitively coupled plasma (CCP) reactor operating at room temperature at radio frequency (RF) of 13.56 MHz. Prior the hydrogen plasma treatment, the chamber was evacuated to a base pressure of 1 mPa and then filled with hydrogen to a 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.

2.2. Reflectance interferometry

The thickness of thin films was estimated by optical reflectance interferometry in wavelength range of 400 ÷ 1000 nm using metallographic optical microscope MTM409 equipped by 10 W halogen lamp as a light source and the BTC112E fiber coupled TE cooled 16 Bit CCD spectrometer. The reflectance was measured as a ratio of the signal reflected from the sample and the signal reflected from silver mirror. The thickness was fitted from the reflection spectra using the tabulated values of the index of refraction of ZnO and the commercial software FilmWizard.

2.3. Electrical resistivity

The Agilent 34410a 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 [14].

2.4. Photothermal deflection spectroscopy

The Photothermal Deflection Spectroscopy (PDS) measures directly the optical absorption of thin films in wavelength range of 250 ÷ 1600 nm with high sensitivity of four orders of magnitude. The heat absorbed in the sample 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 optical absorptance is detected by the position detector monitoring the laser beam deflection. The optical absorption of thin film is evaluated as the ratio of the amplitudes of the deflection of the laser beam at the investigated sample and at the black sample.

2.5. Scanning electron microscopy

Scanning Electron Microscopy (SEM) (MAIA, TESCAN) was used for imaging the ZnO films. The images were taken at accelerating voltage of 10 keV using In-lens detector. The grain sizes were estimated from the images using ATLAS software.

3. RESULTS AND DISCUSSION

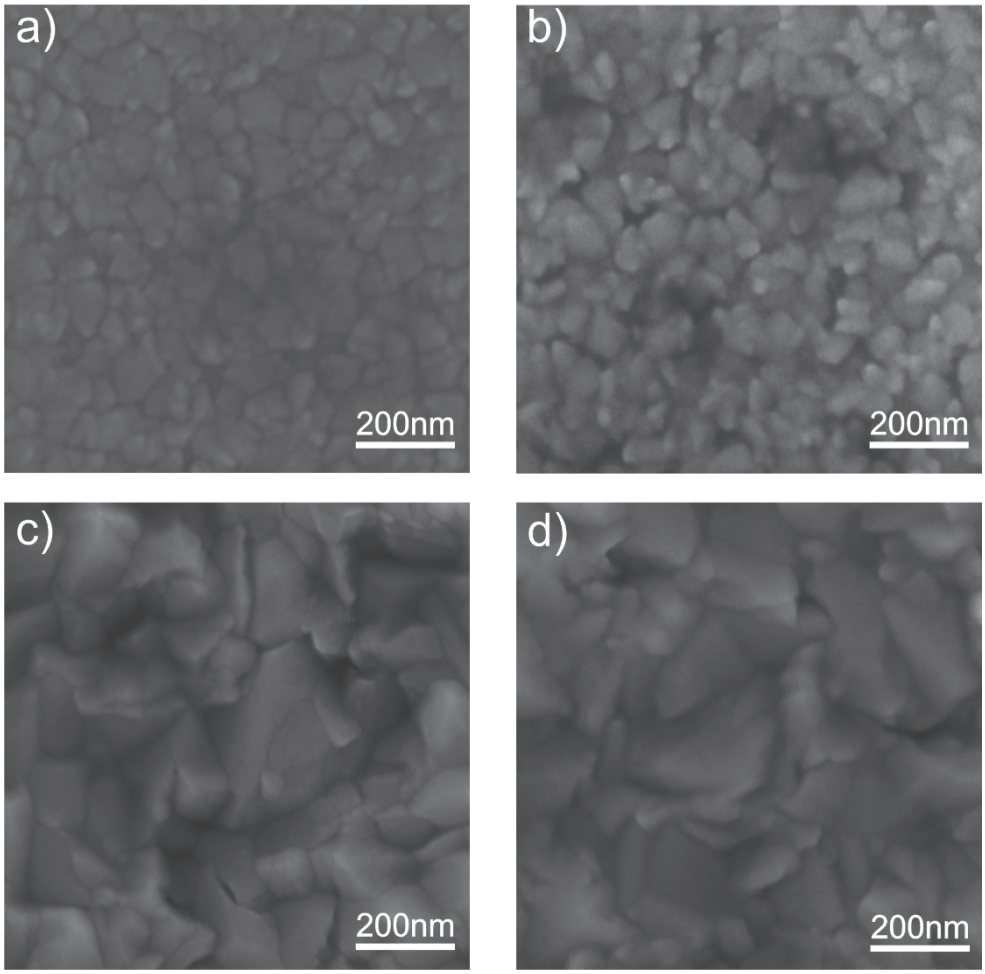

Figure 1 SEM micrographs of as-grown (a, c) and H-plasma treated ZnO films (b, d) with thicknesses of 100 nm (a,b) and 600 nm (c, d)

Figure 1 shows SEM images with the morphologies of the as-grown films as well as these that were after treated in hydrogen plasma. The measured area was 1 μm^2. It is obvious that the thinner film (a, b) consists of smaller grains that the thicker one (c, d). The SEM micrographs indicates the smoothing effect of hydrogen plasma, however the significant plasma etching was not confirmed by the statistical analysis. The grain sizes of the ZnO films are presented in **Table 1**.

Table 1 Grain sizes of the various ZnO film

Sample	Grain sizes (nm)			
	Min. value	Max. value	Mean value	Std. deviation
As-grown (100 nm)	35	123	73	25
H-plasma (100 nm)	33	121	75	24
As-grown (600 nm)	114	411	195	81
H-plasma (600 nm)	36	292	141	66

The 4-point method in the van der Pauw contact configuration was employed to measure the electrical resistance of thin films. From the electrical resistance and thickness values we calculated the electrical resistivity of the ZnO films. The electrical resitivity is higher in thiner films indicating the free carriers mobility deterioratio by surface scattering. In both cases we have found that the electrical resistivity decreases by about 4 orders of magnitude after 10min of hydrogen plasma treatment compared to as-grown ZnO films.

Table 2 Resistivity of ZnO thin film with different thicknesses before and after H-plasma

	As-grown (100 nm)	H-plasma (100 nm)	As-grown (600 nm)	H-plasma (600 nm)
Resistivity ρ (Ωcm)	122	2.45×10^{-2}	55.7	7.07×10^{-3}

The optical absorption spectra of ZnO films are shown in **Figure 2.** The interference fringes are clearly distinguishable in thicker sample spectra. Both spectra reveal the direct optical absorption edge in the near infrared region at about 3.3 eV which is typical for ZnO. After hydrogen plasma treatment the optical absorption in the near infreared region below the photon energy 1.5 eV significantly increases, whereas the change of the optical absorption edge is negligible. This indicates the increase of the free carrier absorption. We reject the theory that the hydrogen increases electrical conductivity by reducing metallic Zn, because in such a case the increase of the optical absorption would be independent of the photon energy. These conclusions must be further confirmed by the Hall effect measurements. We should also notice, that the relative increase of the free carrier concentration is higher in thinner film, indicating that the hydrogen may not fully penetrate the thicker film.

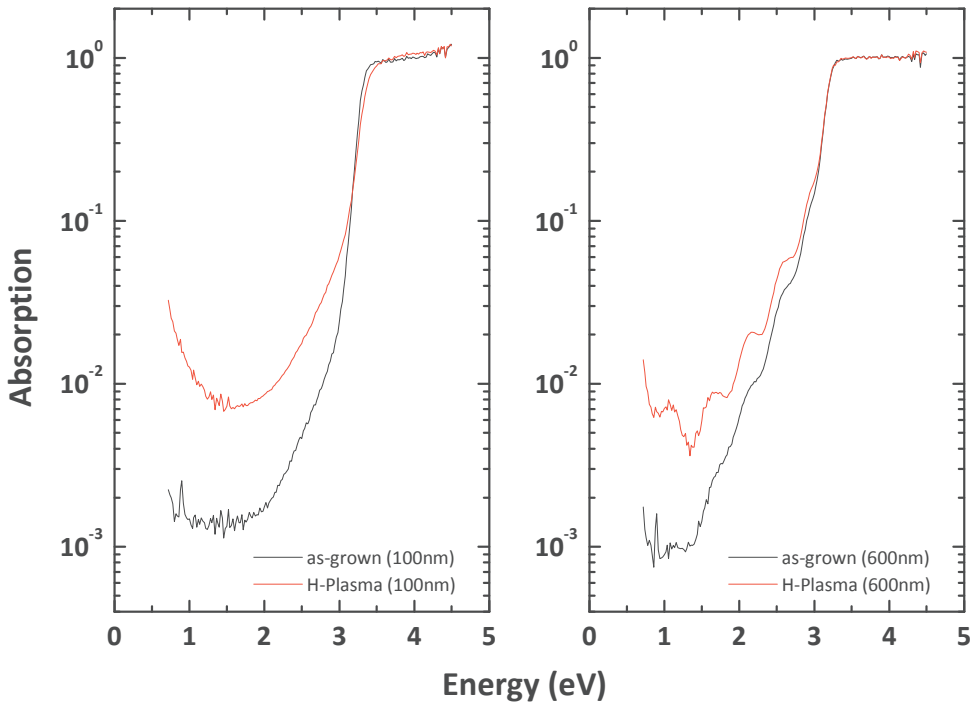

Figure 2 Absorption spectra of as-grown (black) and hydrogen plasma treated (red) ZnO films with thickness of 100 (left) and 600 nm (right)

4. CONCLUSION

We deposited nominally undoped, highly resistive polycrystalline ZnO thin films using DC reactive magnetron sputtering of Zn target in the gas mixture of argon and oxygen plasma. The SEM images show that the crystal

size increases with the film thickness. 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 by 4 orders of magnitude after hydrogen plasma treatment. Moreover, the increase of the infrared optical absorption, related to free carrier concentration, was detected by the photothermal deflection spectroscopy below the optical absorption edge. Therefore, we can conclude that the increase of the electrical conductivity is related to the increase of the free carrier concentration indicating the post-deposition hydrogen plasma doping. Our results must be further confirmed by the Hall effect measurements.

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