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Zinc-acetate 직접 가열에 의한 ZnO막의 제조 및 산소 분위기 영향

논 문 8-4-1

Fabrication of ZnO Films from Directly Heated Zinc-Acetate and Oxygen Effects on the Deposition

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Abstract

ZnO films have been grown easily with the conventional thermal evaporation method on SiO_2 coated Si wafers. Anhydrous zinc acetate has been used as evaporation source. Zinc-acetate was directly heated in the laboratory-made brass boat. Zinc-acetate was sublimed at the boat temperature of about 220 ℃. The substrates were heated to 600 ℃ with home-made tantalium heater. Oxygen has been flowed into the deposition chamber to change the partial pressure of oxygen. X-ray diffraction patterns showed all the films to be amorphous. The films deposited at high oxygen pressure exhibit higher resistivity than films at low pressure. Energy dispersive spectroscopy(EDS) and rutherford backscattering spectrometry(RBS) were conducted on the films to reveal the composition of the ZnO films.

Key words(중요용어): ZnO films(아연 산화막), Evaporation(진공 증착), Directly heated(직접가열), Zinc-acetate(아연-아세테이트), Partial pressure of oxygen(산소 분압), Amorphous(비정질)

1. INTRODUCTION

Much attention has been paid to zinc oxide(ZnO) films due to their unique optical and electrical properties and resulting application as transparent conducting films[1,2] or piezoelectric transducers[3]. ZnO films have been obtained by sputtering[4], metal-organic chemical vapor deposition (MOCVD) [5], and spray pyrolysis[6]. Recently, Leong G. Mar etc.[7] have grown ultra thin ZnO films by thermal evaporation method in which zinc acetete is directly heated and deposited onto the substrate. Anhydrous zinc acetate($Zn(CH_3COOH)_2$) has been known to be a favourable zinc precursor for zinc film deposition by chemical vapor deposition (CVD). The anhydrous zinc acetate is adequate source material for thermal evaporation due to its low sublimation temperature (estimated to be about 234 ℃).

In this paper, we have grown ZnO films up to thickness of 1 μm within 2 hour via conventional thermal evaporation method in which the anhydrous zinc acetate was used as source material. The substrates were heated to 600℃ to crystallize depositing films. X-ray diffraction method were carried out to study the crystallographic characteristics of ZnO films. Oxygen has been flowed into the deposition chamber to change deposition pressure. We expected admitted oxygen to compensate for oxygen deficiencies of ZnO films. Resistivity and activation

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energy were measured. And EDS and RBS measurements were conducted to reveal the compositions of the ZnO films in detail. The role of the ambient oxygen in the growing processes will be discussed.

2. FILM PREPARATION

The ZnO film deposition performed in the conventional evaporator. The laboratory-made brass boat, shown in Fig. 1., was used to heat the zinc acetate. The boat was heated by the ceramic packaged resistive heaters. The boat temperature was monitored and controlled by the personal computer connected to a thermocouple and a current controller. A small hole was placed at the front of the boat to allow the emission of the vapors. Diameter of the hole was 1 mm or 2 mm. Zinc acetate dihydrate loaded into the boat was heated in the evacuated chamber at 100℃ for several hours to remove the water of crystallization. On heating, vacuum deteriorated rapidly. The vacuum is recovered as the water vapor effused from the zinc acetate dihydrate is evacuated, which is an indication that the zinc acetate dihydrate is transformed to anhydrous zinc acetate. After the pressure of the chamber reached 1.0 x 10^{-3} Pa, we heated the boat to 190℃ with normal speed. And then we carefully raised the temperature of the boat with monitoring the pressure variation in the chamber. The pressure rose slowly as the anhydrous zinc acetate was sublimed. The background pressure was 1.0 x 10^{-3} Pa. We opened shutter to deposit films at the pressure of 6.0 x 10^{-3} Pa and the pressure was maintained at (6.0 ± 0.5) x 10^{-3} Pa during deposition. The substrates were heated by the home-made tantalium heater to 600℃. As the resistance of the tantalium heater was as low as 0.1ohm, we used 10 : 1 transformer. Square type(2 mm x 5 mm) resistors were fabricated to measure resistance of the ZnO films from which resistivity was calculated. Aluminum was used for electrodes of the resistors. ZnO film islands and electrodes were patterned by metal masks. The resistance was measured as a function of temperature between 15℃ and 90℃. An activation energy was obtained in this temperature range. We flowed oxygen into the chamber through mass flow controller and needle valve to change the oxygen pressure of the chamber. We raised the chamber pressure to 6.0 x 10^{-2} Pa and executed deposition at 6.5 x 10^{-2} Pa. Metal mask was used to shape step at the film edge. The film thickness was measured at the edge with α-step.

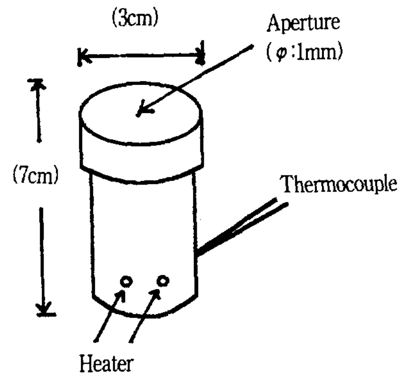


Fig. 1. Configuration of the brass boat used to heat zinc acetate

3. RESULTS AND DISCUSSION

3.1 Deposition of ZnO films

The X-ray pattern of the zinc acetate dihydrate used as source material in this experiments is shown in Fig. 2.(a). Fig. 2.(b) is the X-ray diffraction pattern of the source material heated at 100℃ for several hours as described above. Fig. 2.(b) is perfectly agree with the X-ray pattern of anhydrous zinc acetate put on the JCPDS cards. The brass boat loaded with anhydrous zinc acetate was further heated to sublime it.

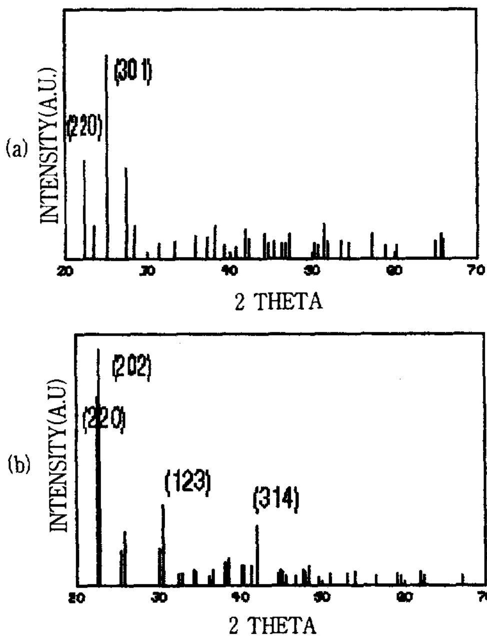


Fig. 2. X-ray diffraction patterns of zinc acetate dihydrate
(a)before dry and (b)after dry

The chamber pressure rises rapidly from the brass boat temperature of 220 ± 5℃ as shown in Fig. 3. We surmise that anhydrous zinc acetate is sublimed at about 220℃. The pressure of the chamber rised slowly during deposition. So we lowered the temperature of the boat to fix the pressure. The temperature decreased within 5℃ for the evaporation period of 2 hours. The depositions were processed in the substrate temperature range 20℃-600℃. In Fig. 4., we plotted the deposition rate as a function of the substrate temperature. In Fig. 4., boat1 and boat2 represent different aperture (diameter of 1 mm and 2 mm respectively). The deposition rate was dependent on the temperature and the diameter of the aperture. The deposition rate is deeply decreased at the substrate temperature of 500℃ which seems to be due to reevaporation. Abrupt decrease in resistivity is also found at the substrate temperature of 500℃(Table 1).

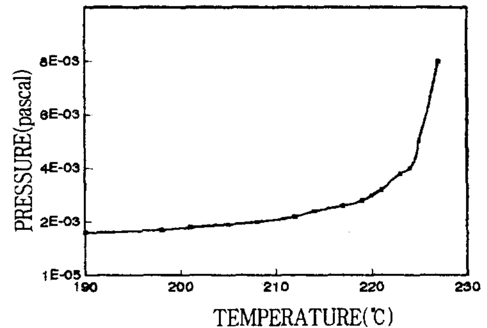


Fig. 3. Chamber pressure variation with source temperature

Deposition rate is as high as 120 Å/min at the substrate temperature of 400℃ with boat2 which is comparable to that of rf sputtering methods.

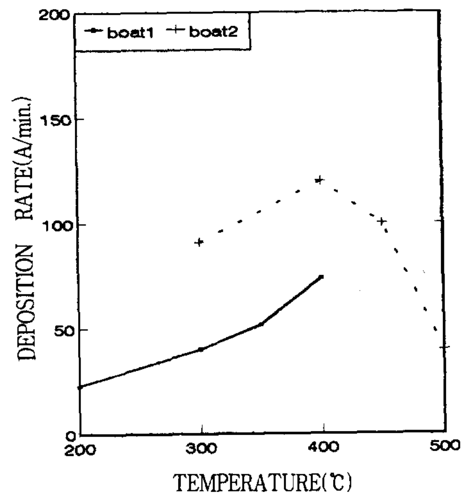


Fig. 4. Deposition rate of ZnO films as a function of substrate temperature

3.2 Properties of the ZnO films

X-ray diffraction patterns were obtained from the ZnO films deposited at the substrate temperature of 20℃-600 ℃. X-ray diffraction patterns showed the films to be amorphous as shown in fig.5.. We measured the current vs. voltage characteristics(I(V)) of the ZnO resistors. The resistors exhibit good ohmic properties as shown in Fig. 6.

Resistivities calculated from I(V) measure-

ments are listed in Table Ⅰ. By raising the deposition pressure to 6.0 $\times 10^{-2}$ Pa with oxygen, its resistivity increased by a factor of 10000. The increase of resistivity may be attributed to the following reasons. (1)The oxygen makes in-situ compensation for oxygen deficiencies in the ZnO films during deposition. (2)The extra oxygen included in the ZnO films acts as traps. (3)The ZnO films are porous by the low-vacuum environments. Resistivities were measured in a temperature range of 20℃-90℃ (R(T)). Some results are shown in Fig. 7.. A sweep direction was shown by arrow. In case of the films deposited at high pressure, a return sweep traced the different line indicated by the arrow. It means some traps in the films. We obtained activation energies from Fig. 7.. The activation energies are also listed in Table Ⅰ. The activation energies(about 0.01 eV) of the

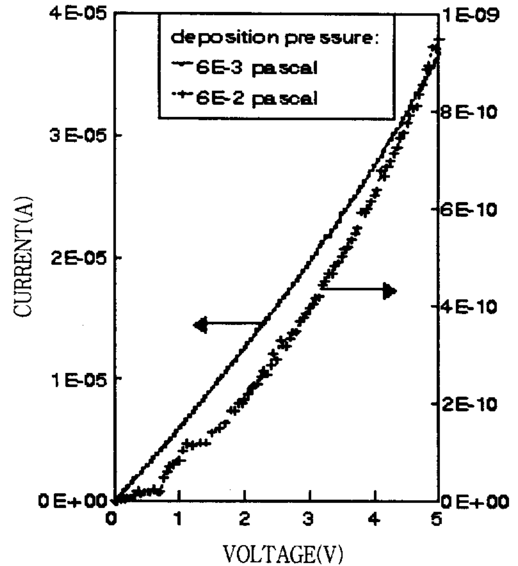


Fig. 6. Current dependence on voltage for two representative ZnO films

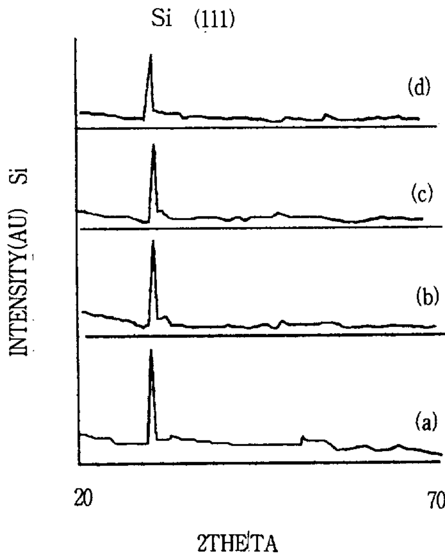


Fig. 5. XRD results of ZnO films.
a) T = 300℃,b) T = 400℃,c) T=500℃,d) T = 600℃

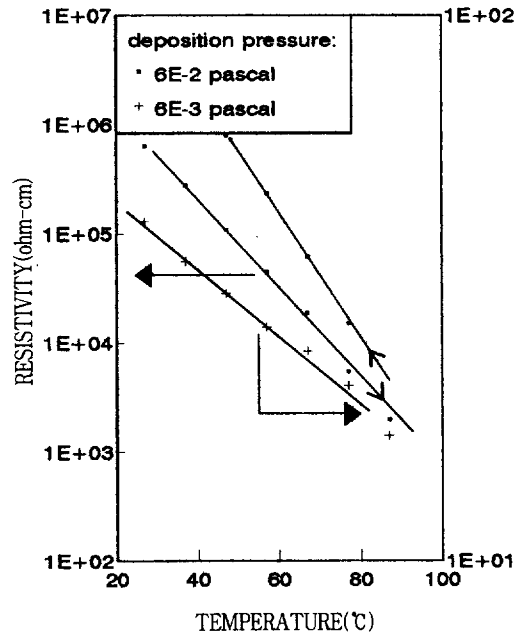
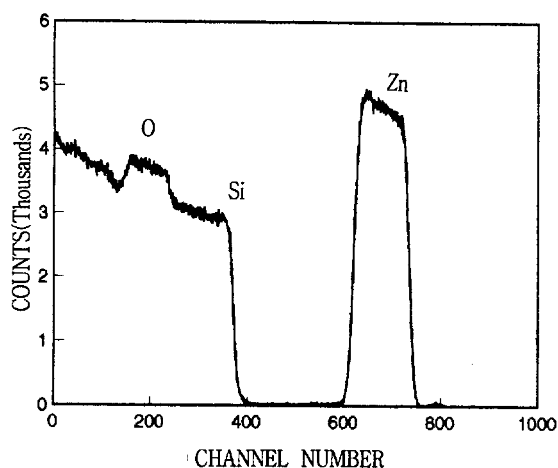


Fig. 7. Resistivity variation with temperature

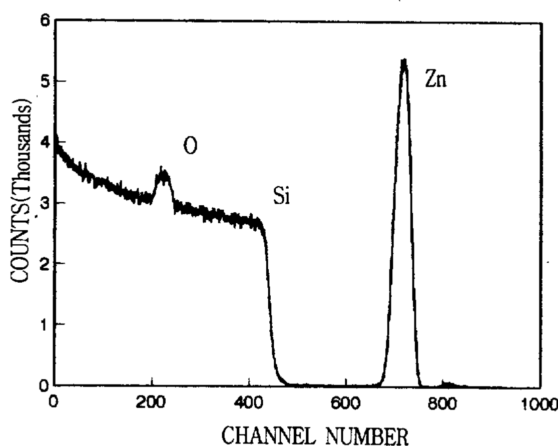
films deposited at the pressure of 6 x 10^{-3} Pa are too low comparing with that of monocrystalline ZnO stoichiometric defects(0.05 eV)[8]. By raising the deposition pressure, the activation energy increases to 0.04 eV. EDS confirmed the presence of zinc and oxygen in the films. Fig. 7. gives RBS spectra of the films deposited at the substrate temperature of 400℃. The deposition pressure of (a) was 6 x 10^{-2} Pa and that of (b) is 6 x 10^{-3} Pa. The measured

Table 1. Results of the Resistivity and activation energy measurements.

Deposition pressure(Pa)	6×10^{-3}			6×10^{-2}
Substrate temp.(℃)	300	400	500	400
Resistivity (Ω-cm)	58	57	0.25	1.2×10^{6}
Activation energy(eV)	0.012	0.013		0.03×0.04



(a)



(b)

Fig. 8. RBS spectra for ZnO films on Si wafer deposited at (a)$6x10^{-2}$ Pa and (b)$6x10^{-3}$ Pa

oxygen to zinc ratios for (a) and (b) are approximatly 1.0. and 1.1, respectively. The obtained ZnO films deposited at different oxygen pressure were not shown oxygen deficiencies. We come to conclusion that more traps in the ZnO films deposited at high pressure may contribute to increment of resistivity.

4. CONCLUSION

It has been shown that it is possible to grow thick films(thicker than 1 um) of ZnO with reasonable deposition rate by conventional thermal evaporation method. Reactive evaporations have been tried by adding oxygen to the chamber. A considerable increase in resistivity and activation energy were obtained by reactive deposition. But RBS measurements exhibit no oxygen deficiencies in the films doposited at different oxygen partial pressure. From the hysteresis in the results of the R(T) measurement, we conclude that the resistivity increase is due to the increment of trap density.

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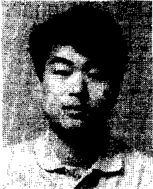

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