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Preparation of ZnO Films by Activated Reactive Evaporation Method

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Synopsis

Zinc oxide films were prepared on silica glass substrates by the use of an r.f. activated reactive evaporation (ARE) method, and were examined by X-ray diffraction (XRD) and scanning electron micrograph (SEM). XRD measurements indicate that the films were c-axis oriented and that an r.f. plasma of Zn and O was necessary for the ZnO film deposition. Substrate temperature, oxygen gas pressure, evaporation rate, r.f. power and inlet position of oxygen gas effect the c-axis orientation, the growth rate and the microstructure of the films. Optimum conditions for a dense film with a fine texture of the surface and having good crystallinity were as follows: the substrate temperature;400°C, the evaporation rate;5.0Å/s, the oxygen pressure;2.0×10^{-4} Torr, the r.f. power;150 to 200W, and the oxygen gas inlet near the substrate. For the film prepared under the optimum conditions, the standard deviation σ of the rocking curve for the (002) diffraction was 1.9deg, smaller than that of the film prepared by using an r.f. sputtering method.

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1. Introduction

A zinc oxide thin film has been used for surface acoustic wave (SAW) device, ultrasonic wave microscope and ultrasonic filter as practical electronic materials. And recent rapid development of the electronic technologies needs zinc oxide films with improved properties. Control of crystallographic orientation is especially necessary for the application to ultrasonic devices[1)2)]. Several fabrication techniques of zinc oxide films have been reported such as the chemical vapor deposition technique (CVD), the dc[3)] or rf[4)] sputtering, the ECR sputtering[5)], and the ion plating. Highly oriented piezoelectric ZnO single crystals was obtained by the ECR sputtering method[5)].

The activated reactive evaporation (ARE) method can prepare the ZnO films with excellent properties and high orientation, because the evaporation rate of Zn metal is well controlled. Fine quality single-crystal YBCO films were have been prepared by this method[6)7)]. However, the fabrication of the ZnO films by this method has not been yet reported.

This paper reports the effect of the evaporation conditions on the properties of ZnO films prepared by ARE method. Crystallographic orientation, film growth rate and microstructure were examined and correlated to substrate temperature, r.f. power, evaporation rate, and oxygen pressure. The properties of thus obtained ZnO films are also compared with those prepared by the ECR sputtering method.

2. Experimental

Fig.1 shows a schematic diagram of the activated reactive evaporation system used (JEOL JST-EB1000). A silica glass substrate was located at 770mm apart from the evaporating source. The substrate temperature during the deposition was kept constant between room temperature and 700°C. Zn metal was evaporated using an electron-beam gun (JEOL JEBG-102UB) and the evaporating rate was controlled by a thickness controller with a quartz thickness monitor. Oxygen gas was lead into the chamber as a reactive gas, the pressure of which was controlled in the range from 5.0×10^{-5} to 3.0×10^{-4} Torr. The oxygen pressure was measured by the ionization vacuum gauge set at the bottom of chamber. During the deposition a plasma was generated by an rf

power supply in order to increase the reactivity of oxygen and zinc. Two positions of the oxygen inlet were used : One was at the bottom of the chamber (B), the other was near the substrate (A). When oxygen was lead through the latter inlet A the local oxygen pressure at the substrate was higher than when it was through the former inlet B, while the background pressure was lower. Table 1 summarized the deposition conditions.

The crystal structure of the films was investigated by X-ray diffraction (XRD) measurements. In order to examine the distribution of the crystallographic orientation, X-ray rocking curves[1)8)] of the films were taken in the following way: Set a ZnO film on a substrate to be parallel to the reference plane of the diffractometer. Then adjust the θ and 2θ axis near 17.22° and 34.44°, respectively, which corresponds to the diffraction angles of the (002) plane. Then fix the 2θ axis, that is, the detector arm at the angle and scan the θ axis, that is the specimen arm around 17.22°. The surface morphology of the films was observed under a scanning electron microscope (SEM).

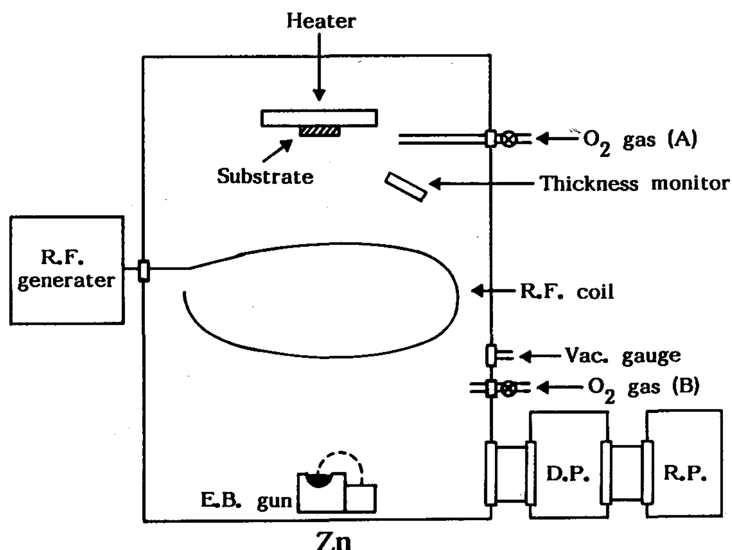

Fig.1 Schematic diagram of activated reactive evaporation system.

Table 1 deposition conditions

substrate	silica glass
substrate temperature	room temperature~700 °C
evaporating source	zinc metal (99.99%)
deposition atmosphere	O_2 : $(0.5\sim3.0)\times10^{-4}$ Torr
r.f. power	0~200 W
film thickness	0~4000 Å

3. Results and Discussion

3.1 Influence of the deposition conditions on the crystallographic orientation

Fig.2 shows the XRD pattern for a ZnO thin film with a thickness of 2000Å prepared on the silica glass (Ts;400°C, the Zn evaporation rate;5.0Å/s, Po_2;2.0×10^{-4} Torr, r.f. power;100W, and O_2 gas;the inlet A). Only the (001) peak was observed, indicating that the obtained thin ZnO film was oriented in the direction of the c-axis perpendicular to the substrate surface. This result is in accord with the Bravis' law[9] concerning to the relation between the close packed

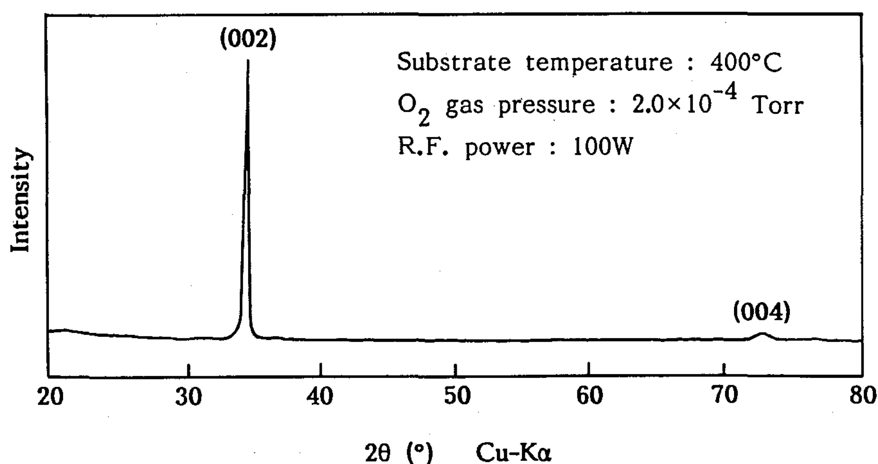

Fig.2 X-ray diffraction pattern of ZnO film prepared on silica glass. (Substrate temperature;400°C, Zn evaporation rate;5.0Å/s, O_2 gas pressure;2.0×10^{-4} Torr, r.f. power;100W, O_2 gas;inlet A, thickness:2000Å)

plane of the film and the substrate plane. Similar orientation relationship was observed for almost all films specimens prepared under various conditions in this investigation. This reveals that the ZnO films with such a orientation easily grow through the activated reactive evaporation.

The rocking curves and their standard deviation σ are given in Fig.3 for the films with a thickness of 2000Å prepared at various substrate temperature. The deposition conditions are as follows : the evaporation rate;5.0Å/s, Po_2;2.0x10^{-4} Torr, r.f. power;100W, and O_2 gas; the inlet A. The film prepared at 400°C has the smallest σ (1.9 deg), suggesting that it exhibits the best orientation. The orientation is a little lower at Ts=600 and 700°C than at Ts=400°C, because σ of the films prepared at 600°C and 700°C are 2.2 and 2.2 deg, respectively. On the other hand, marked decrease in orientation with σ=1.2 deg was observed in the films prepared by the ECR sputtering method. This results from large amounts of lattice strain and oxygen defects which are caused by low thermal energy supplied from the substrate.

In Fig.4 are compared the rocking curves for the ZnO thin films with a thickness of 800Å prepared by various methods : (a)ECR sputtering, (b)rf sputtering (c)ARE. The σ values of (a), (b) and (c) are 1.2, 6 and 2.5 deg, respectively. Thus, the degree of orientation of the films due to ARE is similar to that for ECR sputtering and is much better than that for rf sputtering.

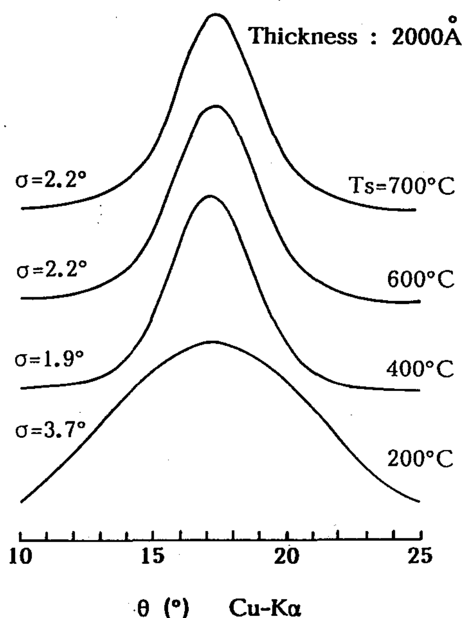

Fig.3 Rocking curves of (002) peak of ZnO prepared on silica glass at various substrate temperatures. (Zn evaporation rate;5.0Å/s, O_2 gas pressure;2.0x10^{-4} Torr, r.f. power;100W, O_2 gas;inlet A, thickness 2000Å)

A remarkable effect of the r.f. power on the film preparation has been noticed. Fig.5 shows the XRD peak of the (002) plane for various r.f. powers of 0, 10 and 100W (the deposition conditions : Ts;400°C, the evaporation

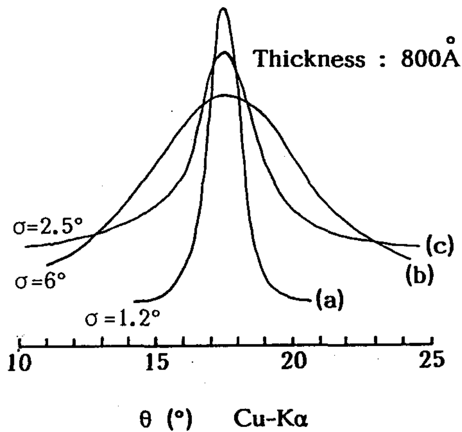

Fig.4 Rocking curves of (002) peak of ZnO with a film thickness of 800Å prepared by (a)ECR sputtering[5], (b)r.f. sputtering[5] and (c)activated reactive evaporation. (Substrate temperature;400°C, Zn evaporation rate;5.0x10Å/s, O_2 gas pressure;2.0×10^{-4} Torr, r.f. power;150W, O_2 gas;inlet A)

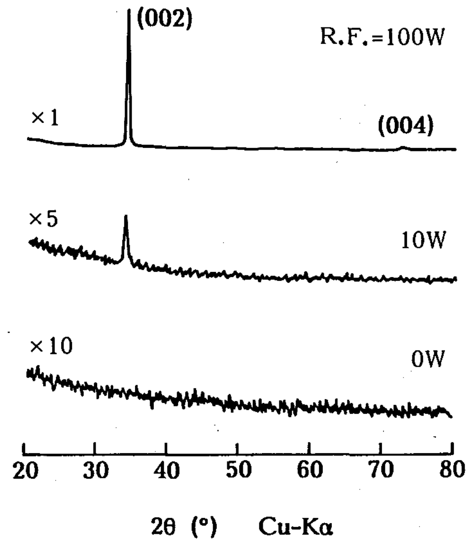

Fig.5 X-ray diffraction patterns of ZnO films under various r.f. powers : 0W, 10W and 100W. (Substrate temperature ;400°C, Zn evaporation rate;5.0Å/s, O_2 gas pressure;2.0×10^{-4} Torr, O_2 gas;inlet A)

rate;5.0Å/s, Po_2;2.0×10^{-4} Torr, O_2 gas;the inlet A, and the evaporation period;17min). No peaks were observed for the deposition without using r.f. (r.f. power=0), suggesting no growth of the film. For the r.f. power of 10W, small amount of the ZnO films grows. In contrast, the r.f. power of 100W enables the growth of the film with a thickness of about 1000Å. These results clearly reveal that oxygen and zinc atoms are activated by the r.f. plasma for the growth of ZnO films in ARE from Zn metal.

3.2 Growth rate of the films

In Fig.6 the growth rate of the thin films is plotted as a function of the r.f. power (Ts;400°C, the evaporation rate;5.0Å/s, Po_2;2.0×10^{-4} Torr). The growth rate was evaluated by dividing the measured thickness values of the films, which are deposited for a constant period (17min), by the deposition period. The filled and open

marks correspond to the films due to the O_2 gas inlets of A and B, respectively. The growth rate obviously depends upon the r.f. power and the position of O_2 gas inlet. It increases with increasing the r.f. power and becomes saturated above 100W. This trend is observed for both of the inlets. The growth rate is higher for the gas inlet A than for the inlet B. Only very thin films (about 300Å) were deposited without the r.f. plasma because Zn atoms are reevaporated through they once are deposited on the substrate, although the film cannot be detected by XRD

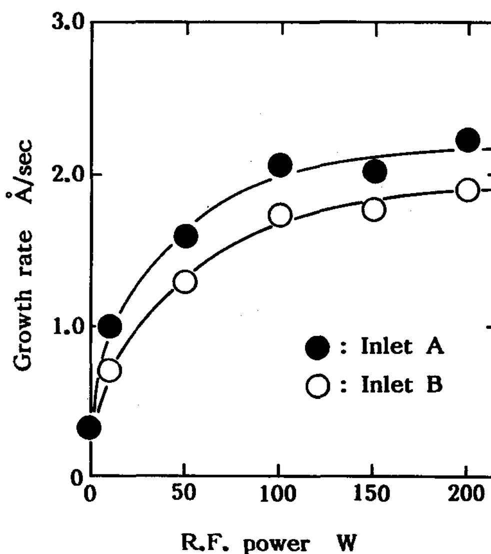

Fig.6 r.f. power dependence of growth rate of ZnO films under two different O_2 gas inlet :(●) A and (○)B. (Substrate temperature; 400°C, Zn evaporation rate;5.0Å/s, O_2 gas pressure;2.0×10^{-4} Torr)

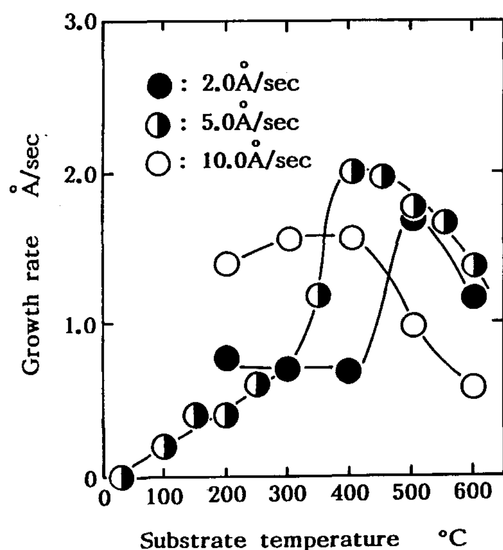

Fig.7 Substrate temperature dependence of growth rate of ZnO films under various Zn evaporation rates : (●)2.0, (◑)5.0 and (○)10.0 Å/s. (O_2 gas pressure;2.0×10^{-4} Torr, r.f. power;(◑)150W and (●,○)100W, O_2 gas;inlet A)

as shown in Fig.5.

Fig.7 shows the variation of the growth rates as a function of the substrate temperature where the Zn evaporation rate were 2.0, 5.0 and 10.0Å/s. The rate was calculated by dividing 5000Å by the time when the thickness of the deposited films reached 5000Å. The other deposition conditions are as follows: Po_2;2.0×10^{-4} Torr, r.f. power;100W and 150W for the evaporation rates of 2.0 and 10.0Å/s, and 5.0Å/s respectively, O_2 gas;the inlet A. For the Zn evaporation rate of 2.0Å/s, the

growth rate is independent of Ts, up to 400°C, while it markedly increased above 400°C and exhibited a maximum at 500°C. For the Zn evaporation rate of 10Å/s, a maximum of the growth rate was observed at approximately 400°C, above which the growth rate decreased as Ts increased. Similar behavior was also observed for the evaporation on rate of 5.0Å/s, where the growth rate reaches a maximum value at 400°C. Thus, it has been indicated that the growth rate increases as the evaporation rate increases. The above results suggest two different possibilities for formation processes of the ZnO thin film in ARE; (1) Zn atoms are deposited before they are reacted with O_2 to the ZnO film, and (2) The reaction of Zn atom and O_2 molecules occurs to ZnO molecules before they reach the substrate and subsequently deposit on the substrate. In the deposition with a constant oxygen pressure and a constant r.f. power, either of the two processes is the rate controlling one. The evaporation rate of Zn determines which is the dominant one. At small Zn evaporation rates, the process (2) is the rate-controlling step. In this case, the growth rate has been observed to increase at high Ts where the thermal energy for nucleation and growth is sufficient, while the Zn reevaporation from the substrate reduces the growth rate at much higher Ts. On the other hand, the process (1) is dominant at high evaporation rates. In this case the reevaporation is less active at low Ts, resulting in higher growth rate. The marked decrease in the growth rate was observed below Ts=300°C at the evaporation rate of 5.0Å/s. We ascribe the decrease to the insufficient thermal energy for nucleation and growth of the ZnO film.

The highest growth rate of the ZnO film in this investigation is approximately 2Å/s at a Zn evaporation rate of 5.0Å/s and Ts~400°C, as shown in Fig.7. Thus, the measured growth rates are always smaller than the Zn evaporation rates. These results suggest that a part of the evaporated Zn contributes to the ZnO formation on the substrate, but the rest part goes out of the chamber without any contribution to the ZnO formation through the processes (1) and (2).

Fig.8 shows the effect of O_2 pressure, Po_2, on the growth rate of the ZnO film (Ts;400°C, the evaporation rate;5.0Å/s, r.f. power;100W, O_2 gas;the inlet A). The growth rate increases with increasing Po_2 below 1.5x10^{-4} Torr and remains a constant in the range from 1.5x10^{-4} to 2.5x10^{-4} Torr. However the rate decreases above 3.0x10^{-4} Torr. This is because the turbulent flow of O_2 gas takes place through the narrow nozzle near the substrate and reduces the ZnO deposition when oxygen

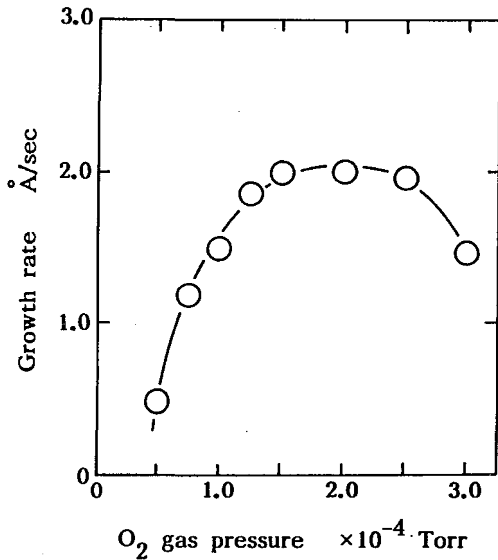

Fig.8 O_2 gas pressure dependence of growth rate of ZnO film. (Substrate temperature;400°C, Zn evaporation rate;5.0Å/s, r.f. power;150W, O_2 gas:inlet A)

is lead into the chamber.

From Figs.3~8, the optimum conditions for the deposition of the ZnO thin films with the best orientation at the highest growth rates were found to be Ts of 400°C, the Zn evaporation rate of 5.0Å/s and Po_2 of (2.0~2.5)x10^{-4} Torr.

3.3 SEM observation of the film surface

The SEM photographs in Fig.9 show the microstructures of the deposited ZnO films prepared with various r.f. powers of (a)50W, (b)100W and (c)200W. (Ts;400°C, Po_2;2.0x10^{-4} Torr, the evaporation rate;5.0Å/s, O_2 gas;inlet A). All the films consist of a great number of ZnO crystallites with about <1000Å diameter. The film surface is fairly smooth. The crystallites are smaller in size and the film is highly denser at 100 and 200W than at 50W. Thus, the dense films were found to need the r.f. powers above 100W. Insufficient activation of Zn and oxygen gas due to low r.f.powers below 100W decreases the nucleation sites of ZnO crystals. As a result, the crystals with larger diameters grow.

Fig.10 illustrates the effects of Ts and Po_2 on the microstructure of the film surface (the evaporation rate;5.0Å/s, r.f. power;150W and O_2 gas;inlet A). The deposition conditions (Po_2, Ts) in this figure are (a)(2.0x10^{-4} Torr, 300°C), (b)(2.0x10^{-4} Torr, 400°C) and (c)(1.0x10^{-4} Torr, 300°C). The films prepared at 300°C under Po_2=2.0x10^{-4} Torr (a) and 1.0x10^{-4} Torr (c) show similar microstructures. On the other hand, the film (b) exhibits denser microstructure than the films (a) and (c).

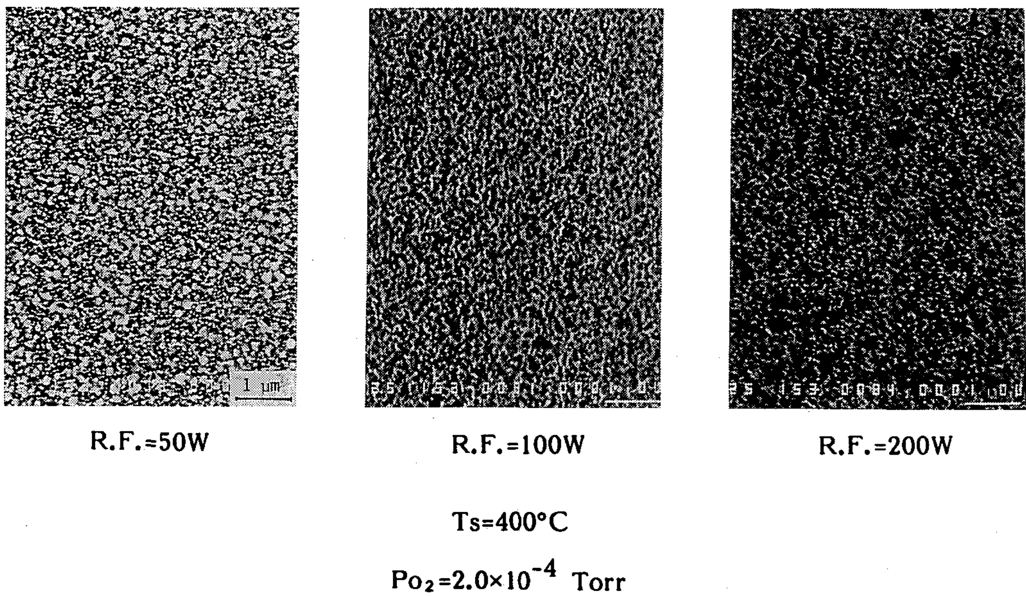

Fig.9 Scanning electron micrographs of ZnO films under various r.f. powers (a)50W, (b)100W and (c)200W. (substrate temperature;400°C, Zn evaporation rate;5.0Å/s and O_2 gas pressure;2.0×10^{-4} Torr, O_2 gas;inlet A)

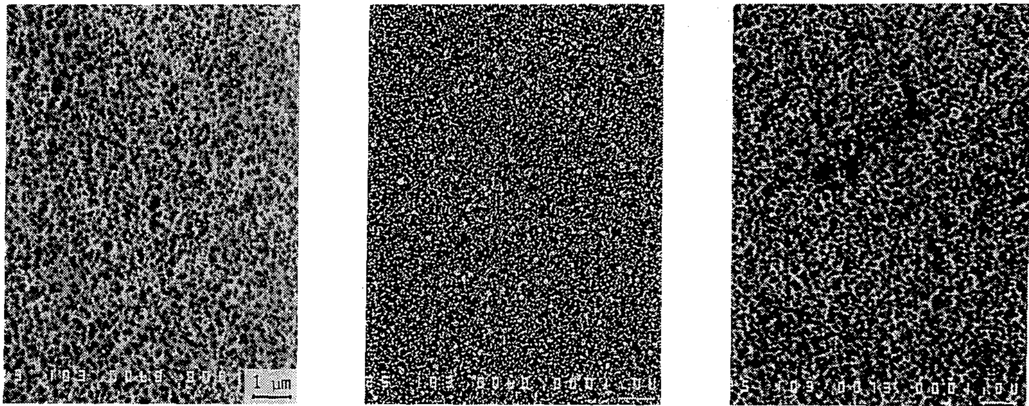

Fig.10 Scanning electron micrographs of ZnO films under various conditions. (a)Substrate temperature;300°C : O_2 gas pressure;2.0x10^{-4} Torr, (b)Substrate temperature;40°C : O_2 gas pressure;2.0x10^{-4} Torr and (c)Substrate temperature;400°C : O_2 gas pressure;1.0x10^{-4} Torr. (r.f. power;150W, O_2 gas;inlet A)

3.4 Influence of the annealing on resistivity

After deposition, annealing of the samples at high temperature of 200~600°C was performed in air. Fig.11 shows the variation of the resistivity as a function of the annealing time and the annealing temperature. Deposition conditions of the samples are as follows : the substrate temperature;400°C, the evaporation rate; 5.0 Å/s, Po_2;2.0×10^{-4} Torr, r.f. power;100W, O_2 gas;the inlet A, and film thickness;2000Å. The as-deposited film is a semiconductor since the resistivity is 1.18×10^{-1} Ωcm. This can be attributed to the oxygen defect in the film. It should be emphasized that rapid increase in resistivity is observed for the annealed at 600°C. But the resistivity remains unchanged at 200°C. SEM observations indicate that the film annealed at higher than 400°C has more smooth surface.

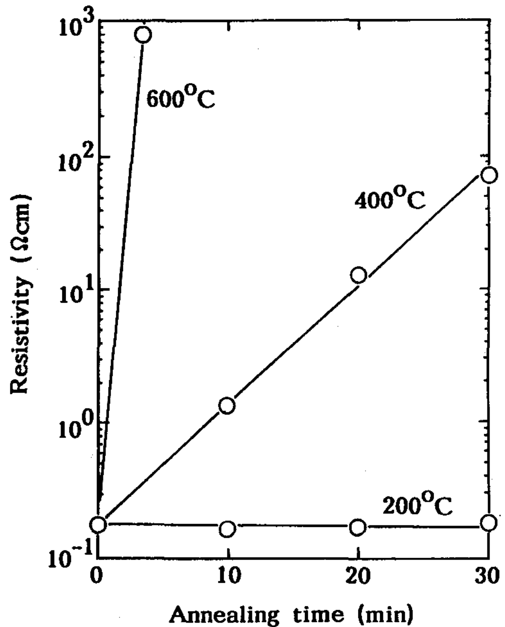

Fig.11 Annealing time dependence of resistivity of ZnO films under various annealing temperatures : 200, 400 and 600°C. (Substrate temperature;400°C, Zn evaporation rate;5.0Å/s, O_2 pressure;2.0×10^{-4} Torr, O_2 gas;inlet A)

4. Conclusions

We have discussed the preparation of ZnO films on silica glass substrate by an activated reactive evaporation method with respect to orientation, crystallinty and surface structure. Highly c-axis oriented ZnO films were obtained in this method. For the films with a thickness of 800Å prepared at Ts=400°C, the standard deviation σ of the rocking curve for the (002) diffraction was 1.9°, smaller than that of the film prepared by using an r.f. sputtering method. No growth of this films was observed for the deposition without using r.f. It indicates that oxygen and zinc atoms should be activated by

the r.f. plasma for the growth of ZnO film. On basis of the growth rate measurements of ZnO film under the various zinc evaporation rates, we suggested two different formation processes of the ZnO thin film. A dominant process depends upon the evaporation rate of Zn. O_2 pressure had an effect on the growth rate of ZnO film. SEM observation indicated that the films have smooth surface. Optimum conditions for a dense film with a fine texture of the surface and having good crystallinty were as follows : the substrate temperature;400°C, the evaporation rate;5.0Å/s, the oxygen pressure;2.0×10^{-4} Torr, the r.f. power;150 to 200W, and the oxygen gas inlet near the substrate.

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