The relation between the microstructure, the orientation and the electrical properties of Al-doped ZnO thin films deposited on the various kinds of substrates by MOCVD

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Al-doped ZnO thin films were prepared on the various kinds of substrates at 600°C by MOCVD. The ZnO thin films on the fused silica and (100)MgO substrates oriented to the c-axis. The film on (012)Al₂O₃ substrate had the (110) orientation. The resistivity of the undoped ZnO film on the fused silica substrate was about 10^0 Ω ·cm at room temperature and was 10 times higher than that on (100)MgO substrate. The electrical resistivity of the film on the (012)Al₂O₃ was 10^{-2} Ω ·cm and was the lowest of the three. The difference of the electrical resistivity among the films on the three kinds of substrates was caused by the difference of the carrier concentration. The electrical resistivity of the Al-doped ZnO thin films had the minimum values for the temperature of Al(C₅H₇O₂)₃ vaporizer, and on the fused silica substrate the electrical resistivity was lowered to the order of 10^{-2} Ω ·cm. The change of the electrical resistivity was considered to be related to the orientation and the structure of the films.

1. INTRODUCTION

ZnO thin films have been applied to sensors, solar cells, SAW device, etc.[1] The orientation and the electrical resistivity are needed to be controlled in order to improve their device characteristics. However, the study of ZnO films has been mainly focused on the preparation of the films with low electrical resistivity at low deposition temperature.[2-4] Therefore, the relation between the orientation, the microstructure and the electrical resistivity has not been made clear. In this paper, Al-dopedZnO thin films were deposited on three kinds of substrates by MOCVD by varying the Al content in the films and discussed with the relation between the electrical resistivity and the orientation and the microstructure of the films.

2.EXPERIMENTAL

Al-dopedZnO thin films were prepared by MOCVD. Zn(C₅H₇O₂)₂ was used as the Zn source, the distilled water and O₂ as the oxygen sources and Al(C₅H₇O₂)₃ as the Al source. The deposition pressure and temperature were held constant at 1.3kPa and 600°C, respectively. Fused silica,(100)MgO and (012)Al₂O₃ substrates were used as the substrates. The Al content in the film was controlled by varying the temperature of Al(C₅H₇O₂)₃ vaporizer [T(Al)] from80° to110°Cand keeping the other parameters constant throughout the experiment. N₂ carrier gas flow rates for transportation of Zn (C₅H₇O₂)₂, H₂O and Al(C₅H₇O₂)₃ vaporizers were held constant at 100,70,30 ml/min, respectively. The gas flow rate of O₂ was kept constant in 100 ml/min. The

temperatures of the Zn(C₅H₇O₂)₂ and H₂O were held constant at 110°Cand40°C,respectively.

An XRD was used for the determination of the orientation and the lattice constants of the films. The degree of the orientation was defined by

(the summation of intensity of orientational planes) / (the summation of intensity of all planes)
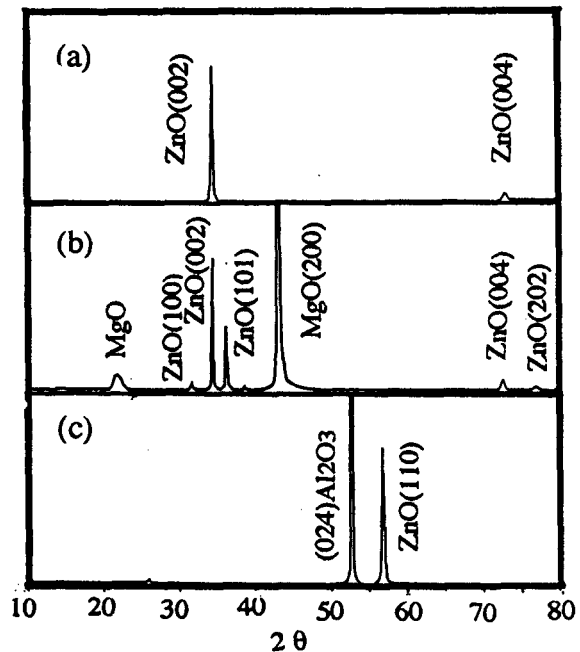

Fig.1 XRD patterns of the films on (a) fused silica, (b) (100)MgO, (c) (012)Al₂O₃ substrates

The surface morphology was observed by SEM. The electrical resistivity and the carrier concentration of the films were measured by the four-probe method at room temperature and by the van der Pauw method, respectively. The electrical resistivity is generally represented by the equation;

$$\rho^{-1} = en\mu$$

where ρ is electrical resistivity, e is elementary charge, n is carrier concentration, μ is mobility. In our experimentals, μ was calculated by the equation using the measurement value of ρ and n.

3. RESULTS and DISCUSSIONS

3.1 The undoped ZnO thin films deposited on various kinds of substrates

Fig.1 shows X-ray diffraction patterns of the undoped ZnO thin films deposited on (a)fused silica, (b)(100)MgO and (c)(012)Al$_2$O$_3$ substrates. Only (00l) refraction of ZnO was observed in the case of the film deposited on the fused silica substrate as shown in Fig.1 (a). The obvious orientation parallel to the substrate of the film was not observed by X-ray pole figure measurement. This result shows that the film on the fused silica substrate had only the c-axis orientation perpendicular to the substrate, orientation of one dimension. In the case of the film on (100)MgO substrate, the strong (00l) refraction was observed together with the weak (h0h) and (h00) refractions as shown in Fig.1(b). The degree of (00l) orientation was 0.6-0.7 and the film with the perfect c-axis orientation was obtained at the substrate temperature of 620℃. It was ascertained by X-ray pole figure that (00l) oriented grains had two different orientational directions parallel to the surface. Thus the film on (100)MgO substrate had orientation of three dimensions. In the case of (012) Al$_2$O$_3$, only (hh0) refraction was observed as shown in Fig.1(c), so that the film had the perfect (110)
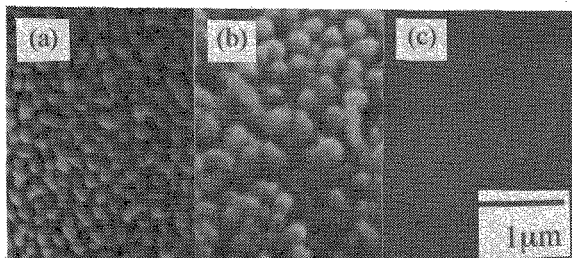

Fig.2 Microstructures of the surfaces of the films deposited on (a) fused silica, (b) (100)MgO, (c) (012)Al$_2$O$_3$ substrates

orientation. The film with the only one kind of direction was observed by pole figure measurement. These results show that the film on (012)Al$_2$O$_3$ substrate had perfect orientation of three dimensions.

The microstructures of the surfaces of the same films as Fig.1 are shown in Fig.2. On a fused silica substrate, the film was made up of the distinct grains with 100-200nm in size. On (100)MgO substrate, the similar grains to those on the fused silica substrate were observed. The grain size was 200-300nm and was bigger than that on the fused silica substrate. The microstructure of the film on the (012)Al$_2$O$_3$ had no distinct grains and had the flat surface as shown in Fig.2 (c).

Fig.3 shows the relation between the inverse of the electrical resistivity and the carrier concentration of the films. The inverse of the electrical resistivity linearly increased with increase in the carrier concentration. This result shows that the mobility was constant regardless of the kinds of substrates, and that carrier concentration determined the electrical resistivity. The mobility calculated from the slope in the Fig.3 was in the order of 10^0cm^{2}v^{-1}s^{-1}.

The change of the electrical resistivity by the kinds of substrates is considered as follows; The carriers of the undoped ZnO have been generally considered to be generated by the nonstoichiometry of ZnO crystal. However, under the major deposition time, ZnO deposits on the pre-deposited ZnO film. As it is hardly considered the substrate influences the nonstoichiometry of the whole film, the non-stoichiometry was considered to be almost the same regardless of the kinds of the substrates. The main reason is considered to be the structural difference among the films. The film on (012)Al$_2$O$_3$ substrate had the perfect three dimensional orientation and did not have the
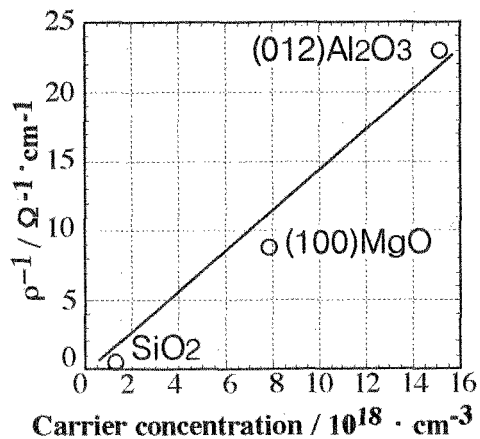

Fig.3 Rrelation between the inverse of the electrical resistivity and the carrier concentration of the films

structure with distinct grains. Therefore, this film had the highest crystal perfection of the three, so that it is considered that the resistivity was the lowest of the three. On the other hand, both films on the fused silica and (100) MgO substrates were made up of the distinct grains. However, the film on the fused silica substrate had orientation of only one dimension, while that on (100) MgO substrate had partial orientation of three dimensions. As the orientation of the film on (100)MgO substrate was higher than that on the fused silica substrate, the electrical resistivity of the part of the junctions of grains on (100)MgO substrate may be considered to be lower than that on the fused silica substrate. Moreover, the effective thickness of the film caused by the structures of the films is also considered to affect the apparent electrical resistivity. The effective thickness means the actual thickness to influence the current of the film. The effective thickness is considered to be related to the crystal perfection of the film along the film thickness, especially the part of the film near the substrate. Therefore, it is considered that as the crystal perfection becomes higher, the distortion part of the structure near the substrate becomes thinner. As a result, the effective thickness is considered to become thicker. Taking account of the results mentioned before, the order of the effective thickness of the film from thick to thin is considered to be as follows; (012)Al$_2$O$_3$, (100) MgO and a fused silica substrates. These results suggest that the apparent electrical resistivity is considered to be also related with the effective thickness.

3.2 The Al-doped ZnO thin films on various kinds of substrate

Fig.4 shows the relation between T(Al) and the degree of the orientation. The film of T(Al)=0 °C means the undoped ZnO film. As the Al content in the film can be considered to increase with T(Al), so that the increase in T(Al) corresponds to the increase in the Al content in the film. The film on a fused silica substrate had the
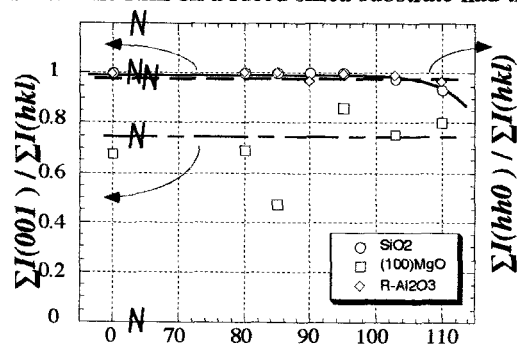
Temperature of Al(C$_5$H$_7$O$_2$)$_3$ vaporizer / °C

Fig.4 Relation between the degree of the orientation and the temperature of Al(C$_5$H$_7$O$_2$)$_3$ vaporizer

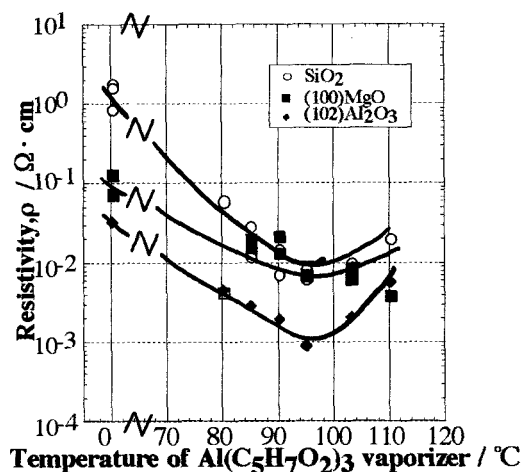Temperature of Al(C$_5$H$_7$O$_2$)$_3$ vaporizer / °C

Fig.5 Relation between the electrical resistivity and the temperature of Al(C$_5$H$_7$O$_2$)$_3$ vaporizer

perfect c-axis orientation below 95 °C of T(Al). Over 95 °C , (h0h) refraction appeared together with (00l) refractions and the degree of the c-axis orientation became lower. The degree of the orientation of the film on (100)MgO substrate was almost constant to be 0.7. On the other hand, in the case of (012)Al$_2$O$_3$ substrate, the perfect (hh0) orientation was kept with increasing T (Al). Then the rocking curves of the films on the fused silica and (012)Al$_2$O$_3$ substrates, whose degrees of orientation were nearly 1, were measured. The half-width of rocking curve of (002) refraction on the fused silica substrate increased from 3.3° to 4.5° with the increase in T(Al) from 0° to 110°C. That of (110) refraction on (012)Al$_2$O$_3$ substrate also increased from 0.67° to 1.4° when T(Al) increased from 0°C to 110°C. On both films, the half-width of rocking curve changed with increase in T(Al). Therefore, it can be concluded that the lattice of ZnO became distorted continuously with increasing the Al content. Furthermore, the half-width of rocking curve of the fused silica substrate was wider than that of (012)Al$_2$O$_3$ in spite of (002) refraction being lower angle than (110) refraction. Therefore, it can be considered that the film on (012)Al$_2$O$_3$ substrate had the higher degree of the orientation than the film on the fused silica substrate.

Fig.5 shows the relation between T(Al) and the electrical resistivity of the same films as shown in Fig.4. The electrical resistivity decreased with the increase in T (Al) below 95°C. The electrical resistivities at 95°C of T (Al) were 10^{-2} Ω・cm, 10^{-2} Ω・cm and 10^{-3} Ω・cm on the fused silica, (100)MgO and (012)Al$_2$O$_3$ substrates, respectively. Over 95°C of T(Al), the electrical resistivity contrarily increased with the increase in T (Al). Even though the value of the electrical resistivity depend on the kinds of the substrates, the tendency of the

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electrical resistivity change with T(Al) was almost the same. The change of the microstructure, lattice parameter and the carrier concentration with T(Al) was investigated only in the case of the film on the fused silica substrate, as follows.

Fig.6 shows the dependence of the surface morphologies of the fused silica substrates on T(Al). As shown in Fig.6(a), the undoped ZnO thin film had the distinct grains. The film of 95°C of T(Al) in Fig.6(b) made up of smaller grains and had smoother surface than those of the undoped film (Fig.6(a)). In the case of the film of 110°C of T(Al), the distinct grains were observed clearer than 95°C of T(Al). The relation between T(Al) and the c-axis lattice parameters of ZnO is shown in Fig.7. When Al was introduced, the lattice parameter decreased. However, the lattice parameter hardly changed with the increase in T(Al).

The carrier concentration and the mobility of the Al-doped ZnO films on the fused silica substrate was measured by the van der Pauw method. The carrier concentration and the mobility of the film of 95°C of T (Al) were 9.01×10^{19} cm^{-3} and 3.3 cm^{2}V^{-1}s^{-1}, respectively. In the case of the film of 110°C, 1.18×10^{19} cm^{-3} and 0.74 cm^{2}V^{-1}s^{-1}, respectively. In the range from 0° to 95°C, the mobilities were almost the same, so that the decrease in the electrical resistivity was caused by the increase in carrier concentration. As shown in Fig.7, the c-axis lattice parameter decreased when Al ions were doped. Therefore, Al ions are considered to replace Zn ions of ZnO lattice and generate carriers. Over 95°C of T(Al), in spite of the increase in the carrier concentration, the electrical resistivity decreased, so that the low mobility caused the high resistivity. In this region, the c-axis lattice parameter was almost constant as shown in Fig.7. This means that Al ions incorporated in the film does not replace Zn ions in ZnO lattice. However, as the half-width of rocking curve increased and the ZnO lattice became distorted continuously with increasing T(Al), so that it is considered that Al ions existed in the films except in the Zn sites of the lattice. Therefore, Al ion not
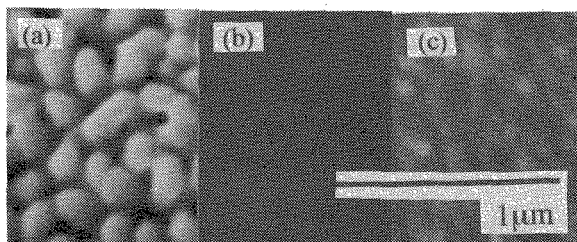

Fig.6 Microstructures of the surfaces of the films deposited on fused silica substrates as a function of the temperature of Al(C₅H₇O₂)₃ vaporizer,T(Al). T(Al); (a)0°C, (b)95°C, (c)110°C
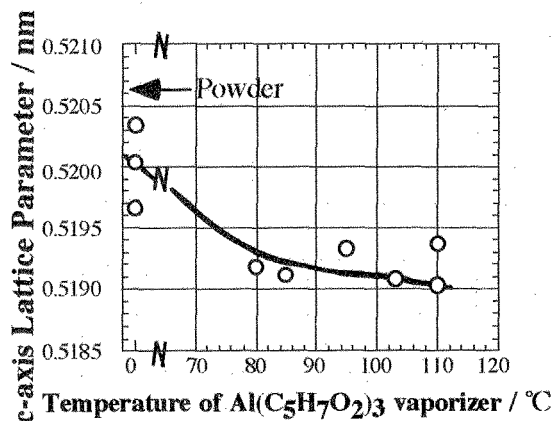
Fig.7 Change of c-axis lattice parameter with the temperature of Al(C₅H₇O₂)₃ vaporizer incorporated at the Zn site is considered to exist in the interstitial site of the ZnO lattice and/or outside of the lattice, grain boundaries. In both cases, the mobility of the electrons is considered to decrease with the increase in Al content. As shown in Fig.6, the distinct grains was observed in the case of the film of 110°C . This microstructure change may be related to the existence of Al ions outside of ZnO lattice.

4. CONCLUSIONS

Al-doped ZnO thin films with low resistivity were prepared on the three kinds of substrates by MOCVD. The resistivity of the undoped ZnO thin films depended on changing the kinds of substrates, and the change of the electrical resistivity corresponded with the change of the carrier concentration. This change was considered to be related with the microstructures of the films ascribed to the kinds of the substrates. On Al-doped ZnO thin films, the electrical resistivity change did the same behavior regardless of the kinds of the substrates. Below 95°C of T (Al), the resistivity decreased with increase in T(Al) and had the minimum value at 95°C of T(Al). This was caused by the increase in the carrier concentration. Above 95°C of T(Al), the electrical resistivity increased contrarily with increase in T(Al). This was caused by the decrease in the mobility.

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