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PREPARATION OF THIN SOLID FILMS IN THE Co-O SYSTEM BY REACTIVE RF SPUTTERING

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Thin solid films in the Co-O system were prepared by reactive RF sputtering and the phase relationships were established as functions of reaction temperature and oxygen partial pressure. Electrical resistivity of grain-oriented Co_3O_4 films was microstructure-sensitive and depended on the crystallite size.

Preparation of thin solid films of metallic oxides by reactive sputtering has been a subject of various studies. Martin$^{1)}$ and Samirant$^{2)}$ have investigated the reaction between sputtered particles and oxygen molecules in a plasma state, suggesting that the oxide is formed in the gas phase, diffusing with energy consumption toward a substrate, and arriving at an adsorption site on the surface of a substrate. The effect of argon ions on the oxide formation on a metal target has also been pointed out.$^{3)}$ However, there can be found only a few studies on the preparation of films in the Co-O system. Hecq et al.$^{4)}$ investigated the growth rate as a function of oxygen partial pressure and phase compositions in the precipitated films obtained by the direct current reactive sputtering. They proposed a reaction model for reactive sputtering in the Co-O system. In the present study, thin solid films in the Co-O system were prepared by reactive RF sputtering varying the oxygen partial pressure and the substrate temperature as main parameters for experimental conditions. Electrical resistance was measured on the obtained films and especially the microstructural effect of Co_3O_4 film on its resistivity was found.

A magnetron-type RF sputtering apparatus (Nichiden Varian, SPF-210H) was used. Cobalt metal of 99.99% pure (Raremetallic Co. Ltd.) was employed for a target material and soda glass or silica glass for a substrate. The distance between a target and a substrate was fixed to be 35 mm. Substrate temperature was varied from room temperature (considering natural temperature increases during sputtering, this should be 40° to 50°C) to 300°C and the mixture of argon and oxygen with various volume ratios was introduced to the reaction chamber. Reactive sputtering was performed at the output power of 150 to 300 W for 1.5 to 2 h. The thicknesses of the obtained films were calculated from scanning electron micrographs of fracture surfaces to be 0.6 to 0.8 μm. The phases present in the films were identified and the crystallite sizes of the preferentially oriented Co_3O_4 films were calculated from X-ray diffraction patterns. Both volume and surface resistances were measured on some films by direct current two-probe technique.

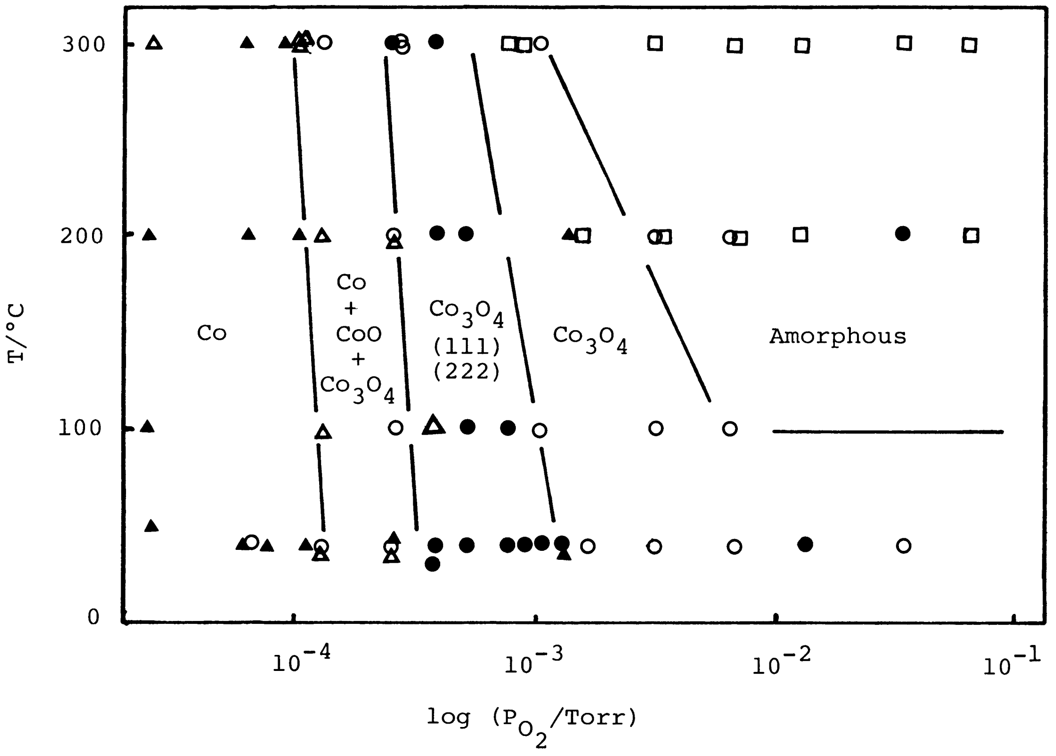

Fig. 1 P_{O_2}-T diagram for the Co-O system.

Figure 1 shows the formed phases for sputtered films as functions of oxygen partial pressure (P_{O_2}) and substrate temperature. It is seen from the figure that rather wide regions exist for pure cobalt metal and Co_3O_4, but that there is no or quite a small region for pure CoO. More characteristic features can be found that (111) planes of Co_3O_4 are highly oriented parallel to the substrate surface at $P_{O_2} \simeq 10^{-3}$ Torr and an X-ray amorphous phase appears above 100°C at high P_{O_2}. The crystalline phases known to exist at thermodynamic equilibrium in the Co-O system are Co, CoO, Co_3O_4, and Co_2O_3, and the phase diagram is well established for high temperature above ~900°C.$^{5)}$ Since a low-temperature phase diagram is not reported, it cannot be judged if the phases shown in Fig.1 represent an equilibrium state. However, the phase boundaries extrapolated from high temperature do not coincide with solid lines in Fig. 1, which indicates that the phases present in a sputtered film are not in a perfect equilibrium state. Specifically the existence of the amorphous phase in the Co-O system has never been reported.

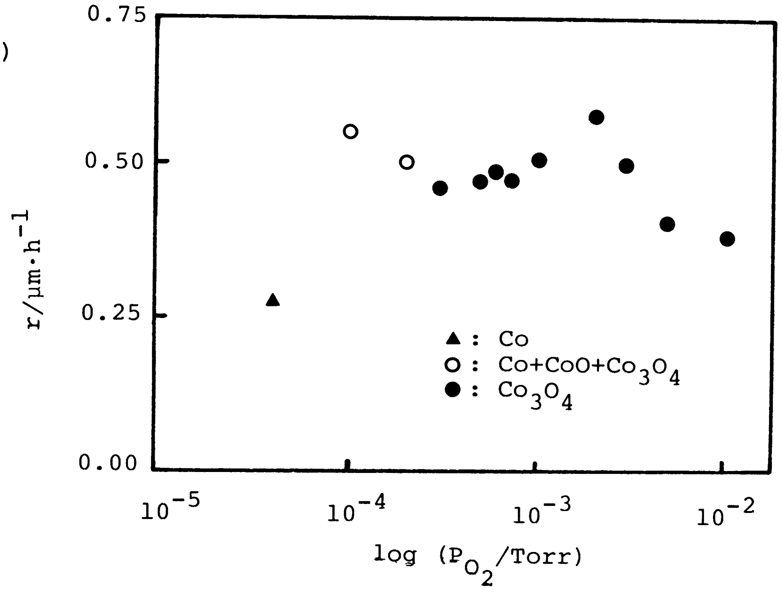

Fig. 2 Growth rate vs. P_{O_2} at room temperature.

In Fig. 2 is shown the growth rate vs. P_{O_2} relation at room temperature. The growth rate of cobalt metal is very small because the total gas pressure is low and hence the sputtering efficiency is low. As the oxygen partial pressure is increased, the growth rate increases up to $\sim 1\mathrm{x}10^{-4}$ Torr and then decreases rather abruptly in the P_{O_2} region where a highly oriented Co_3O_4 film is formed. Though the reason for the decrease in growth rate should be subject to further investigation, it may be related to the fact that (111) plane is the closest packed plane of oxygen ions. As P_{O_2} is further increased, the growth rate increases again up to $\sim 2\mathrm{x}10^{-3}$ Torr and then decreases. This observation is consistent with the previous report on the mechanism for RF sputtering$^{6)}$ that if the gas pressure is high, the growth rate is low as sputtered particles are scattered by collision with gas molecules before reaching the surface of a substrate.

For electrical resistance measurements cobalt metal electrodes were formed on the film surfaces. Both volume and surface resistances were measured at room temperature and the electrical contact between an electrode and a film was perfectly ohmic in all cases. The results are shown in Fig. 3. Both volume and surface resistances reveal similar dependences on P_{O_2}. The characteristic feature in Fig. 3 should be that both resistances for highly oriented Co_3O_4 film become minimized at P_{O_2}=6-8x10^{-4} Torr. Cobalt oxide, Co_3O_4, is reported to be a nonstoichiometric compound with a small metal ion deficiency$^{7)}$ and electrically a p-type semiconductor confirmed by thermoelectromotive force measurements.$^{8)}$ However, electrical conductivity (reciprocal of resistivity) for sintered polycrystalline Co_3O_4 was found to be independent of P_{O_2} at 500°-800°C.$^{9)}$ Hence, the decrease in resistances for grain-oriented Co_3O_4 films cannot be explained merely by the decrease in the electron hole concentration and is considered to be strongly related to the microstructural effect of films.

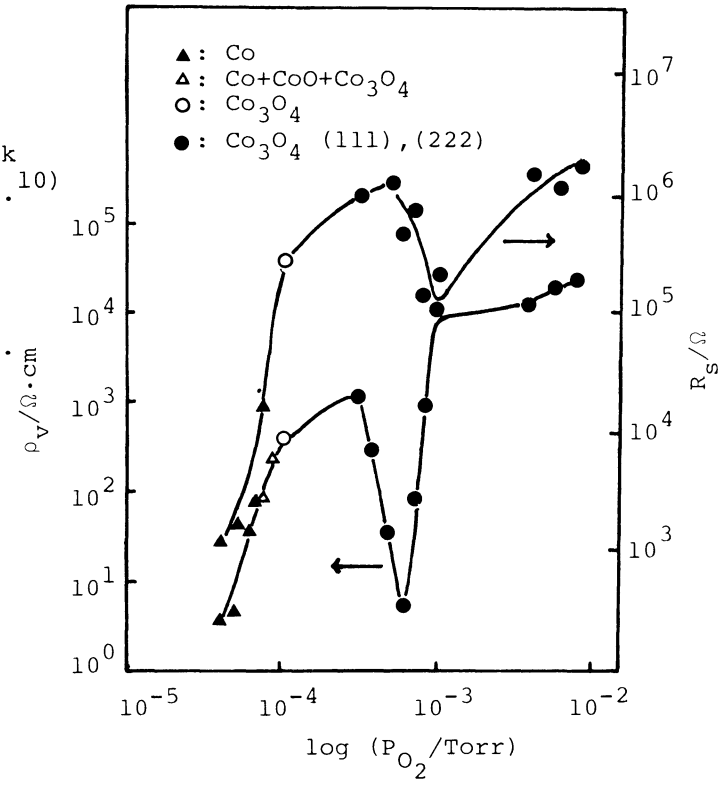

Fig. 3 P_{O_2} dependences of volume resistivity (ρ_V) and surface resistance (R_S) at room temperature.

The crystallite size for a grain-oriented Co_3O_4 film was evaluated from the half-width of (111) diffraction peak using the well-known Scherer's equation.$^{10)}$ The results are shown in Fig. 4. The crystallite size for the film obtained at room temperature showed a maximum value of about 95 nm at P_{O_2} ≃6x10^{-4} Torr. When the P_{O_2} was fixed at 6x10^{-4} Torr and the substrate temperature was varied, the crystallite size decreased at higher temperatures. As shown in Fig. 5, the volume resistivity for the film with similar thicknesses decreased as the crystallite size increased. Judging from the present observations that surface resistance for the film has shown a similar dependence on P_{O_2} to volume resistance and was quite large compared with volume resistance, the grain boundaries in polycrystalline Co_3O_4 films are thought to possess high

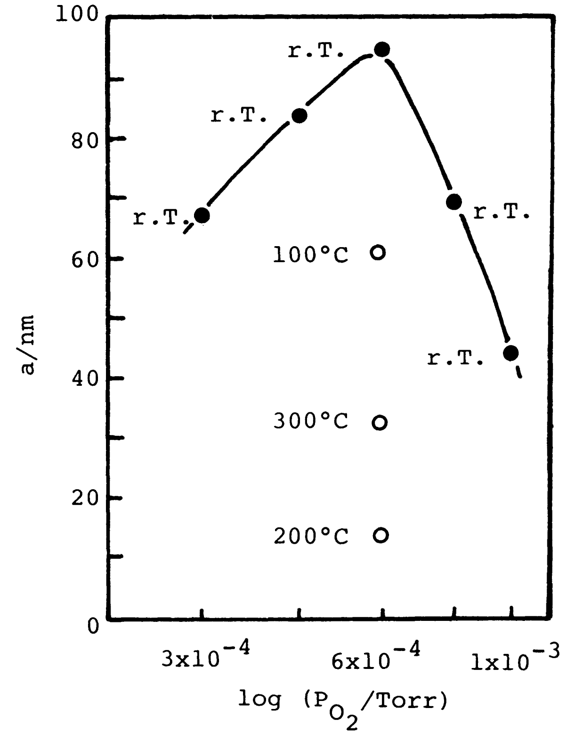

Fig. 4 P_{O_2} and temperature dependences of the crystallite size for grain-oriented Co_3O_4 films.

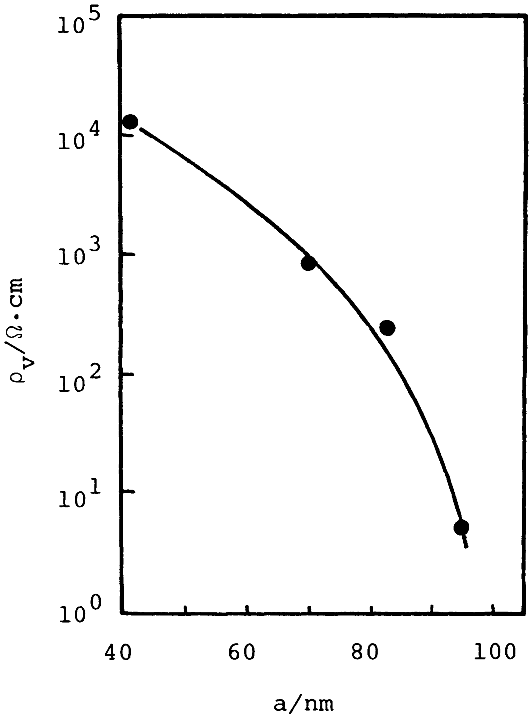

Fig. 5 Crystallite size vs. volume resistivity for grain-oriented Co_3O_4 films.

resistance. If the crystallite size increases, the density of grain boundaries decreases and thus the contribution of grain boundary resistance to the total resistivity decreases. Consequently, the resistivity of a sputtered Co_3O_4 film is microstructure-sensitive and specifically the grain boundary effect is unambiguous.

Acknowledgment

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References

1) B. L. Saint-Martin, Ph.D thesis, Strasbourg, 1969.
2) M. Samrant, Ph.D thesis, Strasbourg, 1970.
3) L. Holland, The Vacuum Deposition of Thin Films, John Wiley & Sons, New York, 1956.
4) M. Hecq, A. Hecqet, and J. Van Cakenberghe, Thin Solid Films, 42, 97(1977).
5) B. Fisher and D. S. Tannhauser, J. Chem. Phys., 44[4], 1663(1966).
6) F. Shinoki, Researches of Electrotechnical Laboratory, No.806, 1(1980).
7) E. J. W. Verwey and J. H. de Boer, Rec. Trav. Chim., 55, 531(1936).
8) K. Koumoto and H. Yanagida, J. Am. Ceram. Soc., 64[11], C-156(1981).
9) K. Koumoto and H. Yanagida, Jpn. J. Appl. Phys., 20[2], 445(1981).
10) H. P. Klug and L. E. Alexander, X-ray Diffraction Procedures, John Wiley & Sons, New York, 1974.

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