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Preparation of cobalt oxide films by plasma-enhanced metalorganic chemical vapour deposition

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Co oxide films were prepared on glass substrates at 150–400 °C by plasma-enhanced metalorganic chemical vapour deposition using cobalt (II) acetylacetonate as a source material. NaCl-type CoO films were formed at low O_2 flow rate of 7cm^3 min^{-1} and at a substrate temperature of 150–400 °C. The CoO films possessed (1 0 0) orientation, independent of substrate temperature. Deposition rates of the CoO films were 40–47 nm min^{-1}. The CoO film deposited at 400 °C was composed of closely packed columnar grains and average diameter size at film surface was 60 nm. At high O_2 flow rate of 20–50 cm^3 min^{-1}, high crystalline spinel-type Co_3O_4 films were formed at a substrate temperature of 150–400 °C. The Co_3O_4 film deposited at 400 °C possessed (1 0 0) preferred orientation and the film deposited at 150 °C possessed (1 1 1) preferred orientation. Deposition rates of the Co_3O_4 films were 20–41 nm min^{-1}. Both Co_3O_4 films with (1 0 0) and (1 1 1) orientation had columnar structure. The shape and average size of the columnar grains at the film surface were different; a square shape and 35 nm for (1 0 0)-oriented Co_3O_4 film and a hexagonal shape and 60 nm for (1 1 1)-oriented film, respectively.

1. Introduction

Thin films of the principal Co oxides, NaCl-type CoO and spinel-type Co_3O_4, and their similar compounds are attractive as solar thermal absorbers [1], protective layers [2], perpendicular magnetic recording medium [3] and magneto-optical recording medium [4]. In recent years, much attention has been paid to (1 0 0)-oriented NaCl-type oxide films (MgO) and (1 0 0)-oriented spinel-type oxide films ($MgAl_2O_4$) used as buffer layers on perovskite-type oxide films [5, 6]. Such oxide materials used as the buffer layers must satisfy the following conditions; chemical stability, similar symmetry of oxygen ion lattice and close value of lattice constants between the perovskite-type oxides and oxide materials of the buffer layers. Thin films of both NaCl-type CoO and spinel-type Co_3O_4 also satisfy these conditions. Therefore, thin films of CoO and Co_3O_4 with (1 0 0) orientation could potentially be used as the buffer layers.

In the past, Co oxide films have been prepared by various deposition processes, such as evaporation [7], sputtering [8] and chemical vapour deposition [9]. Plasma-enhanced metalorganic chemical vapour deposition (PE-MOCVD) process is now widely used in the fabrication of semiconductor devices. This process is known to have several advantages, such as low-temperature film growth and good surface morphology over a large area. However, there has been no report about the preparation of cobalt oxide films by PE-MOCVD. Recently, we have developed a PE-MOCVD process using cobalt acetylacetonate complex as a source material for preparing high-quality (1 0 0)-oriented NaCl-type CoO films at substrate temperatures of 150–400°C [10]. The (1 0 0) orientation of the films were independent of the type of substrate, such as glass, fused silica and stainless steel.

In the present study, we investigated the relationship between deposition conditions, and crystal orientation and deposition rate of Co oxide films with NaCl-type structure and spinel-type structure prepared by PE-MOCVD. Microstructures of the Co oxide films were also described.

2. Experimental details

The PE-MOCVD apparatus in the present study has been described in a previous article [10]. It consists of a stainless-steel vaporizer and a reactor with parallel-plate electrodes. The substrate was placed on the top electrode and r.f. power (13.56 MHz) was supplied to the bottom electrode. Diameters of the top and bottom electrodes were 160 and 215 mm, respectively. Distance between the electrodes was 30 mm. Some magnets were placed in a coaxial circle below the bottom electrode in order to increase the plasma density where the film was deposited. The magnetic field strength in the deposition region was 130 G.

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TABLE I Deposition conditions of Co oxide films

Vaporizing temperature	120 (°C)
Carrier gas (N_2) flow rate	10 ($cm^3\ min^{-1}$)
O_2 flow rate	3–50 ($cm^3\ min^{-1}$)
r.f. plasma power	400 (W)
Substrate temperature	150–400 (°C)
Total pressure	4–9 (Pa)
Deposition time	15 (min)

The source material used was cobalt acetylacetonate complex $Co(C_5H_7O_2)_2 \cdot 2H_2O$ and was heated in a vaporizer at 120 °C. The hydrated water dissociated at 95 °C in the early stage of heating. A gas line was heated to 150 °C. The Co oxide films were obtained as follows. The vapour of the source material was introduced into a reactor through a gas line using nitrogen as a carrier gas under reduced pressure. Oxygen was also introduced into the reactor. Then, the plasma was generated across the electrodes and the deposition was carried out on a preheated substrate at 110 min^{-1}. The substrate used was soda-lime glass. Deposition conditions are summarized in Table I.

The crystal structure and orientation of the films were analysed using X-ray diffraction (CuK_α). Thicknesses were measured using a stylus profilometer. Auger electron spectroscopy (AES) was utilized to detect contamination of carbon and nitrogen in the films. Microstructures of the films were observed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Crystal structure, orientation and deposition rate

The relationship between O_2 flow rate, and crystal structure and orientation of Co oxide films were investigated at a constant substrate temperature of 400°C. Fig. 1 shows X-ray diffraction patterns of Co oxide films deposited at O_2 flow rates of 3–50 $cm^3\ min^{-1}$ under the conditions shown in Table I. When the O_2 flow rate was as low as 3 $cm^3\ min^{-1}$, the deposited film was amorphous. High crystalline and (1 0 0)-oriented NaCl-type CoO films were formed at the O_2 flow rate of 7 $cm^3\ min^{-1}$. The value of the lattice constant for CoO film was 0.422 nm, which was smaller than that for bulk CoO (=0.4260 nm). As the O_2 flow rate increased to 10 $cm^3\ min^{-1}$ a thin film of spinel-type Co_3O_4 coexisted with the (1 0 0)-oriented NaCl-type CoO that was formed. Single phase films of spinel-type Co_3O_4 were formed at O_2 flow rate of more than 20 $cm^3\ min^{-1}$. The Co_3O_4 films possessed a preferred orientation of (1 0 0) and the degree of the (1 0 0) orientation increased with increasing O_2 flow rate. The value of the lattice constant for the Co_3O_4 film deposited at O_2 flow rate of 50 $cm^3\ min^{-1}$ was 0.812 nm, which was larger than that for bulk Co_3O_4 (=0.8084 nm).

Fig. 2 shows the deposition rate of the films deposited at 400 °C as a function of O_2 flow rate. In the range of O_2 flow rate from 3 to 20 $cm^3\ min^{-1}$, the deposition rate of the films were around 40 nm min^{-1}. In the formation range of (1 0 0)-oriented Co_3O_4 films, the deposition rate decreased rapidly from 40 to 20 nm min^{-1} with increasing O_2 flow rate from 20 to 50 $cm^3\ min^{-1}$.

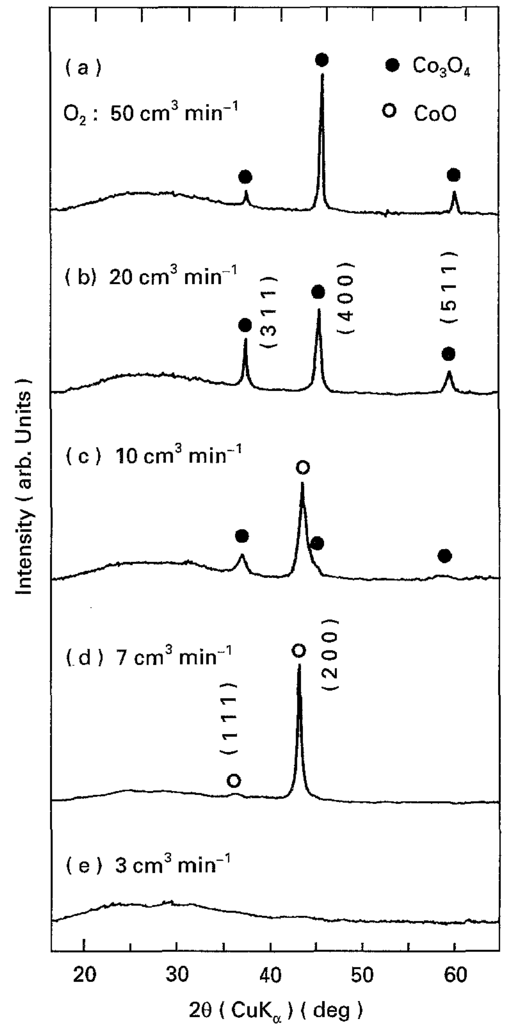

Figure 1 X-ray diffraction patterns of Co oxide films deposited at O_2 flow rate of 3–50 $cm^3\ min^{-1}$ and at substrate temperature of 400 °C.

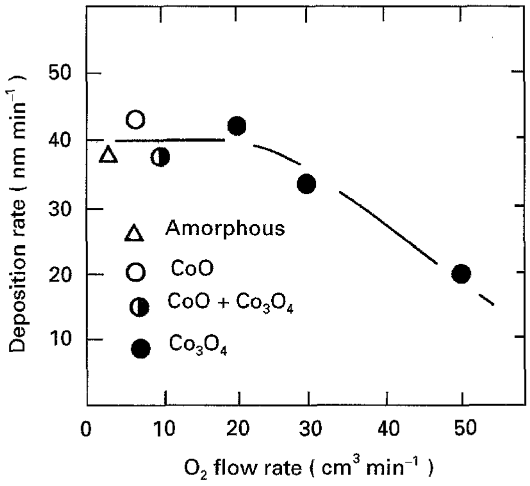

Figure 2 Deposition rate of Co oxide films deposited at 400 °C as a function of O_2 flow rate.

The relationship between substrate temperature, and crystal structure and orientation of CoO films were investigated. Fig. 3 shows X-ray diffraction

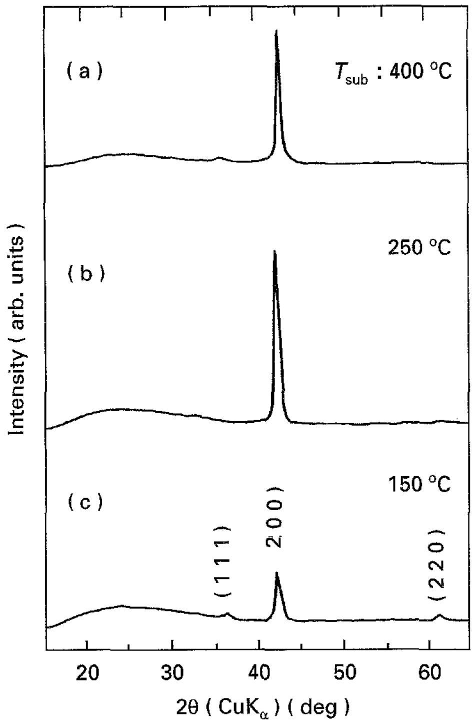

Figure 3 X-ray diffraction patterns of CoO films deposited at O_2 flow rate of $7\,cm^3\,min^{-1}$ and at substrate temperatures of (a) 400 °C, (b) 250 °C and (c) 150 °C.

patterns of CoO films deposited at O_2 flow rate of $7\,cm^3\,min^{-1}$ and at substrate temperatures of 150–400 °C under the conditions shown in Table I. Crystalline CoO films with NaCl-type structure were obtained at substrate temperatures of 150–400 °C, though the degree of crystallinity of the films decreased on decreasing the substrate temperature from 400 to 150 °C. The CoO films possessed a preferred orientation of (1 0 0), independent of the substrate temperature. The values of the lattice constant of the films increased from 0.422 to 0.426 nm, which equalled the value for bulk CoO, with decreasing the substrate temperature from 400 to 150 °C. In the preparation of oxide films on glass substrates by the PE-MOCVD process, the films initially nucleated in a random orientation [11]. The crystal orientation of the film, therefore, is determined by the method for growth of the nucleation. When the film grows from the initial nuclei, the crystal plane of the nuclei with minimum surface free energy may remain parallel to the film surface because the growth rate of the crystal plane with minimum surface free energy is slower than that of the other crystal planes. In an ionic crystal with NaCl-type structure, the (1 0 0) plane is the most densely packed plane and (1 0 0) orientation is known to minimize the surface free energy according to surface stability theory [12], suggesting the origin for the (1 0 0) orientation of NaCl-type CoO films.

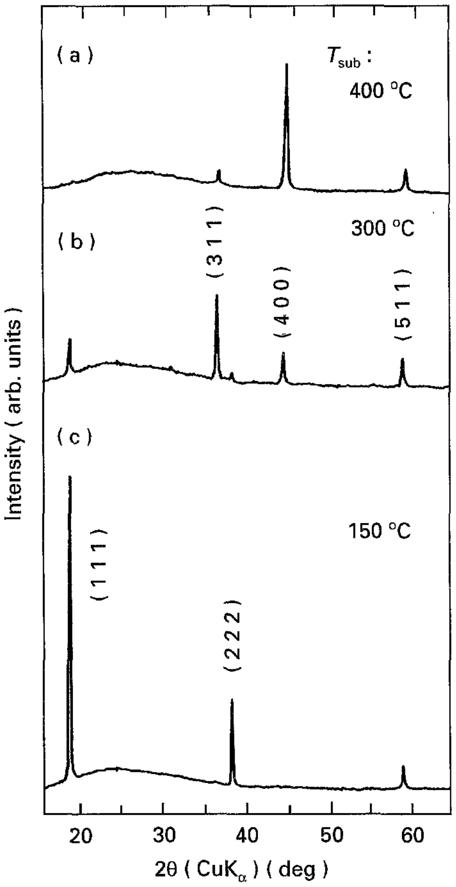

Figure 4 X-ray diffraction patterns of Co_3O_4 films deposited at O_2 flow rate of $50\,cm^3\,min^{-1}$ and at substrate temperatures of (a) 400 °C, (b) 300 °C and (c) 150 °C.

The relationship between substrate temperature, and crystal structure and orientation of Co_3O_4 films were investigated. Fig. 4 shows X-ray diffraction patterns of Co_3O_4 films deposited at O_2 flow rate of $50\,cm^3\,min^{-1}$ and at substrate temperatures of 150–400 °C under the conditions shown in Table I. Highly crystalline Co_3O_4 films with spinel-type structure were obtained at substrate temperatures of 150–400 °C. As the substrate temperature decreased from 400 to 300 °C, the orientation of the Co_3O_4 films were changed from (1 0 0) to random, as shown in Fig. 3a and b. The film deposited at 150 °C possessed a preferred orientation of (1 1 1), as shown in Fig. 3c. The value of the lattice constant for the Co_3O_4 films was 0.812 nm, which was larger than that for bulk Co_3O_4 (= 0.8084 nm), and it is independent of substrate temperature. We have investigated the relationship between the substrate temperature and crystal orientation of spinel-type iron oxide (Fe_3O_4) films deposited by PE-MOCVD using iron (III) acetylacetonate complex $Fe(C_5H_7O_2)_3$ as a source material [13]. The Fe_3O_4 films deposited at 400 °C posessed (1 0 0) preferred orientation, which was the same orientation of the spinel-type Co_3O_4 films in the present study. However, the Fe_3O_4 films deposited at 150 °C had poor crystallinity with random orientation and the Fe_3O_4 films with (1 1 1) preferred orientation were not obtained at substrate temperatures of 150–450 °C. These results indicate that the crystal orientation of the spinel-type Co_3O_4 films deposited by PE-MOCVD was different from that of spinel-type Fe_3O_4 films at low substrate temperatures. In this PE-MOCVD process, cobalt contained in the source material of $Co(C_5H_7O_2)_2$ is divalent (Co^{2+}) and Co_3O_4 is an oxide composed of both Co^{2+} and Co^{3+}, while iron contained in the source material

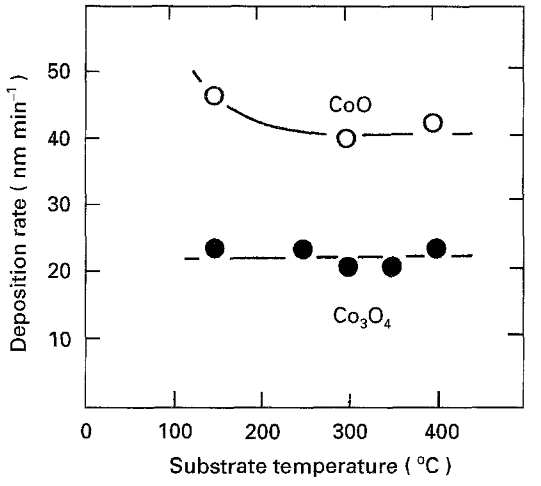

Figure 5 Deposition rate of CoO films and Co_3O_4 films as a function of substrate temperature. The CoO films and the Co_3O_4 films were deposited at O_2 flow rate of 7 and 50 cm^3 min^{-1}, respectively.

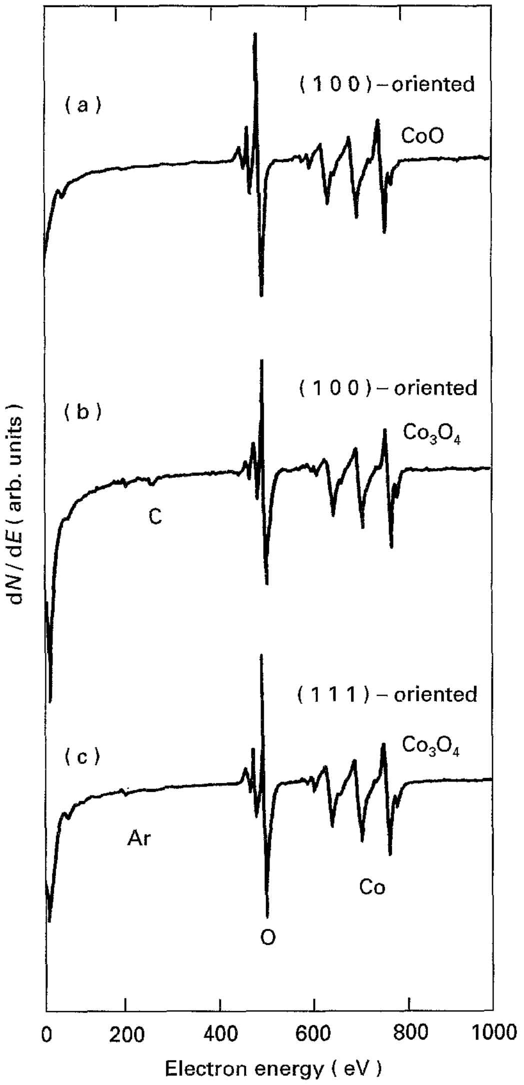

Figure 6 AES spectra at a depth of 100 nm from the film surface of (a) (1 0 0)-oriented CoO film deposited at 400 °C, (b) (1 0 0)-oriented Co_3O_4 film deposited at 400°C and (c) (1 1 1)-oriented Co_3O_4 film deposited at 150°C.

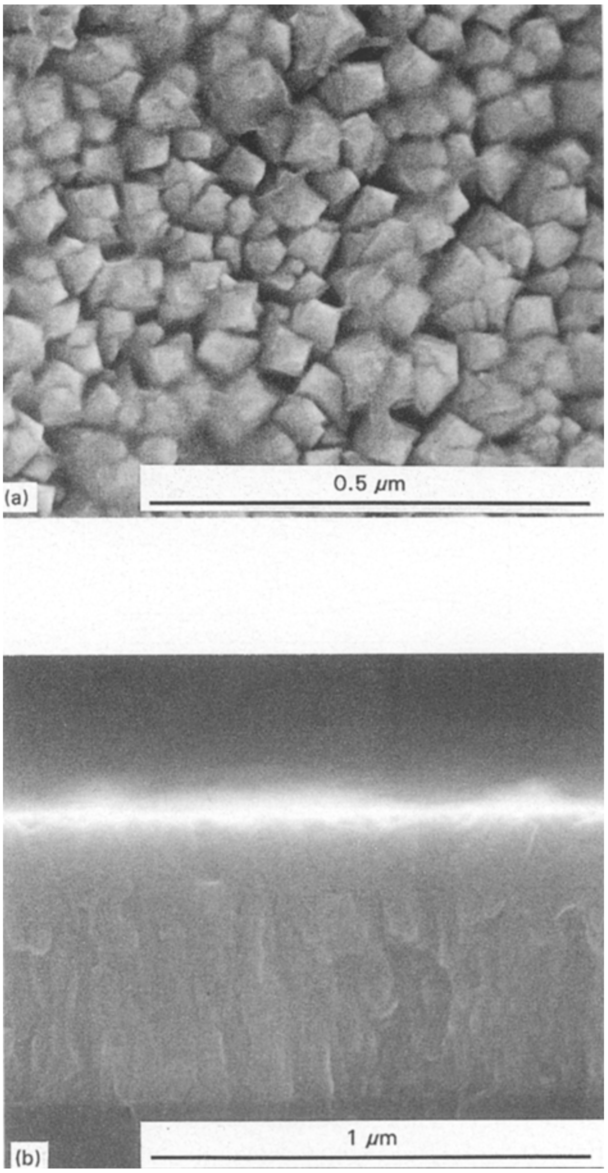

Figure 7 SEM images of (a) surface and (b) cross-section of (1 0 0)-oriented CoO film deposited at 400 °C.

$Fe(C_5H_7O_2)_3$ is trivalent and Fe_3O_4 is an oxide composed of both Fe^{2+} and Fe^{3+}. These suggest that the Co_3O_4 films were prepared in a powerful oxidizing ambient. Since the (1 1 1) plane is the most densely packed plane of O^{2-} in a spinel-type structure, the (1 1 1) orientation of Co_3O_4 films arose from the deposition condition of the powerful oxidizing ambient at the low substrate temperature of 150 °C.

Fig. 5 shows the deposition rate of the CoO films deposited at O_2 flow rate of 7 cm^3 min^{-1} and Co_3O_4 films deposited at O_2 flow rate of 50 cm^3 min^{-1} as a function of substrate temperature. The deposition rate of the CoO films decreased from 47 to 40 nm min^{-1} when the substrate temperature was increased from 150 to 300 °C and took an almost constant value of 40 nm min^{-1} above 300 °C. The deposition rate for the Co_3O_4 films was 22 nm min^{-1} and was independent of substrate temperature from 150 to 400 °C, though the orientation of the Co_3O_4 films changed from (1 1 1) to (1 0 0).

3.2. Microstructure

Fig. 6a, b and c show AES spectra at a depth of 100 nm from the film surface of the (1 0 0)-oriented

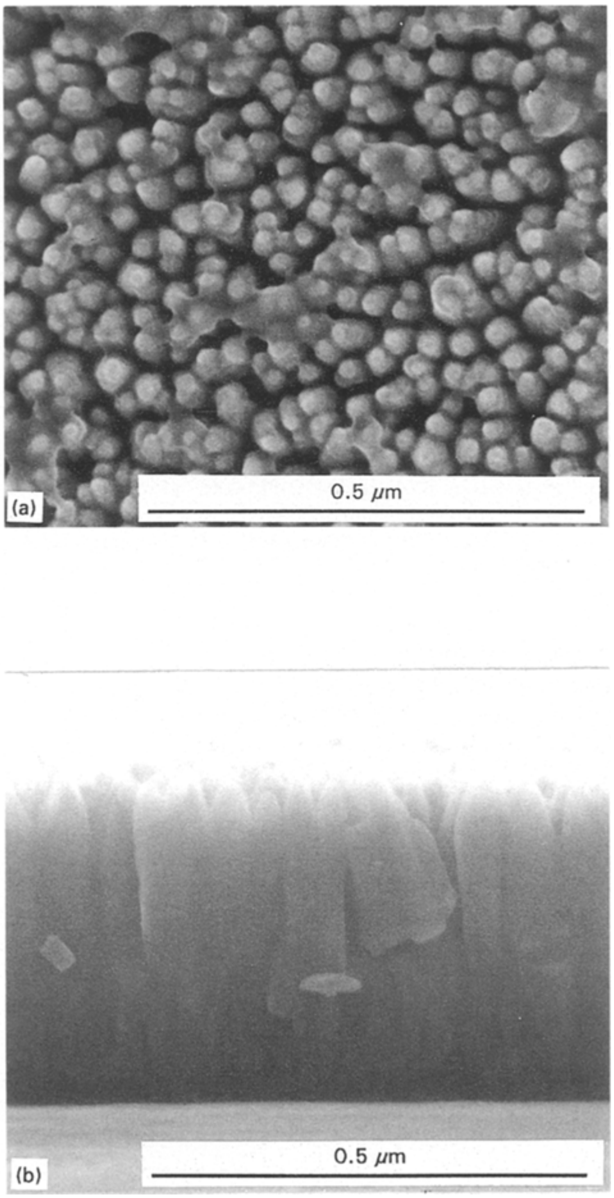

Figure 8 SEM images of (a) surface and (b) cross-section of (1 0 0)-oriented Co_3O_4 film deposited at 400 °C.

CoO film, the (1 0 0)-oriented Co_3O_4 film and the (1 1 1)-oriented Co_3O_4 film, respectively. Ar, O and Co elements were detected in all films. The Ar element comes from AES sputtering source. C element was detected only in (1 0 0)-oriented Co_3O_4 films.

Morphologies of the deposited Co oxide films were investigated using SEM. Fig. 7a and b show SEM images of the surface and cross-section of the (1 0 0)-oriented CoO film deposited at 400 °C, respectively. Film thickness was 640 nm. The film was composed of closely packed columnar grains which grew perpendicular to the film surface. The average diameter size at the film surface was about 60 nm. Figs 8a and b, and 9a and b show SEM images of the surface and cross-section of (1 0 0)-oriented Co_3O_4 film deposited at 400 °C and (1 1 1)-oriented Co_3O_4 film deposited at 150 °C, respectively. The film thicknesses of the CoO film and Co_3O_4 film were 360 and 340 nm, respectively. Each Co_3O_4 film had a columnar structure, as shown in Figs 8b and 9b. However, the shape and the average size of the columnar grains of each Co_3O_4 film at the film surface were different; a square shape and 35 nm for (1 0 0)-oriented film and a hexagonal shape and 60 nm for (1 1 1)-oriented film, as shown in Figs 8a and 9a, respectively. These indicate that the shapes of the columnar grains at the film surface of (1 0 0)-oriented film and (1 1 1)-oriented film correspond to the shapes of crystal planes of (1 0 0) and (1 1 1) in a spinel-type structure, respectively. Besides, the surface of the (1 0 0)-oriented Co_3O_4 film had a characteristic structure with minute protrusions, while the (1 1 1)-oriented film had a smooth surface. The average height of each protrusion of the (1 0 0)-oriented film was 40 nm.

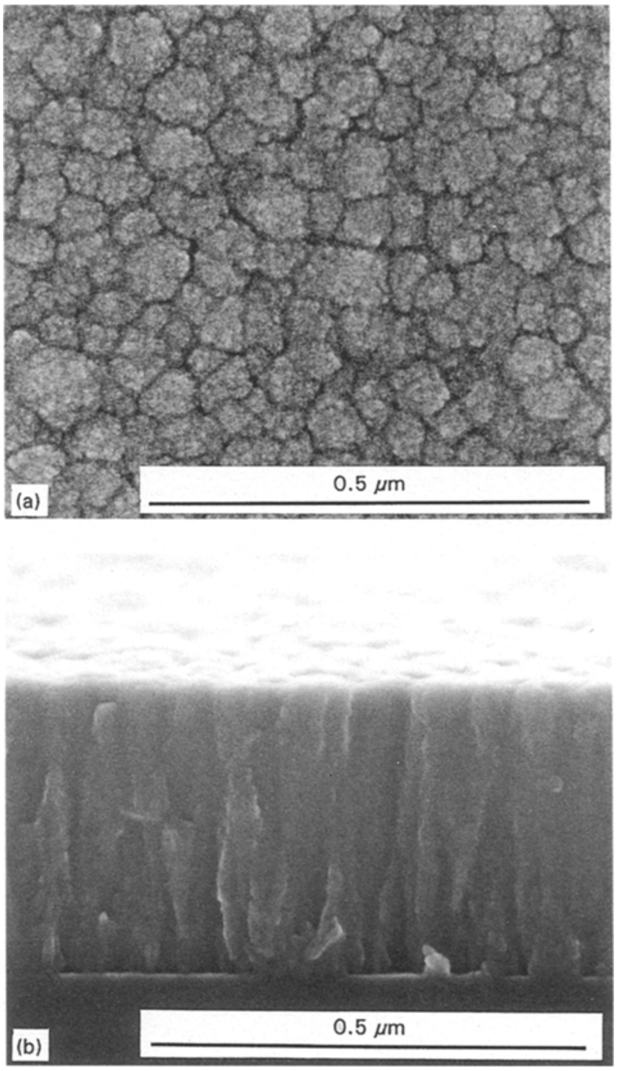

Figure 9 SEM images of (a) surface and (b) cross-section of (1 1 1)-oriented Co_3O_4 film deposited at 150 °C.

4. Conclusions

Co oxide films with NaCl-type and spinel-type structures were prepared on glass substrates at 150–400 °C by PE-MOCVD. The relationship between deposition conditions, and crystal structure and orientation of the films were investigated. With O_2 flow rate as low as 3 $cm^3 min^{-1}$, amorphous films were formed. As the O_2 flow rate increased to 7 $cm^3 min^{-1}$, crystalline CoO films with a NaCl-type structure were formed at substrate temperatures of 150–400 °C. The CoO films possessed (1 0 0) preferred orientation, independent of the substrate temperature. With O_2 flow rate as high as 20–50 $cm^3 min^{-1}$, highly crystalline Co_3O_4 films with a spinel-type structure were formed at 150–400 °C. The Co_3O_4 films deposited at 400 °C possessed (1 0 0) orientation. However, the orientation of the films were changed from (1 0 0) to random to (1 1 1) with decreasing substrate temperature from 400 to 300 to 150 °C. All of the (1 0 0)-oriented CoO films, (1 0 0)-oriented Co_3O_4 films and (1 1 1)-oriented Co_3O_4 films had a columnar structure. The average diameter sizes at the film surface were 60 nm for the (1 0 0)-oriented CoO films, 35 nm for the (1 0 0)-oriented Co_3O_4 films and 60 nm for (1 1 1)-oriented Co_3O_4 films.

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