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Cobalt thin films prepared by chemical vapor deposition from cobaltous acetate

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Cobalt thin films were prepared by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw material was cobaltous acetate which is nontoxic and easy to handle. At a reaction temperature of 300 °C, [111]-oriented polycrystalline films can be obtained on amorphous substrates. Increasing the H_2 partial pressure over the requirement for both the highest deposition rate and lowest resistivity promotes the crystallization with [111] preferential orientation of the film without affecting the crystallite size. Cobaltous acetate appears to offer a viable alternative to cobalt acetylacetonate for low-temperature cobalt film production.

Cobalt thin films are attractive in their application to the memory elements. The cobalt layers have traditionally been prepared by vacuum deposition and electrolytic method in liquid phase. An alternative is to deposit cobalt by chemical vapor deposition (CVD) methods:[1] the pyrolysis of cobaltous acetylacetonate or cobalt nitrosyl tricarbonyl at 400–450 °C; the thermal decomposition or hydrogen reduction of CoI_2 vapor at a temperature higher than 800 or 600 °C; the pyrolysis of cobalt dicyclopentadienyl at 400–450 °C; or hydrogen reduction (at 400–450 °C) of $CoCl_3$ vaporized at 60–150 °C. A relatively low-temperature (325–350 °C) process is hydrogen reduction of cobaltous acetylacetonate.[2]

In this letter, cobaltous acetate, which is nontoxic and readily available, is proposed as a source material in the low-temperature atmospheric-pressure CVD method. The films were deposited by hydrogen reduction of cobaltous acetate on various flow rates of hydrogen gas, and effects of H_2 flow rate on deposition rate, resistivity, and crystallinity of the film are discussed.

Cobaltous acetate tetrahydrate ($(CH_3COO)_2Co \cdot 4H_2O$) of reagent grade was used as the source material. It is easier to obtain and cheaper than cobaltous acetylacetonate. Figure 1 shows a schematic representation of the experimental setup. Cobaltous acetate was heated at a temperature of 300 °C and the generated gas was entrained by nitrogen carrier gas. The flow rate of the carrier gas was 300 cm^3/min. Hydrogen gas was injected into the nozzle and mixed with the source gas. The flow rate of hydrogen gas was ranged from 300 to 1000 cm^3/min.

A 76×26 mm borosilicate glass plate was used as the substrate. The substrate was placed in the closed-tube reactor heated by an external electric furnace. The substrate temperature was 300 °C. The total pressure in the reactor was an atmospheric pressure.

The composition of the film was measured by x-ray photoelectron spectroscopy. The crystallinity of the film was analyzed by the x-ray diffraction method with Cu $K\alpha$ radiation. The electric resistivity was measured by the van der Pauw method.

Shiny smooth cobalt films were formed homogeneously on the borosilicate glass substrates at the reaction temperature of 300 °C. The films were grown by the hydrogen reduction of cobaltous acetate. In an inert (nitrogen) atmosphere, no film was obtained. The films were highly adherent and showed no apparent peeling on glass substrates.

Figure 2 shows the deposition rate of cobalt film as a function of H_2 flow rate. The deposition rate increases with increasing H_2 flow rate from 300 to 600 cm^3/min. The highest deposition rate is obtained at a H_2 flow rate above 600 cm^3/min. Figure 3 shows the resistivity of cobalt film as a function of H_2 flow rate. The resistivity decreases with increasing H_2 flow rate from 300 to 600 cm^3/min and above 600 cm^3/min it shows the lowest value which is close to the resistivity for bulk cobalt (6.24×10^{-6} Ω cm at 20 °C). Thus, the partial pressure of hydrogen gas in its lower values affects the resistivity and the deposition rate. When the H_2 flow rate is over 600 cm^3/min, the deposition rate and the resistivity each show constant value independent of the H_2 partial pressure.

Figures 4(a)–4(d) show the x-ray diffraction patterns of the ~100-nm-thick cobalt films deposited on the borosilicate glass substrates. All patterns show peaks at $2\theta = 44.1°$. The peak was admitted in the x-ray diffraction pattern at the H_2 flow rate larger than 600 cm^3/min. That is, the cobalt film is composed of crystallite with a predominant cubic structure with [111] preferential orientation. Furthermore, Fig. 4 shows that the intensity of the Co (111) peak increases with increasing flow rate of H_2 gas. The full width at half maximum of the diffraction peak (111) yielded the crystallite size of ~17 nm, which is independent of H_2 flow rate. Thus, an extra H_2 partial

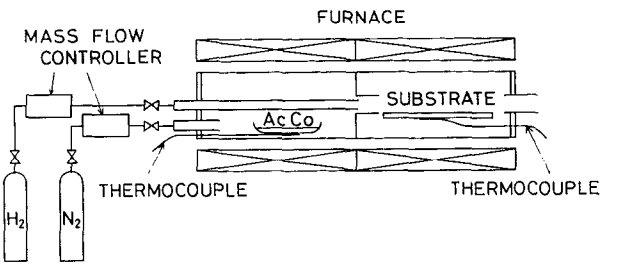

FIG. 1. Schematic representation of experimental equipment.

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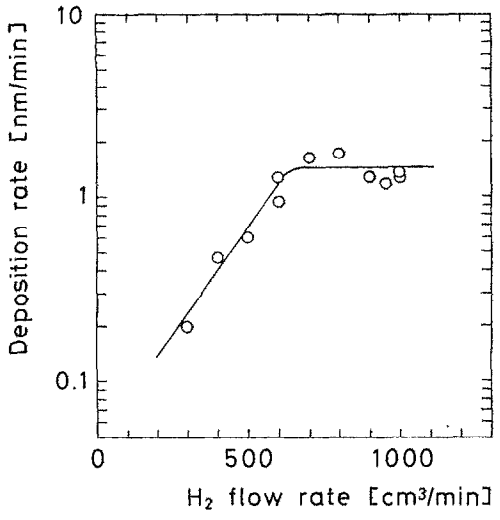

FIG. 2. Deposition rate of cobalt film as a function of H_2 flow rate.

pressure over the requirement for both the highest deposition rate and lowest resistivity promotes the crystallization with [111] preferential orientation of the film without affecting the crystallite size.

In conclusion, cobalt thin films were prepared by a low-temperature atomspheric-pressure chemical vapor deposition method. The raw material was cobaltous acetate which is nontoxic and easy to handle. Polycrystalline films were obtained at a reaction temperature of 300 °C. Increasing the H_2 partial pressure over the requirement for both the highest deposition rate and lowest resistivity promotes

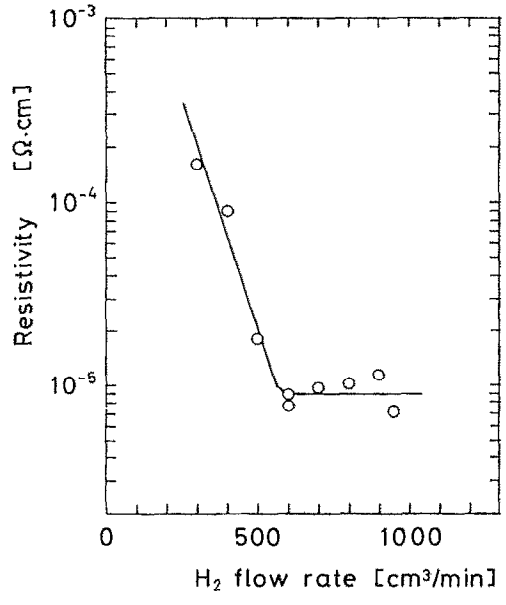

FIG. 3. Resistivity of cobalt film as a function of H_2 flow rate.

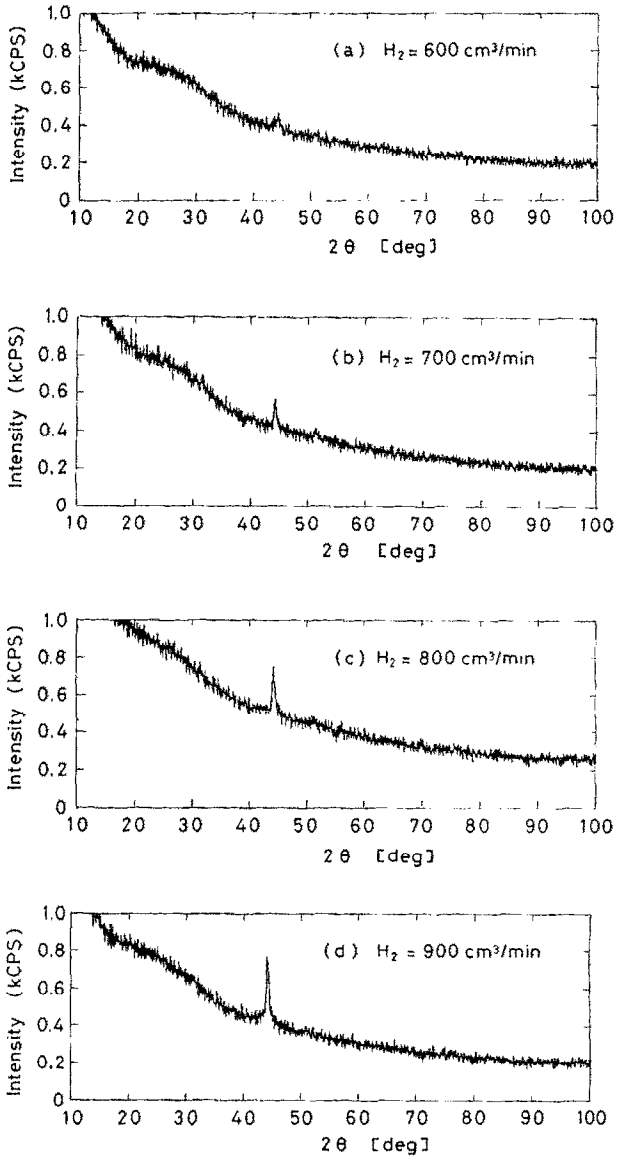

FIG. 4. X-ray diffraction pattern of ~100-nm-thick cobalt film for H_2 flow rate: (a) 600 cm^3/min, (b) 700 cm^3/min, (c) 800 cm^3/min, and (d) 900 cm^3/min.

the crystallization with [111] preferential orientation of the film without affecting the crystallite size. Cobaltous acetate appears to offer a viable alternative to cobaltous acetylacetonate for low-temperature cobalt film production.

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[2] E. J. Jablonowski, Cobalt **14**, 28 (1962).