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Electrodeposition of Sm-Co from Formamide Solution

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Anhydrous samarium chloride, cobalt chloride and their coexisted solution of formamide were electrolyzed at constant current. From the results of XPS analysis of the deposits, their metallic states were found in the inside of the film. Cobalt rich codeposited film showed the saturation magnetization of 840 emu/cc and the coercive force of 18.1 Oe.

The rare earth metal-iron group alloys are widely noticed as high-powered magnet or photo-magnetic recording material. If such a metal thin film were prepared by electrodeposition, the production efficiency would be greatly improved and the application field would expand extensively. However, electrodeposition of rare earth metals is difficult because of their negative oxidation-reduction potentials. From the aqueous solution, it is impossible as hydrogen evolution proceeds. Moeller and Zimmerman[1] succeeded in the deposition of yttrium, neodymium and lanthanum from anhydrous ethylenediamine(en) solution. Only a few examples such as Gd-Co from formamide,[2] and Dy-Fe from dimethylformamide[3] were reported. Karai et al.[4] tried the electrodeposition of Sm-Co from propylene carbonate, but they could not detect the metallic state of Sm and Co.

In the present paper, we reported the successful example of the

electrodeposition of Sm-Co from the formamide solution containing $SmCl_3$ and $CoCl_2$, where magnetic characteristics and XPS analysis were carried out. Electrolytic solution was made up from reagent grade anhydrous samarium chloride($SmCl_3$) and anhydrous cobalt chloride($CoCl_2$) dissolved in formamide treated by Molecular Sieves(3A) to dry the solvent. The solubility of $SmCl_3$ is small and less than about 0.01 mol/dm^3. Within this range, the molar ratio of Sm to total concentration, i.e., (Sm + Co) was changed. En was added, if necessary. As a cathode, ITO, copper or gold, the size of which was 1 cm x 1 cm, was used. Platinum plate was used as a counter electrode. Constant current electrolysis was carried out by using Potentio-Galvanostat(Hokuto Denko HAB-151) at room temperature of 25 $\pm$ 2 ^{o}C. The quantity of Sm and Co deposited on the substrate was analyzed by atomic absorption method. XPS analysis was performed using a Shimadzu ASIX-1000. Magnetic properties of the deposit were measured by a vibrating sample magnetometer(Model 1660-CTS, DMS Co.).

The surface color and the character of the deposited film depended on the electrolytic current density and the Sm content in the film. If the current density was less than 8 mA/cm^2, the obtained film surface was smooth and black in color and had a metallic luster in the case of Sm content in the film larger than 50 mol%. The film obtained at the larger current density than 10 mA/cm^2 had crevasses on the surface. Total current efficiency was about 35% at the current density of 6 mA/cm^2 in the solution of Sm/(Sm+Co) = 37.5% bath. In order to confirm the oxidation state of Sm and Co deposited on the substrate, an XPS investigation was performed. Figure 1 shows Sm $3d_{5/2}$ X-ray photoelectronic spectra of Sm deposited on Au substrate obtained from the solution containing only $SmCl_3$ with 0.3 mol/dm^3 en. The dotted and the solid lines show the binding energy of Sm_2O_3 and Sm metal, respectively. So, the deposit around the surface is Sm_2O_3, but inside of the film seems to be metallic state, because the observed photoelectronic peak's value came close to the value due to Sm metallic state binding energy as etching time increased. In the case of Co obtained from the solution containing only $CoCl_2$, though the main deposit is oxide(CoO), metallic state may be present in the

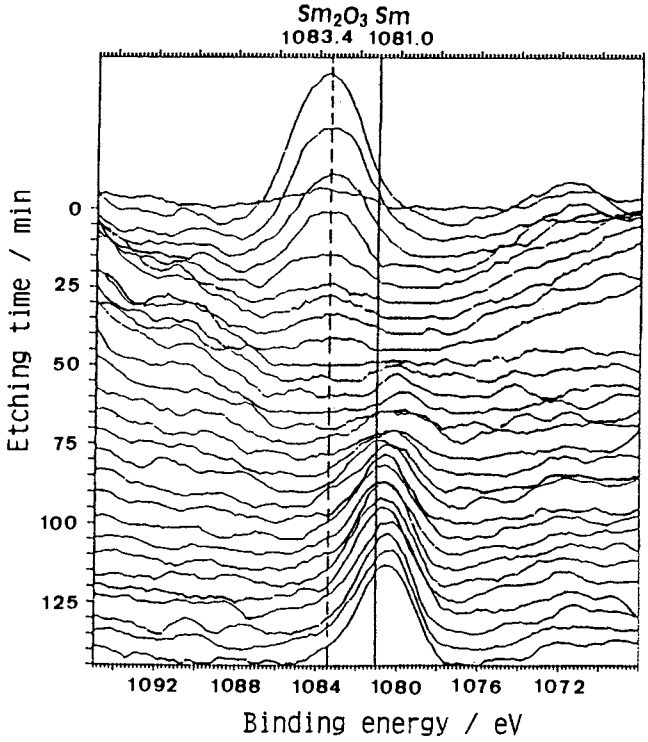

Fig. 1. Sm $3d_{5/2}$ X-ray photoelectron spectra of Sm deposit on Au obtained at 10 mA/cm^2 for 10 min from only Sm^{3+} containing bath.

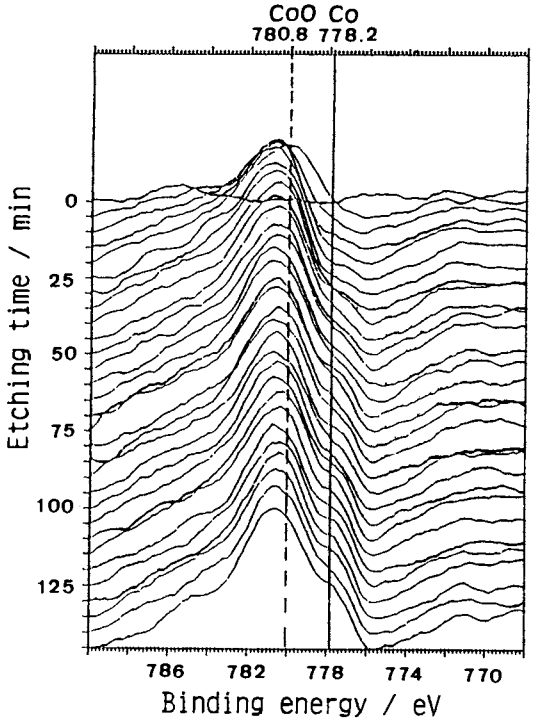

Fig. 2. Co $2p_{3/2}$ X-ray photoelectron spectra of Co deposit on Au obtained at 10 mA/cm^2 for 10 min from only Co^{2+} containing bath.

inside of the film because the shoulder which seemed to be corresponding to Co metal state in Co $2p_{3/2}$ X-ray photoelectronic spectra appeared as etching time went on(Fig. 2). The spectra of Sm-Co codeposit on ITO were reproduced in Fig. 3, the film composition of which is 21% in Sm concentration obtained at 10 mA/cm^2 for 1h electrolysis from Sm/(Sm + Co) = 37.5 mol% bath. The photoelectronic peaks due to

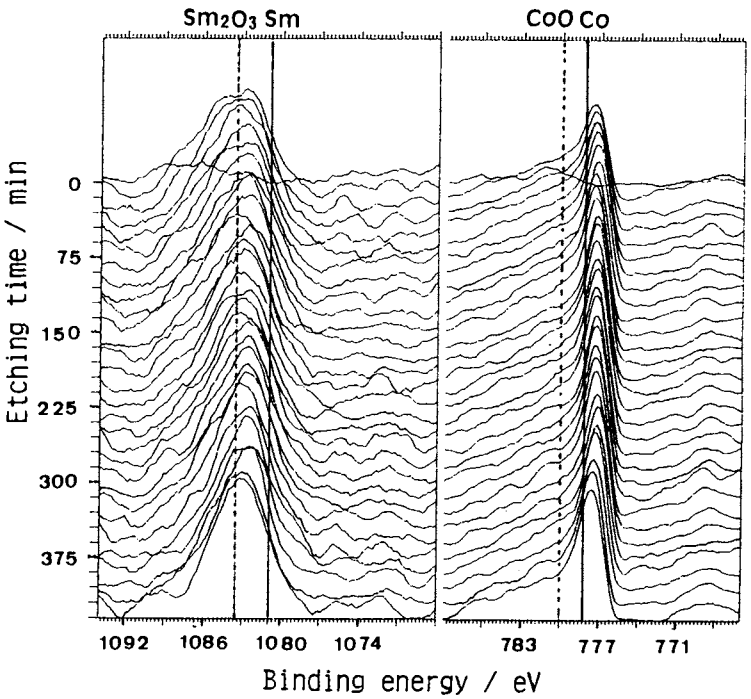

Fig. 3. Sm $3d_{5/2}$(left) and Co $2p_{3/2}$(right) X-ray photoelectron spectra of Sm-Co codeposit on ITO obtained at 10 mA/cm^2 for 1h from Sm/(Sm+Co) 37 mol% bath.

Sm $3d_{5/2}$ and Co $2p_{3/2}$ did not change in their binding energy from the surface to the inside of the film different from Sm and Co film cases(Figs. 1, 2). Considering the binding energy of their peaks, their oxidation states in the codeposited film seem to be not an oxide and a metallic state of pure metal, but a characteristic state such as an intermtallic compound.

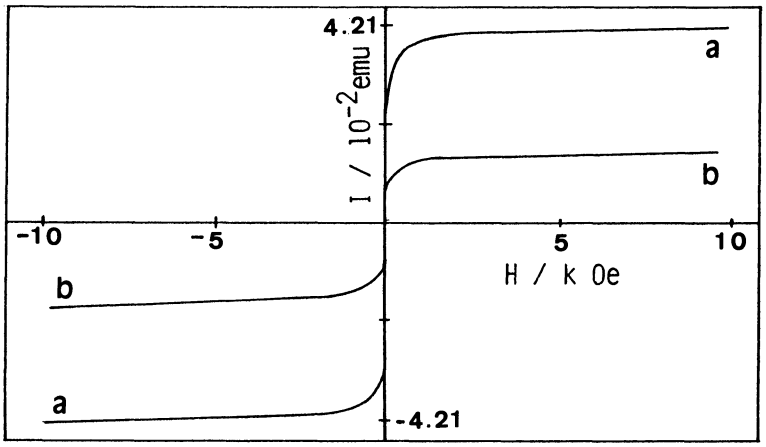

Fig. 4. Magnetization curves of Sm-Co codeposit from Sm 37.5 mol% bath on ITO obtained at (a) 10 mA/cm^2 for 1h electrolysis (film composition, Sm:Co=21:79) and (b) 2 mA/cm^2 for 5h electrolysis (film composition, Sm:Co =55:45).

Figure 4 indicates the magnetization curves of two sorts of film, the size of which is 0.5 cm x 0.5 cm x 2 μm. A cobalt rich film showed a higher saturation magnetization with a value of 840 emu/cc. By enlarging the Fig. 4, a small hysteresis was observed and the coercive force was 18.1 Oe. This value is smaller than the value expected for the Co 79% film. The reason is unknown at present. From all the results stated above, electrolytic deposition of Sm, Co and Sm-Co from formamide is possible and the deposits contain metallic states.

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