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Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 15(4), 499-506
Issue Date	1981-12
Doc URL	http://hdl.handle.net/2115/37996
Type	bulletin (article)
File Information	15(4)_499-506.pdf

Deposition Rate and Chemical Composition of Copper-Nickel Alloys by R. F. Sputtering

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(Received June 30, 1981)

Abstract

Variation of deposition rate of copper-nickel alloys with argon ion bombardment was studied using an r. f. sputtering apparatus along with the characterization of deposited films. The Deposition rate was determined by both thickness and weight of the deposited films. Thickness of the films were measured by means of multiple -beam interferometry. Weight of deposition was measured by means of atomic absorption spectrochemical analysis. The films were also studied and characterized by means of X-ray diffraction and scanning electron microscopy. The deposited films had exactly the same composition with the corresponding target alloys and were homogeneously alloyed with a preferential orientation with (111) plane parallel to the glass substrate surface. The deposition rate was not a simple function of the target composition, but showed a minimum around 80-90 at%Cu, where the deposition rate was 40-50% smaller than the predicted value. The phenomenon was attributed to the morphologically pronounced rugged surface of those target alloys.

1. Introduction

Sputtering techniques have been greatly expanded in applications such as thin film production for coatings, micropatterning of electronic devices and so forth. It is of great importance to elucidate properties of deposition films on a substrate material as well as to estimate the sputtering yield or rate for such applications, Sputtering yield of many kinds of materials has been determined by various methods[1,2]. However, there are only a few measurements made on sputtering yield of alloys and compounds. From a view point of industrial applications, sputtering phenomena of alloys and compounds may be exceedingly important, because of the widerange of practical use in alloy and compound films.

In the present study, film formation of Cu-Ni alloys by r. f. sputtering was examined systematically. Properties of deposited films were examined by means of multiple-beam interferometry, X-ray diffraction and atomic absorption spehtrochemical analysis. They were compared with those of the target materials. Sputtering rate was measured as a function of the composition of the target materials. It was found that the sputtering rate was not a simple function of bulk composition of the

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alloys. A minimum deposition rate arose around 80-90at%Cu alloys. However, the composition of all of the films was exactly the same as that of the corresponding target alloys.

2. Experimental

Pure copper (99.99%), nickel (99.9%) and five Cu-Ni alloys were used in the present study. The alloys were prepared from pure nickel and copper by argon-arc melting and then cold-rolled into plate form. Compositions of the alloys were 4at%, 34at%, 69at%, 80at% and 90at%Cu. The dimensions of each target was 82.5 mm in diameter and 0.5-1.5 mm in thickness. The target materials were washed with acetone or methyl alcohol using a supersonic washing device and dried for 30 minutes in hot air (80℃) before use. High purity argon (99.99%) was used as the sputtering gas without further purification.

A conventional r. f. sputtering apparatus was used in the present study. Details of the apparatus were described elsewhere[3]. A target was mounted on a holder of 80 mm diameter. It was mounted on the holder with four fixing bolts made of stainless steel. They were covered with alloy foils having exactly the same composition as the target material in order to avoid sputtering of the bolts to contaminate the target and deposited films. The films were usually deposited at a time on several glass plates ($15\times15\ \mathrm{mm}^2$) placed around the center of the holder. Specimens for X-ray diffraction were prepared on a larger glass plate ($25\times75\ \mathrm{mm}^2$). The substrate holder was cooled by circulating water inside of it during sputter-deposition.

After mounting a target and substrates, the apparatus was evacuated down to 5×10^{-4} Pa by an oil diffusion pump. Subsequently, the apparatus was baked out at 70℃ for 30 minutes. This procedure gave rise to the decrease the residual pressure to 5×10^{-5}Pa. Argon gas was admitted into the the apparatus through a variable leak valve to keep the pressure constant at 10Pa, which was measured by a Pirani gauge. The argon gas was discharged with applying r. f. power of 2.0 KV, 200 mA and the frequency of 13.56 MHz. Distance between the target and the substrate was 30 mm. Before the films were deposited on the substrates, the target was sputter-cleaned for 30 minutes with closing a shutter to prevent the deposition of sputtered particles. Sputter-deposition of a given target was carried out with varing sputtering time from 2 to 7 minutes in order to determine deposition rate. All of the sputtering experiments were carried out under the same sputtering conditions.

Thickness of a film on a substrate which was placed at the center of the substrate holder was measured by means of multiple-beam interferometry (Tolansky method)[4]. The weight of copper and nickel deposited and chemical composition of the film were determined by atomic absorption spectrochemical analysis. The films which were formed on several substrates in a given sputtering time were dissolved into hot 6 N-HNO_3 solution of 5.00 ml and diluted with distilled water to 250.0 ml. The concentration of nickel and copper in the solution was measured using an atomic abosrption spectrochemical analyzer which was calibrated precisely using standard solutions containing various known amounts of those elements. Compositions of the target materials were determined by the same method. Other films were used for X-ray diffraction and scanning electron microscopy to examine the crystallography and morphology. These properties of the films were compared with those of the targest.

3. Results and Discussion

Film properties as mentioned above were examined for all of the alloys following the same methods and procedures.

Fig. 1 shows a relation between target and film compositions. It was found that the composition of the films was the same as that of the target for a given target–film pair within experimental errors. Similar results have been observed by many investigators[1,2].

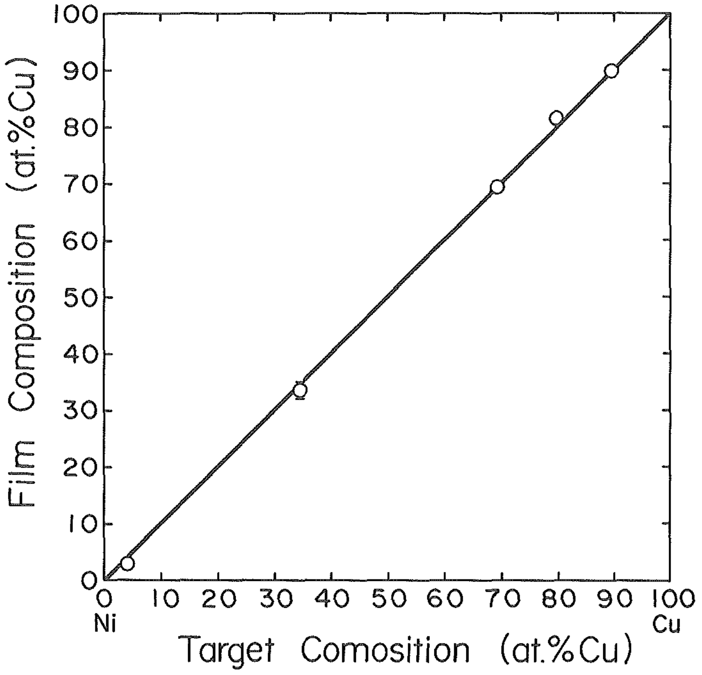

Fig. 1 Variation of the fiilm composition with target composition

Fig. 2 shows an example of increase in film thickness with sputtering time for several alloys. The thickness increased linearly with the time in each case. Such a linearity was found for all other films not quoted in the figure. Identical relations were observed between the weight of deposited copper and nickel. This indicates that the deposition rate was kept constant under the sputtering conditions adopted in the present study. Therefore, the films were formed in a steady state for each of the films.

Fig. 3-a shows the relation between the deposition rate and the composition of

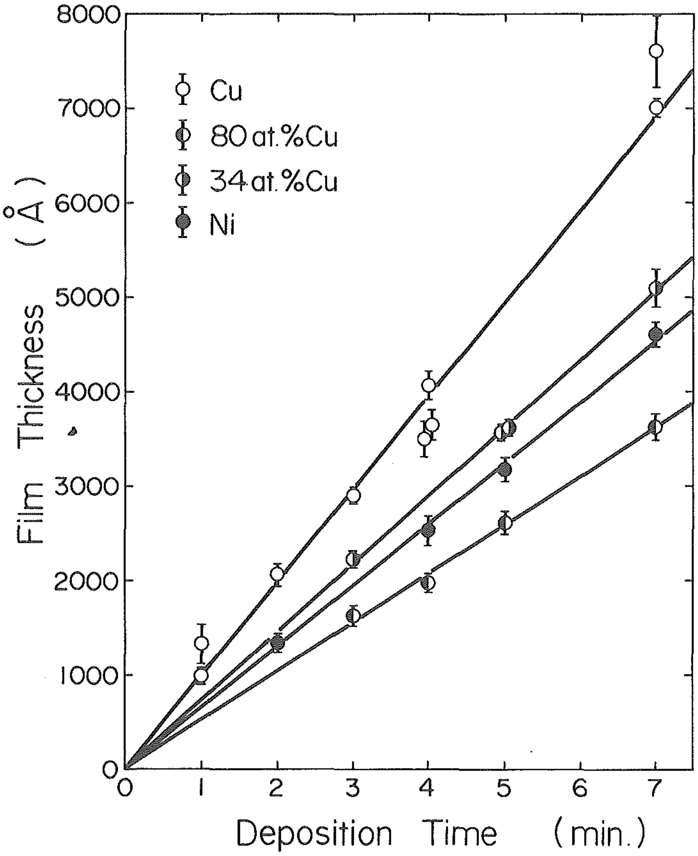

Fig. 2 Variation of film thickness with sputtering time

target materials. The deposition rate was calculated from the slope in straight lines as shown in Fig. 2. Fig. 3-b shows an identical relation, however the deposition rate was calculated from the linear relation between the weight of deposited films and sputtering time. Both Fig. 3-a and Fig. 3-b show that deposition rate of the films was not a simple function of the target composition and a pronounced minimum arised around 80-90at%Cu. These relations are not consistent with the prediction in a selective sputtering model[5,6].

Sputtering rate R of a Cu-Ni alloy will be described as below according to the model.

$$R = JN_a[\gamma_{Cu}X^s + \gamma_{Ni}(1-X^s)] \tag{1}$$

where X^s is the atomic fraction of copper on the target surface, J is the flux of the incident ions, $\gamma_{Cu} = S_{Cu}/N_{Cu}$, $\gamma_{Ni} = S_{Ni}/N_{Ni}$, here S_{Cu} and S_{Ni} are the sputtering yields of copper and nickel, respectively, and N_a, N_{Cu} and N_{Ni} are the atomic densities of the alloy, copper and nickel, respectively. In a steady state, surface composition of Cu-Ni alloys is described in relation to the bulk composition of the targets as

$$\gamma_{Cu}X^s/[\gamma_{Cu} + \gamma_{Ni}(1-X^s)] = X^b \tag{2}$$

where X^b is the atomic fraction of copper in bulk. As mentioned above, each film was deposited in a steady state in the present study, eqn. (2) is valid. Elimination of X^s from eqns (1) and (2) results in

$$R = JN_a\gamma_{Cu}/[X^b + K(1-X^b)] \tag{3}$$

where $K = \gamma_{Cu}/\gamma_{Ni}$, which was evaluated as 1.52 from Fig. 3-a and 1.72 from Fig. 3-b.

The relation predicted by eqn (3) was plotted as the dotted lines in Fig. 3-a and Fig. 3-b, using the observed values of K. It is seen that the experimental results fulfill the relation (3) for the alloys having compositions below 50 at%Cu. The results suggests that the sputtering yields of both the elements remained almost constant in those alloys. The same conclusion has been obtained by many investigations on selective sputtering of Cu-Ni alloys[5-8] although sputtering conditions were milder than those in the present study and constancy of the ratio of the sputtering yield was indicated over the entire composition range. On the other hand, the present results diverged remarkably from relation (3) for the alloys having composition over 50at%Cu.

Besides a similar trend in variation of deposition rate with target composition between those shown in Fig. 3-a and Fig. 3-b, some differences were found between them: the ratio of the deposition rate of copper to that of nickel was 1.52 in Fig. 3-a, while it was 1.72 in Fig. 3-b. The latter agreed quite well with those appearing in the literature[1,2]. In addition the extent of divergence of the experimental results from relation (3) differed slightly between them.

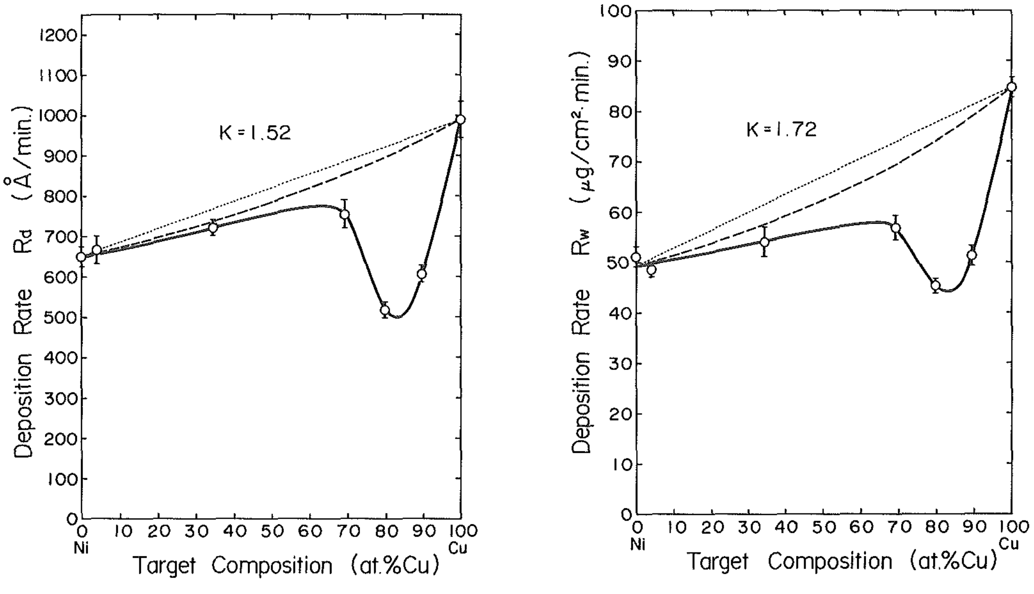

Fig. 3 (a) Variation of deposition rate, R_d, with target composition
(b) Variation of deposition rate, R_w, with target composition

Fig. 4 shows the variation of density of the films with their composition. The density was evaluated from the thickness and the weight of the films. The density of the bulk alloys are shown by a dotted line in the figure. It is seen that the

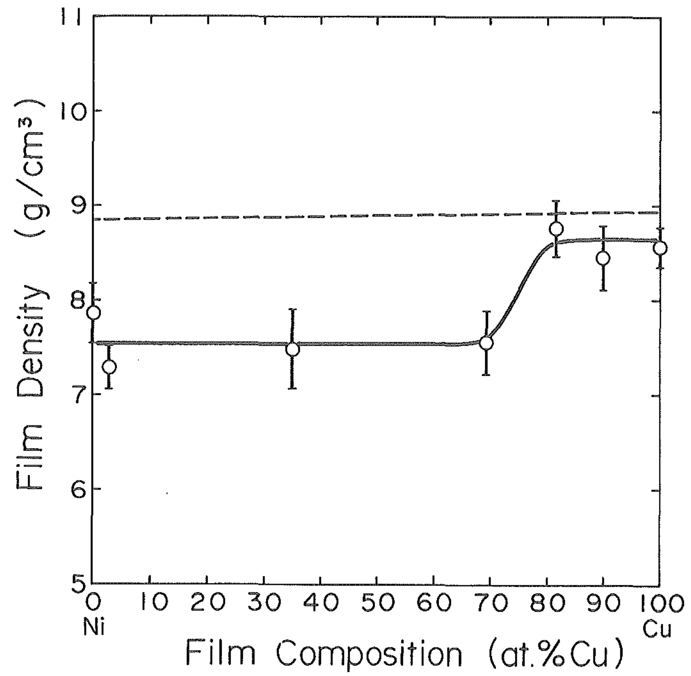

Fig. 4 Variation of the density of films with their composition

density of the films having a composition of over 80at%Cu were fairly close to that of the bulk alloys, while the films having lower compositions had smaller density than the corresponding alloys. X-ray diffraction of the films revealed that the films were alloyed homogeneously and oriented preferentially with the (111) plane parallel to the glass substrate.

It is apparent from the above results that the deviation of the deposition rate from relation (3) is not due to film properties, but arises from the target porperties. However, examination of the crystallography of the target materials showed no characteristic features by which the deviation can be explained. On the other hand, observation of the target surface by SEM revealed some features which explain the deviation. Fig. 5 shows SEM photographs of the target surfaces along with the corresponding film surfaces. The former was observed after the final run of the sputtering experiment (10 times sputtering experiments were done, in which about 10μm of the surface layer was assumed to be removed). The latter was observed after depositing of films approximately 0.5μm in thickness. Photographs show that surface morphology was quite different between the targets and the films. Although many small patches of crystallites were observed on the films, the surfaces were fairly smooth. On the other hand, surfaces of the targets were rough due to sputter-etching. The morphology of these surfaces differed from each other. Nickel and copper have many grooves on their surfaces which presumably correspond to the grain boundaries and the surface of an individual grain was fairly flat. The alloys

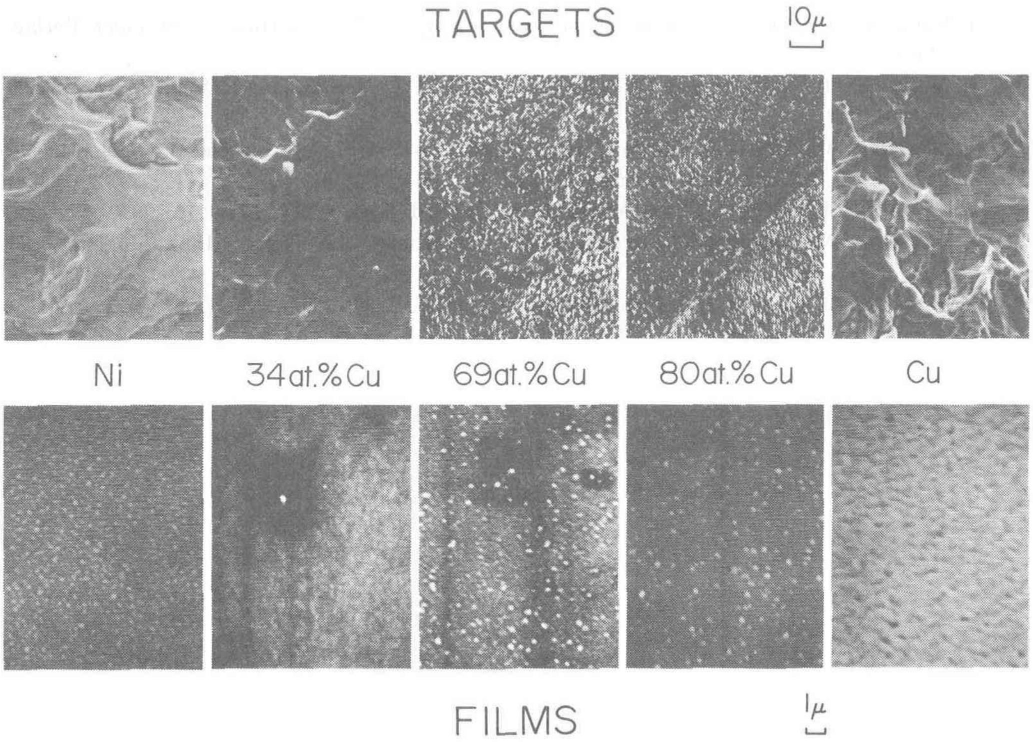

Fig. 5 SEM photographs of targets and films

having composition of 69, 80 and 90at%Cu have more rugged surfaces than the other as seen in the figure. It is considered therefore that the deviation of the deposition rate from relation (3) observed in the present study arose from the rugged surface morphology.

4. Summary

Homogeneous Cu-Ni alloy films were formed on glass surfaces by means of r. f. sputtering of Cu-Ni alloy targets with argon ions. The composition of the films was exactly the same as that of the targets. The crystallites were oriented preferentially with a (111) plane parallel to the glass surfaces. The films having a composition of over 80at%Cu showed a similar density to that of bulk alloys, while those having a composition below 70at%Cu exhibited a smaller density than the bulk alloys.

Deposition rate of the alloys varied depending on the composition of the targets, however it deviated from the prediction in a selective sputtering model. Remarkable decrease in the deposition rate was found for the alloys having the composition around 80-90at%Cu. It was concluded that this phenomenon was closely related to the rugged surface morphology of these target materials.

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