STUDY ON ELECTROLYTICALLY DEPOSITED COPPER FILM ON STAINLESS STEEL SURFACE FOR RF COUPLERS

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Abstract

A copper (Cu) film is electrolytically deposited on a stainless steel-made RF coupler used in a particle accelerator machine. The coupler after electroplated with a Cu film goes to a heat-treatment process for the brazing of components of the coupler. The brazing is performed at a temperature of ~800 °C in a high-temperature vacuum furnace. A residual resistivity ratio (RRR) of the Cu film decreases owing to the high-temperature heat-treatment process. We have been aiming to achieve a desired RRR value after the heat-treatment process. In this study, we have conducted an analysis of a Cu film, which was electrolytically deposited on a stainless-steel surface with an intermediate Cu strike layer, to find atomic diffusion from stainless steel to the Cu film due to heat-treatment. The impact of heat-treatment on the RRR value of the Cu film was evaluated.

INTRODUCTION

Copper (Cu) films are applied to the stainless steel (SUS) made RF couplers for the accelerator machines. An electroplating process is used to deposit the Cu film on the SUS316L surface [1,2]. The fabrication process for the STF-2 RF couplers after the Cu plating follows annealing at 800°C [2]. The annealing process reduces residual resistivity ratio (RRR) values of the Cu film [1,2]. The decrease in the RRR value was attributed to the diffusion of (nickel) Ni from the Ni strike layer, which was applied between the SUS substrate and Cu film to improve the adhesion of Cu film with the substrate, and elements of SUS into the Cu film in the annealing process. The Cu flash layer instead of Ni layer might improve the RRR value of the film as mentioned in ref. [1].

In this work, we show a study on RRR measurement and characterization of Cu films deposited with a Cu strike layer on a SUS316L substrate. The final aim of this work is to obtain a high RRR value of a Cu film after annealing at 800°C.

EXPERIMENTS

Cu Film Deposition

A Cu film was deposited on a SUS316L surface which was first coated with a thin Cu film called a Cu strike layer. The Cu film and the thin strike layer both were deposited by electroplating method. The electroplating of the Cu film was conducted in a $CuSO_4$ solution bath. Four Cu plated SUS samples (sample 8-1 to 8-4) and a bare SUS sample with size similar to the electroplated samples were prepared to evaluate RRR values of the Cu films. An additional sample (sample 9-2) was prepared for depth profile analysis to measure the concentrations of elements present in the film. Table 1 shows the names of prepared samples with the thicknesses of the Cu films. The thicknesses mentioned in Table 1 were calculated from the weight gain of the sample due the electroplating of the Cu films.

Table 1: Electroplated Sample Names and Thicknesses of the Deposited Cu Films

Sample	Thickness (μm)
8-1	13.3
8-2	12.1
8-3	9.5
8-4	7.5
9-2	13.3

Annealing of Samples

The electroplated and SUS samples were annealed in a vacuum furnace at 800°C for five minutes. The maximum pressure at 800°C was measured to be 2.2×10^{-3} Pa.

RRR Measurement

RRR measurements of the electroplated and SUS samples were conducted with the four-probe method in STF, KEK. The electroplated samples and SUS sample were prepared in a size of ~4.5×150 mm for the RRR measurements. The measurements were repeated for the samples after the annealing process was applied to the samples. The electrical resistances of the samples were measured at temperatures of 300 and 4 K. The RRR measurement system with the fixed samples is shown in ref. [3].

Film Characterization

The film was characterized with a scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDX), and glow discharge mass spectroscopy (GDMS).

RESULTS AND DISCUSSION

Adhesiveness of the Film to Substrate

The Cu strike layer had strong adhesion to the SUS substrate and was not peeled off in a testing conducted with an adhesive tape, ultrasonic rinsing, and scratching the film. The Cu film also had strong adhesion to the Cu strike layer and was not peeled off in the aforementioned tests. The impact of the annealing was also observed on the film adhesion. The cross-section of the film after annealing was observed with SEM and the film-substrate interface position

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*E-mail addresses: vchouhan@e-marui.jp & vchouhan@post.kek.jp was confirmed by EDX mapping. The image showed no exfoliation of the film from the surface. The results showed that strong adhesion between the Cu film and SUS surface was obtained without applying a Ni strike layer.

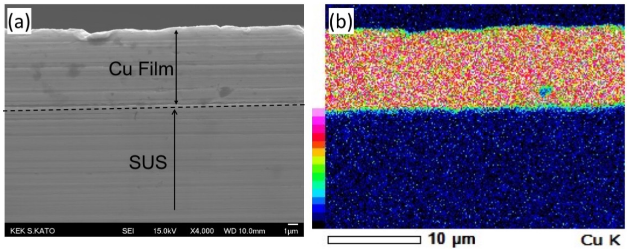

Figure 1: Cross-sectional view of a Cu film deposited on a SUS substrate with an intermediate Cu strike layer. (a) SEM image and (b) corresponding EDX map showing the Cu film and film-substrate interface.

RRR of Cu Films

The electrical resistances of the electroplated and SUS samples before and after annealing were measured in a temperature range between 4 and 300 K. Sample resistance versus sample temperature curves for the non-annealed and annealed samples are shown in Fig. 2. The resistances of the Cu films were estimated by eliminating the resistance of the SUS substrate from the sample resistances. The parallel resistance model was used for eliminating the resistance of the SUS substrate. The film resistance was estimated by the following relation:

$$R_f = \frac{R_t R_{SUS}}{R_{SUS}-R_t},$$

where R_f, R_{SUS}, and R_t are the resistances of Cu film, SUS substrate, and total resistance of the sample. Here, resistance of the substrates (R_{SUS}) was considered to be equal to the resistance of the SUS sample since the sizes of the substrates and SUS sample were almost same.

The RRR values of the films were calculated from the estimated film resistances at 300 and 4 K. The RRR values of the electroplated and SUS samples before and after annealing are shown in Fig. 2 (c). The RRR values were found to be the highest for the sample 8-1 in both annealed and non-annealed cases. The comparison of RRR values before and after annealing revealed that the RRR values significantly reduced for the annealed Cu films whereas no change in the RRR value of the substrate after annealing was noticed.

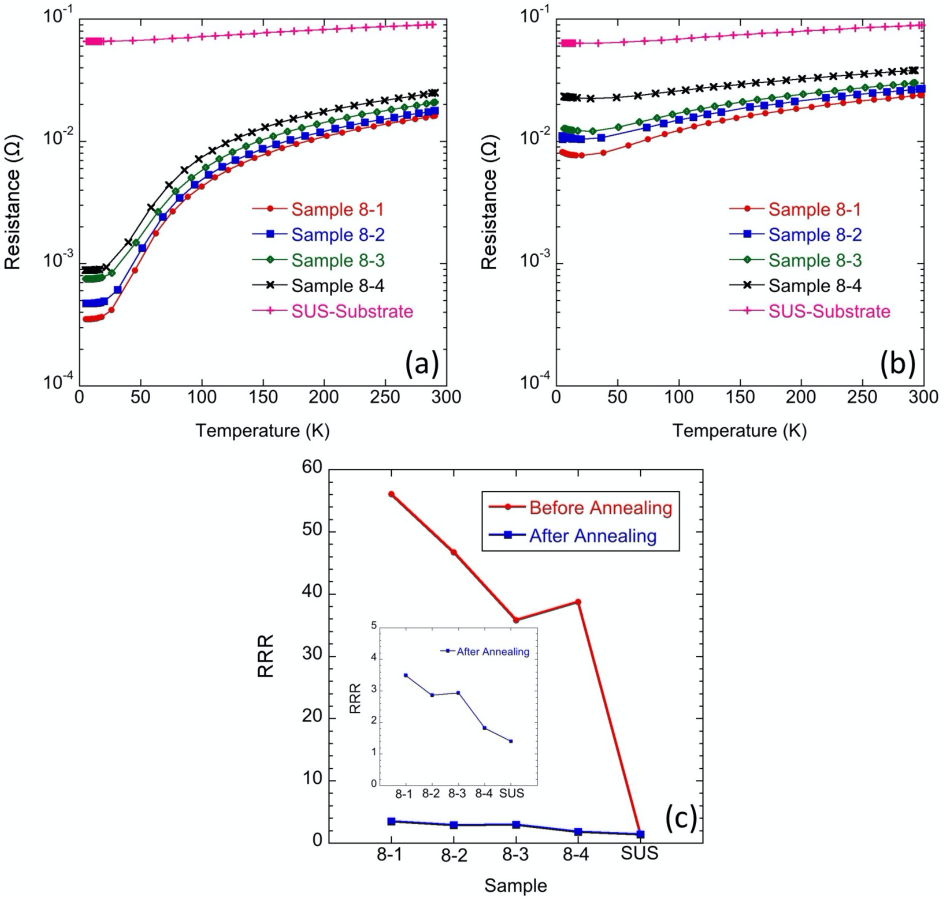

Figure 2: Resistances of the electroplated samples and SUS substrate sample as a function of sample temperature before (a) and after annealing (b) of the samples. (c) RRR values of the Cu films of all four samples and SUS sample. The inset in (c) shows zoomed-in vertical axis to show the RRR values of the annealed samples.

Surface Images and EDX Analysis

The surface of the deposited Cu film on the SUS substrate was observed before and after the annealing. The grains were not visible on the as-deposited surface. To estimate the grain size in the as-deposited Cu film, the Cu film surface was chemically etched. SEM images of the etched surface and an annealed surface are shown in Fig. 3. The images revealed that an average grain size in the annealed film was significantly larger than that in the as-deposited film.

The annealed surface was analyzed with EDX. The analyzed position and the EDX spectra are shown in Fig. 4. The EDX analysis showed that no serious contaminants were present on the surface. Further study will be conducted to compare the surfaces of all the four electroplated samples.

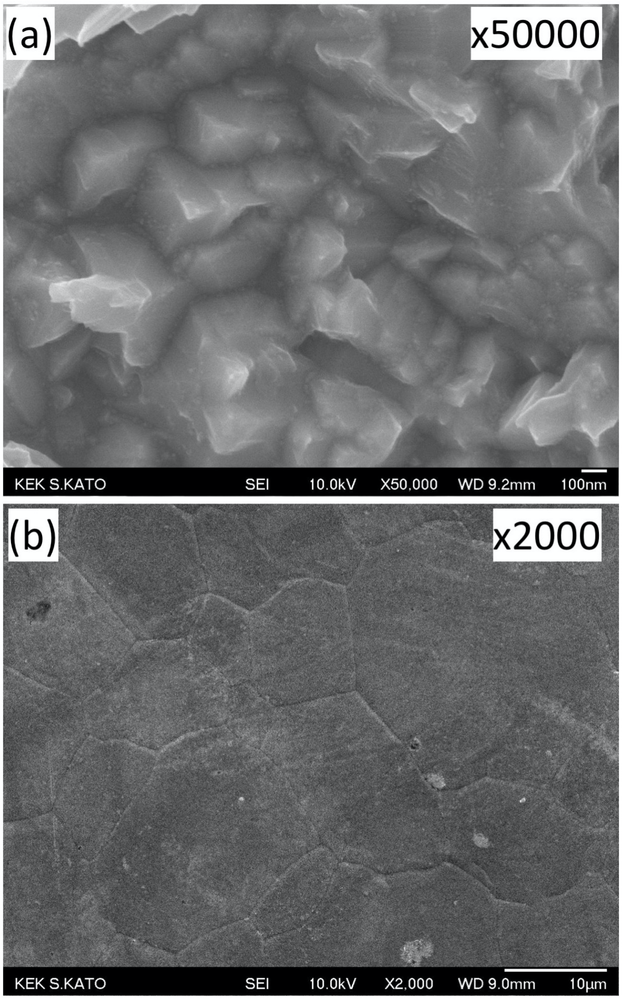

Figure 3: SEM images of (a) non-annealed surface after chemical etching and (b) annealed surface.

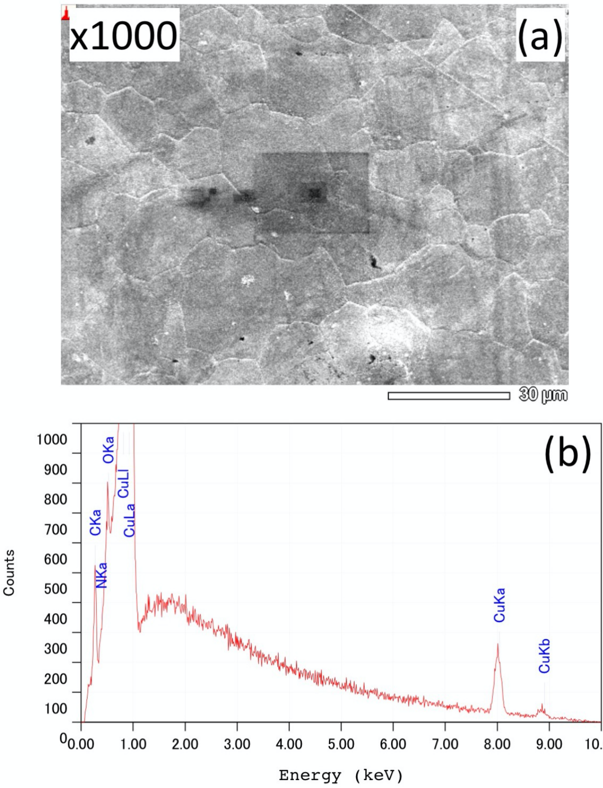

Figure 4: An annealed Cu film surface (a) and the corresponding EDX spectrum (b).

Depth Profile with GDMS

The sample 9-2 prepared with a Cu film thickness of ~13 µm in a size of 25 × 25 mm was annealed under the same conditions. The film after the annealing process was characterized with the GDMS to obtain a depth profile of diffused elements in the Cu film. The GDMS analysis was conducted in National Institute for Materials Science (NIMS) Japan. The depth profile of the film is shown in Fig. 5. The crater depth was measured with a mechanical profile and the same was ~57 µm. The depth profile showed that mainly iron (Fe), Ni, and Chromium (Cr) diffused from the SUS substrate to the Cu film where concentration of the diffused Fe was the highest. Fe concentration in the Cu film near the Cu-SUS interface was high and drastically reduced towards the film surface. The top surface up to a depth of ~6 µm contained Fe with less than 0.1 at%. Similar trends of atomic concentrations of Cr and Ni in the film were observed. Diffusion of other elements (aluminum and silicon) of the substrate in the film was not high and their atomic concentrations were found to be very low in the film. The atomic concentration ratios in the film for Al and Ni over Fe were 4 and 1.5 times higher than that in the SUS substrate. This showed that diffusion rates of Al and Ni in the Cu film were higher than that of Fe and Cr. Diffusion of Cu from the film to substrate was also observed and was higher compared to the diffusion of elements from the substrate to the film. Hydrogen concentration in the film was measured to be higher in the film near the top surface and a gradual decrease in the concentration towards the film-substrate interface was observed.

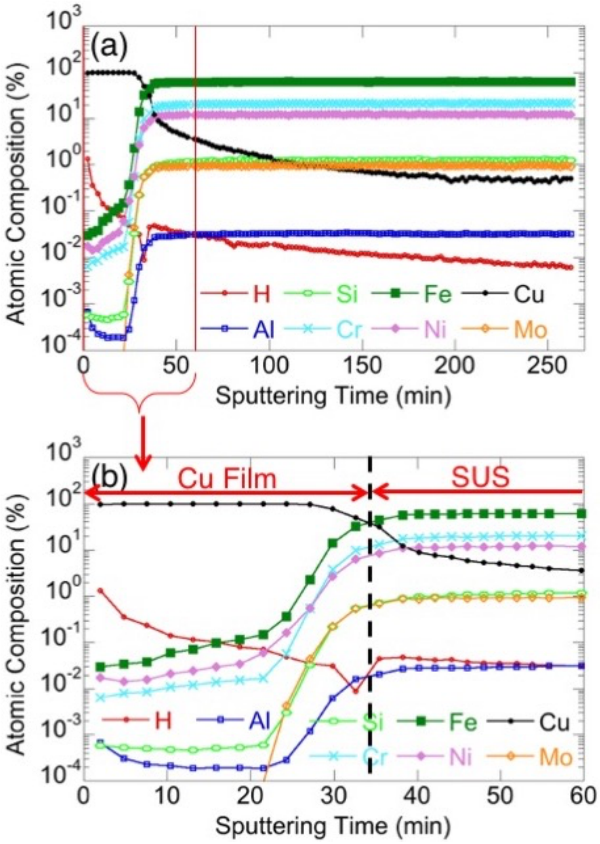

Figure 5: Depth profile of the Cu film deposited on the SUS substrate. The profile was measured with GDMS. (a) The profile up to a depth of ~57 μm and (b) the depth profile with zoom-in horizontal axis showing sputtering time.

DISCUSSION

The sample 8-1 showed higher RRR values compared to other samples. The higher RRR might be related to the thicker Cu film. The annealing at 800°C significantly degraded the RRR values of the films, although the average grain size was much larger compared to that in the as-deposited films. The larger grain size might reduce the electron scattering at the grain boundaries and an improved RRR is expected. The lower RRR values might be due to the diffused impurities from the furnace atmosphere and SUS substrate to the film. Depth profile showed SUS elements which were diffused from the substrate and H that might came from the furnace atmosphere. Although the film deposited in this study were without an intermediate Ni layer, the RRR value decreased. It appears that the diffused impurities even in the small concentration might degrade the RRR value. The sample 8-1 with thicker Cu film obvious contained less impurity concentration in the top several microns compared to the thinner film. The lower impurity concentration might keep the RRR value of the film higher than that for other samples having thinner Cu films. The impact of impurity concentration on RRR value might dominate over the impact of larger grain size. A previous study [1] showed that a lower annealing temperature of ~400°C was effective to obtain a higher RRR value and the impact of larger grain dominated over the impact of diffused impurities at this temperature.

CONCLUSION AND FUTURE WORK

Cu films with different thicknesses were deposited by electroplating process on SUS316L substrates. A Cu strike layer instead of a Ni layer was applied on the substrate before deposition of Cu film. The films were strongly adhered to the substrates and have not exfoliated after annealing process. The grain size became significantly larger after the annealing process. An RRR value was measured to be higher for a thicker Cu film. However, the annealing process degraded the RRR values of the films significantly. The depth profile measured with GDMS showed that impurities including Fe, Ni, Cr, Al, and Si diffused from the substrate to the film. H might diffuse from the furnace atmosphere to the film. It appears that the present impurities diffused from the substrate and furnace might be responsible for the lower RRR values of the Cu films.

Further study is required to confirm the effect of the impurity concentration on RRR value. Moreover, RRR values of Cu films with Ni and Cu strike layers are required to be compared to understand the impact of Cu strike layer. Cu strike layer with thicker Cu film will also be tested. A higher RRR value might be obtained for a thicker Cu film with a Cu strike layer.

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