Transactions of the Materials Research Society of Japan 32[3] 603-608 (2007)

Microwave Heating of Thin Cu Film

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Thin Cu films with different thickness and microstructure were prepared using evaporation with a quartz substrate, followed by microwave irradiation in air (frequency of microwave:2.45 GHz, incident flux of microwave:563 W, irradiation time: 600 s). Microwave heating of thin Cu film is quite anomalous. The abrupt temperature rise and drop occur at early stage of microwave irradiation, then continuous temperature rise appears. The temperature change is caused by various combinations of the change in the rate of temperature rise (ΔT) due to the ratio of a thickness to resistivity of thin Cu film, the increases in ΔT due to Cu-oxide and resistivity rise at elevated temperature, and the decreases in ΔT due to Cu particle growth during microwave irradiation and heat radiation from the surface of thin Cu film.

Keywords: microwave heating, thin Cu film, thickness, resistivity

1. INTRODUCTION

Metal bulk is excellent reflector of microwave energy and in general is not heated significantly by microwave. Recently, there has been much interest in microwave heating and sintering of metal powder [1-6]. Novel microwave measurement technique involving the transmission of a microwave signal through a resistive film has been demonstrated in order to measure the sheet resistance of thin metal films [7]. The authors have reported microwave application for heating of a thin Au film used in a surface plasmon resonance analysis [8]. However, there have been few reports regarding microwave heating of thin metal film, and also its mechanism has not been well understood.

A part of incident microwaves penetrates into the metal from the surface. Depth of penetration, that is, skin depth relates to a conductivity of the metal. The conductivity of thin film drops below that of the metal bulk because of surface scattering (Fuchs and Sondheimer theory (F-S theory)) [9,10]. Thin metal film prepared by PVD, such as sputtering and evaporation, consists of many microstructural defects such as lattice defects, lattice distortion, grain boundaries, micro-voids, impurities, and so on. The ratio of microstructural defects to the whole microstructure in thin metal film is considerably large compared to metal bulk and powder. Therefore, physical properties of thin metal film differ from those of metal bulk and powder. Mayadas and Shatzkes [11] reported that a major portion of the total resistivity in polycrystalline films comes from electron scattering at grain boundaries (M-S theory). Havemann and Davis [12] reported that the conductivity in thin Ni-Fe alloy film becomes considerably low as compared to the value obtained from the F-S theory. Furthermore, Steinhoegl *et al.* [13,14] have proposed a model that the F-S theory has been combined with the M-S theory. Thus, physical properties in thin metal film depends upon both the thickness and microstructure. Therefore, microwave characteristics of thin metal film may also differ from that of metal powder.

In the present study, microwave characteristics of thin Cu film used in a field of electronic devices were examined to clear the effects of thickness and microstructure on microwave heating of thin Cu film.

2. EXPERIMENTAL PROCEDURE

Thin Cu films with different thickness and microstructure were prepared using evaporation method (Hitachi Co. Ltd., HUS-5GB). A substrate was quartz and its shape was 10×13×1 mm. Evaporation pressure was 1.33×10^{-2} Pa. No heating of the substrate was performed. A thickness of thin Cu film was controlled by changing a distance from basket to substrate, h , and evaporating time, t_E . Figure 1 shows a schematic diagram of microwave irradiation test. A 2.45 GHz, 1.8 kW microwave generator was used as microwave source. Distribution of a microwave field was complex because of a multi-mode microwave cavity. A thin Cu film was placed at the height of 90 mm from the bottom because it received the maximum incident flux of microwave. Microwave irradiation was conducted at 1 kW for 600 s in air. A net incident flux of microwave to thin Cu film was 563 W.

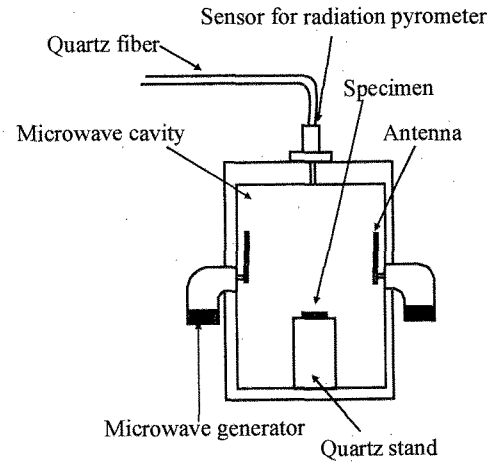

Fig.1 Schematic diagram of microwave irradiation test.

A temperature of thin Cu film was measured using a glass fiber type of radiation pyrometer (Chino Co. Ltd., IR-FL3). Microwave cavity was shielded to prevent the entrance of light. Surface morphology and thickness of thin Cu film were examined by an atomic force microscopy (AFM, Digital Instruments Co. Ltd., Nano Scope III). A resistivity of thin Cu film was measured using four-point probe technique at room temperature. Characterization of thin Cu film was conducted using X-ray photoelectron spectroscopy (XPS, Shimadzu Co. Ltd., ESCA-1000).

3. RESULTS

Figure 2 shows the temperature change of thin Cu film with a thickness of 47.2 nm (h:115 mm, t_E:120 s) during microwave irradiation. The radiation pyrometer used in the present study was unable to measure a temperature lower than 373 K because of a detection limit of the sensor. No temperature detection which appears in Fig.2 is due to this. As shown in Fig.2, the abrupt temperature rise and drop occurred at early stage, then no temperature detection appeared. Thus temperature change was quite anomalous.

Figure 3 shows AFM images of this thin Cu film. As shown in Fig.3(b), Cu particle growth was observed. This results from microwave heating of thin Cu film.

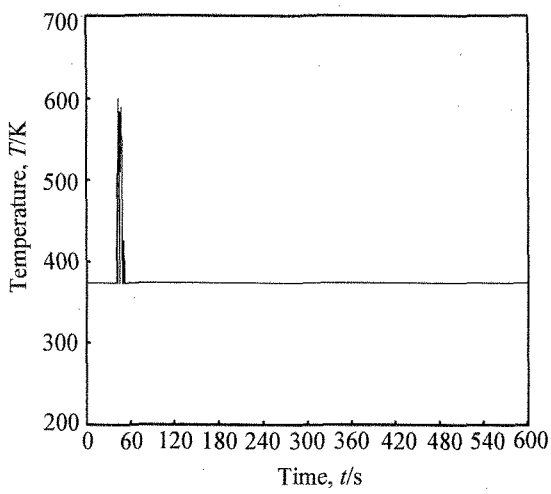

Fig.2 Temperature change of thin Cu film with a thickness of 47.2 nm (h: 115 mm, t_E:120 s) during microwave irradiation.

In thin Cu film with a thickness of 280 nm (h:115 mm, t_E: 600 s), no temperature detection was observed during microwave irradiation. Figure 4 shows AFM images of this thin Cu film. There was little morphological difference between (a) as-evaporated and (b) after microwave irradiation. This results from no microwave heating in this thin Cu film.

Figure 5 shows the relationship between Cu particle size, which is measured from AFM image, and a thickness of thin Cu film prepared by changing t_E under the same h (115 mm). Although the thickness of as-evaporated thin Cu film increased with increasing t_E, Cu particle size was nearly constant regardless of the thickness. As shown in Fig.5, thin Cu film was difficult to heat using microwave irradiation when the thickness exceeded about 200 nm.

Thin Cu films were prepared by changing h under the same t_E (120 s). Figure 6 shows the temperature change of thin Cu film with a thickness of 96.8 nm (h:100 mm, t_E:120 s) temperature rise appeared. The rate of its continuous rise

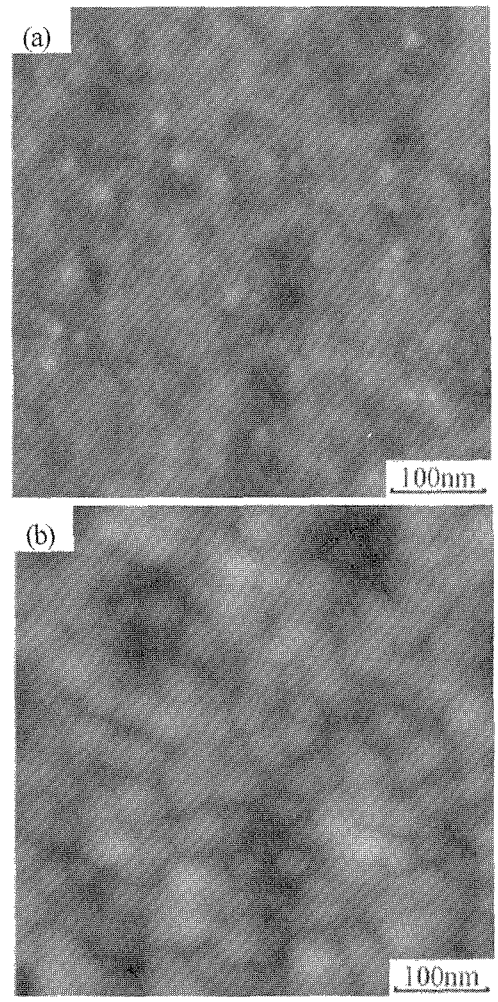

Fig. 3 AFM images of thin Cu film with a thickness of 47.2 nm (h:115 mm, t_E:120 s). (a) as-evaporated, and (b) after microwave irradiation.

decreased with increasing microwave irradiation time. At late stage of microwave irradiation, the temperature remained almost unchanged (525 K).

Figure 7 shows AFM images of this thin Cu film. As shown in Fig7(a), Cu particle size of as-evaporated thin Cu film was larger than that of Fig.4(a). As shown in Fig.7(b), a significant growth of Cu particles due to microwave heating was observed.

In thin Cu film prepared by evaporating at h of 80 mm, no temperature detection was observed during microwave irradiation. The thickness of as-evaporated thin Cu film increased with decreasing h. Figure 8 shows the relationship between Cu particle size and thickness of thin Cu film. Cu particle size of as-evaporated thin Cu film increased with increasing thickness. This is because Cu particles are deposited at high temperature as h is short. The change in Cu particle size after microwave irradiation was anomalous. As shown in Fig.8, thin Cu film with a large thickness was difficult to heat using microwave irradiation.

Figure 9 shows XPS spectra (depth analyses) of as-evaporated thin Cu film with a thickness of 47.2 nm (h:115 mm, t_E:120 s). In Cu2p spectra a set of clear peaks of metallic

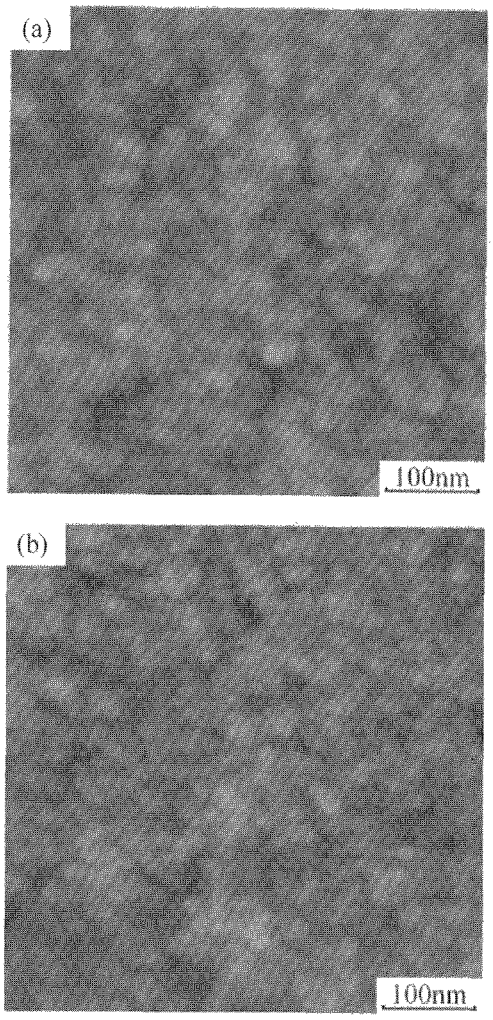

Fig. 4 AFM images of thin Cu film with a thickness of 280 nm (*h*:115 mm, t_E:600 s). (a) as-evaporated, and (b) after microwave irradiation.

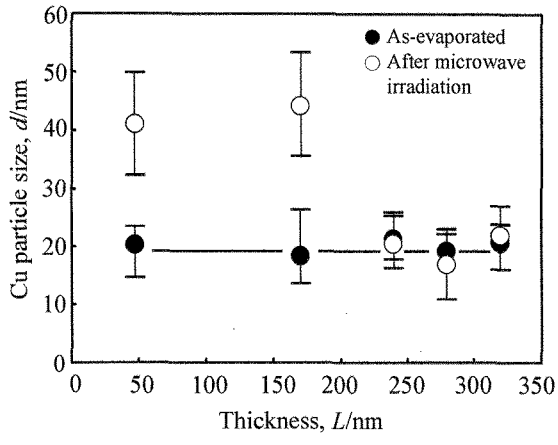

Fig. 5 Relationship between Cu particle size and a thickness of thin Cu film prepared by changing t_E under the same *h* (115 mm).

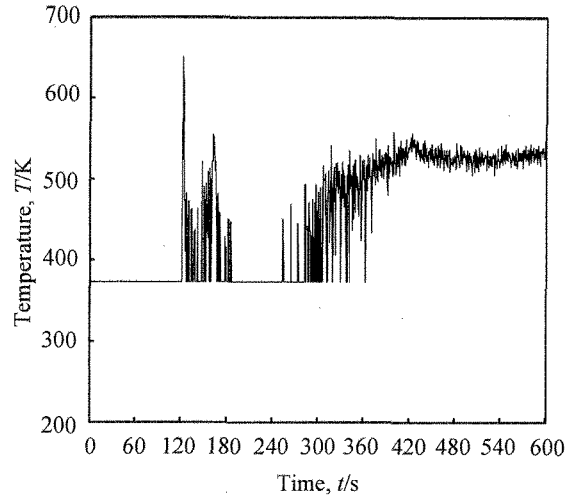

Fig. 6 Temperature change of thin Cu film with a thickness of 96.8 nm (*h*:100 mm, t_E:120 s) during microwave irradiation.

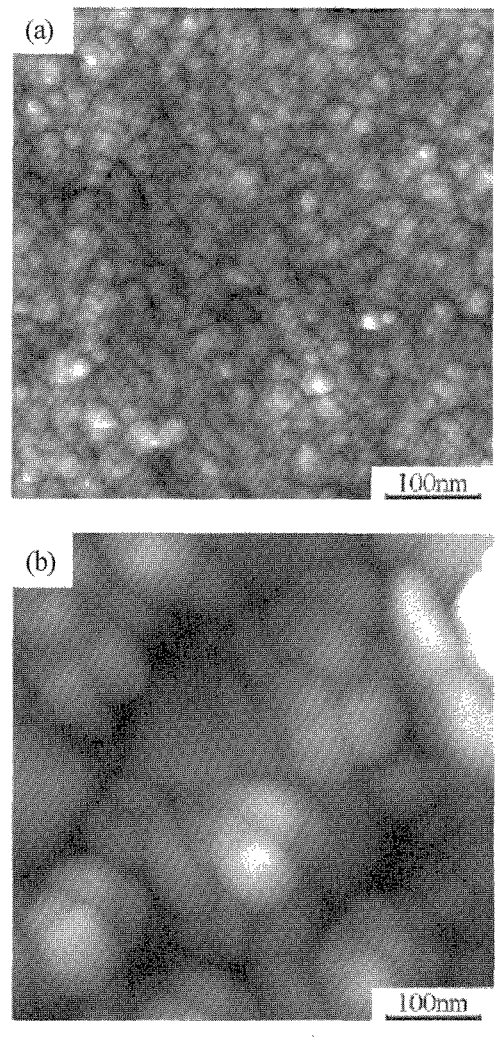

Fig. 7 AFM images of thin Cu film with a thickness of 96.8 nm (*h*:100 mm, t_E:120 s). (a) as-evaporated, and (b) after microwave irradiation.

Cu ($2p_{3/2}$=932.4 eV, $2p_{1/2}$=952.2 eV) appeared, but a peak of Cu-oxide ($2p_{3/2}$=933.6 eV) was not clear. On the other hand, a clear peak of Cu-oxide appeared in O1s spectra of the surface (sputtering time of 0 s in Fig.9). A peak intensity of Cu-oxide decreased with a depth from the surface.

Figure 10 shows XPS spectra of as-evaporated thin Cu film with a thickness of 96.8 nm (h:100 mm, t_E:120 s). The amount of Cu-oxide was larger than that in Fig.9. Thus the amount of Cu-oxide increased with decreasing h. This is because Cu particles are deposited at high temperature as h is short, resulting in promotion of Cu oxidation.

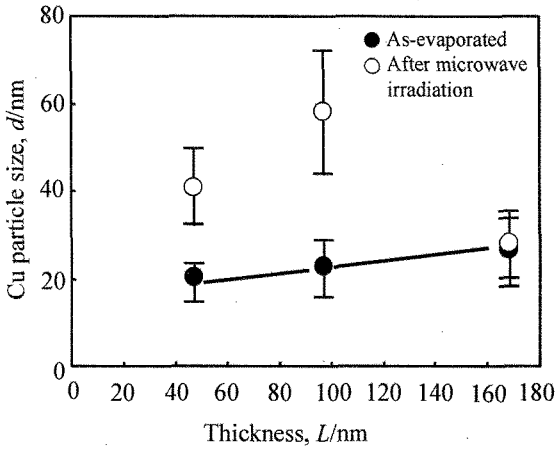

Fig.8 Relationship between Cu particle size and thickness of thin Cu film prepared by changing h under the same t_E(120 s).

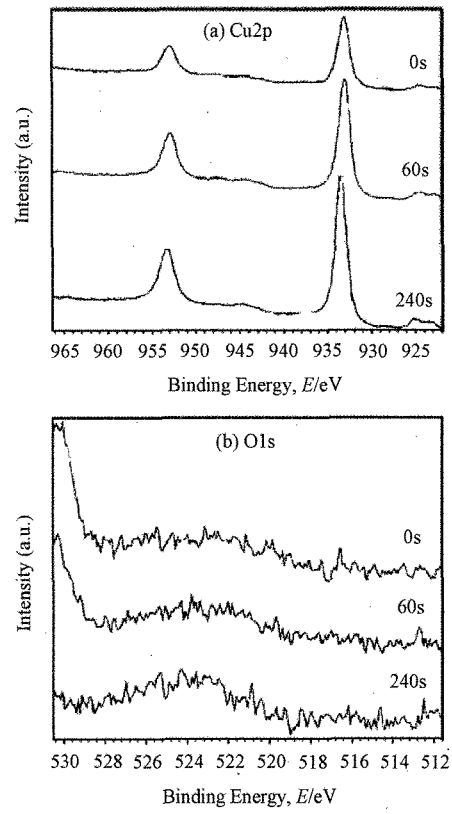

Fig. 10 XPS spectra of as-evaporated thin Cu film with a thickness of 96.8 nm (h:100 mm, t_E:120 s).

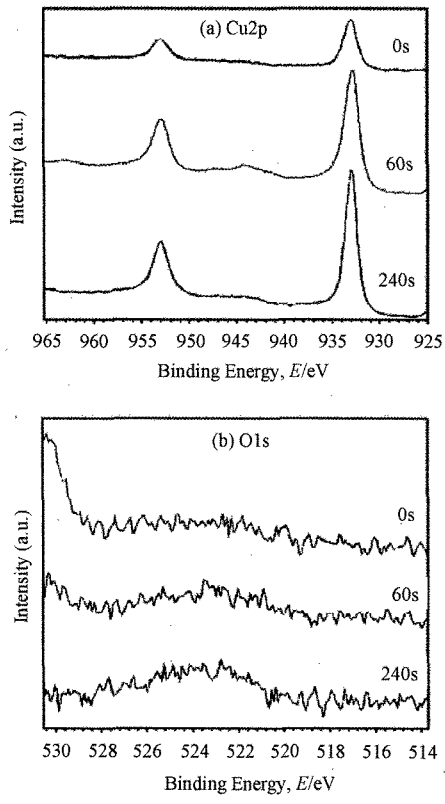

Fig. 9 XPS spectra of as-evaporated thin Cu film with a thickness of 47.2 nm (h:115 mm, t_E:120 s).

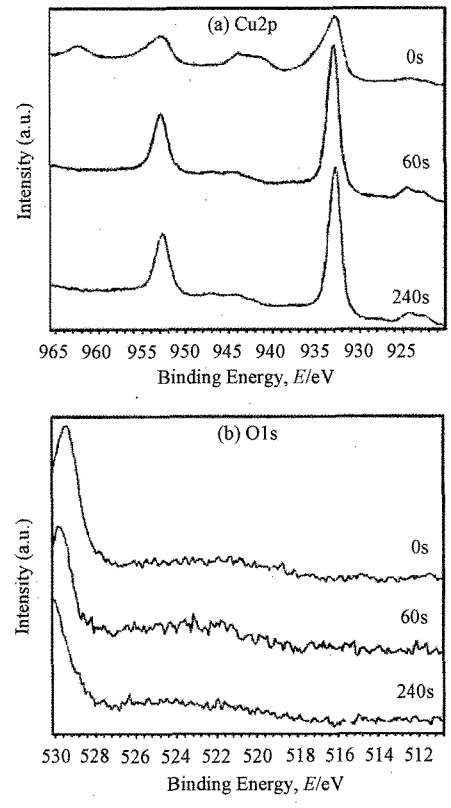

Fig. 11 XPS spectra of microwave irradiated thin Cu film with a thickness of 96.8 nm (h:100 mm, t_E:120 s).

Figure 11 shows XPS spectra of this thin Cu film after microwave irradiation. In Cu2p spectra, peak-broadening due to a presence of Cu-oxide was observed. A clear peak of Cu-oxide was confirmed in O1s spectra of the interior of thin Cu film, too. These results suggest that a large amount of Cu-oxide was formed by heating in air.

4. DISCUSSION

Although metal bulk reflects most of incident maicrowaves, a part of incident microwaves penetrates into the interior from the surface. Depth of penetration, that is, skin depth (defined as the distance from the surface into the material at which the power drops to e^{-1} of the original value) is given by [15]

$$\delta = (2/\omega\alpha_0\sigma)^{1/2} \tag{1}$$

where δ is the skin depth, ω angular frequency ($\omega=2\pi f$, where f is frequency of microwave), μ_0 free space permeability, and σ conductivity. Substituting the value of σ for Cu in bulk (σ =59.5×10^6 Ω^{-1}/m) [16] into eq.(1), we obtain δ=1.32 μm. This value is larger than the thickness of thin Cu film used in the present study. This suggests that most of incident microwaves permeate through the thin Cu film.

Bosman *et a.l* [15] have studied microwave absorption of contaminant (supposing as thin film disk) on a microwave window. According to the results, the temperature rise of the contaminant was expressed as:

$$\lambda = 2\pi c/\omega \tag{2}$$

$$\delta/\lambda = s/2\pi\delta \tag{3}$$

$$L/s = L\lambda/2\pi\delta^2 \tag{4}$$

$$\Delta T = 100\,\mathrm{K}\cdot\frac{a}{1\,\mathrm{mm}}\cdot\frac{L/s}{(1+L/s)^2}\cdot\frac{A}{10^8\,\mathrm{W/m^2}}\cdot\frac{1}{\kappa/(10^3\,\mathrm{Wm^{-1}K^{-1}})} \tag{5}$$

where ΔT is the rate of temperature rise, λ free space wave length, c the speed of light in vacuum, a the radius of thin film disk, L the thickness of thin film disk, A the average incident flux of microwave, and κ the thermal conductivity of thin film disk. Replacing thin Cu film square (10×13 mm) used in the present study by a disk with equivalent area, we obtain a = 6.43 mm. Dividing incident flux of microwave (563 W) by the area of thin Cu film, we obtain A =4.33×10^6 W/m^2.

When a, A and κ are constants in eq.(5), ΔT depends on L/s. Substituting eqs.(1) and (2) and ρ=1/σ into eq.(4),

$$L/s = 60\pi L/\rho \tag{6}$$

As a result, ΔT depends on L/ρ as the following equation:

$$\Delta T = 100\mathrm{K}\cdot\frac{a}{1\mathrm{mm}}\cdot\frac{60\pi L/\rho}{(1+60\pi L/\rho)^2}\cdot\frac{A}{10^8\,\mathrm{W/m^2}}\cdot\frac{1}{\kappa/(10^3\,\mathrm{Wm^{-1}K^{-1}})} \tag{7}$$

From a combination of the F-S and M-S theories, the resistivity of thin Cu film is given by the following equation [13]:

$$\rho = \rho_0\left\{\frac{1}{3}\Big/\left[\frac{1}{3}-\frac{\alpha}{2}+\alpha^2-\alpha^3\ln\left(1+\frac{1}{\alpha}\right)\right]+C_0(1-P)\frac{U}{S}l_0\right\} \tag{8}$$

$$\alpha = \frac{l_0}{d}\frac{R}{1-R} \tag{9}$$

where ρ is the resistivity of the thin Cu film, ρ_0 the resistivity of Cu in bulk, l_0 the mean free path within a grain, d the average distance of the grain boundaries, R the reflectivity coefficient at grain boundary, P the specularity parameter, C_0 a constant (C_0 =1.2), U the perimeter and S the area of the cross-section of the thin Cu film. The first term on right side of eq.(8) shows the contribution of grain boundary scattering, and the second term shows the contribution of surface scattering.

The values of R=0.50 for Cu [13] have been reported. Figure 12 shows a comparison of measured resistivity, ρ_m, which is obtained using four-point probe technique, with calculated resistivity, ρ_c, which is obtained by substituting the value of R, l_0=40 nm [13], P=0.5 (with respect to epitaxial single crystal)[17], ρ_0=0.0167 μ Ωm [16], and the value of d (Cu particle size shown in AFM image) into eqs.(8) and (9). In the case of R =0.45, good agreement with experimental data was achieved.

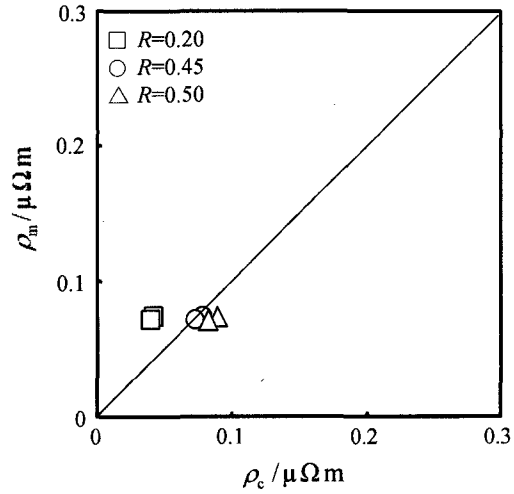

Fig.12 Comparison of measured resistivity, ρ_m, with calculated resistivity, ρ_c.

Figure 13 shows a relationship between ρ and thickness of thin Cu film for R=0.45. As shown in Fig.13, ρ increases with decreasing thickness of thin Cu film (the contribution of surface scattering). Also ρ increases with decreasing d (the contribution of grain boundary scattering).

Figure 14 shows a relationship between ΔT obtained by substituting R=0.45, P=0.5, l_0=40 nm and κ=393 J/(mK) [16] into eqs.(7), (8) and (9) and L/ρ in thin Cu film. As shown in Fig. 14, ΔT depends on L/ρ. When only the thickness of thin Cu film is increased under the same particle size, L/ρ increases considerably with not only an increase in L but also a decrease in ρ due to surface scattering, resulting in a decrease in ΔT. On the other hand, when only a particle size is increased under the same film thickness, L/ρ increases with a decrease in ρ due to grain boundary scattering, resulting in a decrease in ΔT.

However, mentioned above, temperature change of thin Cu film was anomalous. As-evaporated thin Cu film contains Cu-oxide (Figs.9 and 10). Since Cu-oxide has a large dielectric loss, it contributes to an increase in ΔT. It is well known that ρ for metal rises at elevated temperature [16]. This phenomenon contributes to an increase in ΔT (Fig.14) .

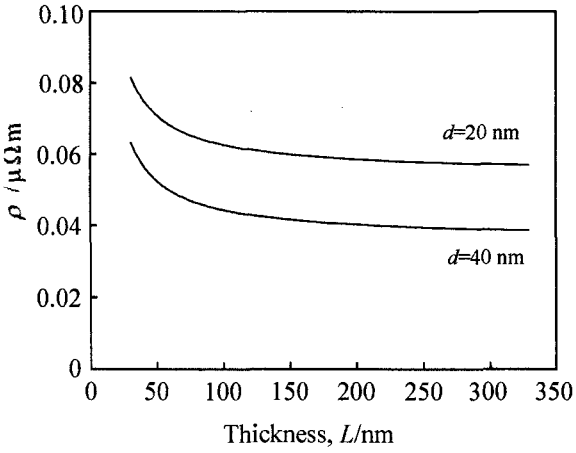

Fig. 13 Relationship between ρ and thickness of thin Cu film for R=0.45.

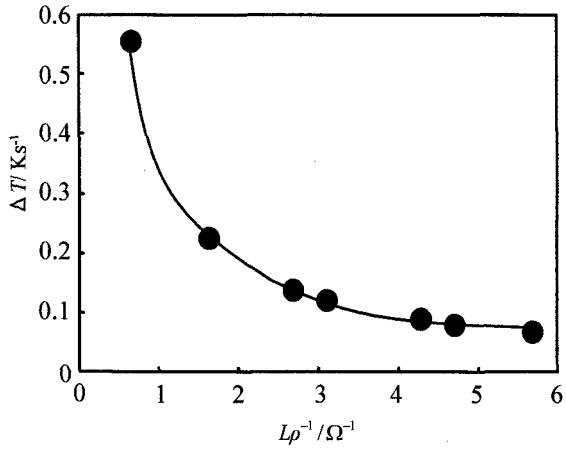

Fig.14 Relationship between ΔT and L/ρ in thin Cu film.

On the other hand, Cu particle growth due to microwave heating causes a decrease in ΔT (Figs.13 and 14). As a result, temperature change is attributed to various combinations of the increase or decrease in ΔT due to L/ρ, the increases in ΔT due to Cu-oxide and temperature dependence of ρ, and the decreases in ΔT due to Cu particle growth during microwave heating and heat radiation from the surface of thin Cu film. The abrupt temperature rise which is observed at early stage of microwave irradiation in thin Cu film with a relatively small thickness is caused by low L/ρ and Cu-oxide. Subsequent temperature drop is attributed to Cu particle growth due to microwave heating. In the case of thin Cu film with a small amount of Cu-oxide, thereafter no temperature detection appears (Fig.2). This is because resultant ΔT is very low. When the amount of Cu-oxide is large, the temperature drops down slowly as shown in Fig.6. This is caused by a large contribution of Cu-oxide heating. Then, by the increases in ΔT due to Cu-oxide and temperature dependence of ρ, the temperature rises again. At late stage of microwave irradiation, the temperature remains unchanged. This is because heat balance between microwave heating and heat radiation from the surface of thin Cu film is achieved. In the case of thin Cu film with a large thickness, no temperature detection appeared as shown in Figs.(5) and (8). This arises from very large L/ρ.

5. CONCLUSIONS

Thin Cu films with different thickness and Cu particle size were prepared using evaporation with a quartz substrate, followed by microwave irradiation in air (frequency of microwave:2.45 GHz, incident flux of microwave:563 W, irradiation time: 600 s). The following conclusions were obtained:

(1) Microwave heating of thin Cu film is quite anomalous. The abrupt temperature rise and drop occur at early stage of microwave irradiation, then continuous temperature rise appears.

(2) Temperature change is caused by various combinations of the change in the rate of temperature rise (ΔT) due to the ratio of a thickness to resistivity of thin Cu film, the increases in ΔT due to Cu-oxide and resistivity rise at elevated temperature and the decreases in ΔT due to Cu particle growth during microwave irradiation and heat radiation from the surface of thin Cu film.

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(Received January 15, 2007;Accepted February 23, 2007)