LOW RESISTIVE COPPER THIN FILM DEPOSITED WITH ULTRA-HIGH PURITY TARGET AND ECR-ION BEAM SPUTTERING

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Abstract: A thin film process using ECR-ion beam sputtering with ultra pure (99.999999%) copper target was investigated for improving transportation properties in the film. The electric resistivity of the thin film was 40% lower than that of using a commercial-grade purity target. And the optical qualities evaluated by the transmission and reflection spectrum measurements were also indicate slower relaxation characteristics of the free carriers. These results evidenced the efficacy of the target purity for defects/impurity less copper thin film.

Key words: copper, thin film, resistivity, ultra high purity, wiring, electrode.

1. INTRODUCTION

Wires in electric circuits (IC) or micro electro-mechanical system (MEMS) takes charge of important roles as channels of energy and information transmitting to organize functions of sub-systems in the device, which are corresponded with a peripheral vascular system or nervous system in animals. To transmit energy or signal smoothly, the electric resistivity of wires should be as small as possible, while the width should be small for compactness and agility of the device.

The wire structures of copper are often used as wiring in IC or MEMS because of its large conductivity. The origin of the electric resistivity is scattering of free carrier drift by phonons and atomic defects, i.e. impurities, grain boundaries in wires and roughness of the surfaces. The quantity of such atomic defects is depended on process conditions of wires. The wires in IC or MEMS are constructed by a thin film process and pattern transcription process, such as lithography with etching, lift-off or damascene process. Whichever the processes are selected, smaller density of the stoppage of electric flow in the fundamental metal film is preferable for small-loss wiring.

In this paper, a thin copper film process using electron cyclotron resonance (ECR) type ion beam sputtering method with ultra high purity target is examined aiming to explore the metallic film process for small loss wiring in energy harvesting MEMS devices. Reducing infusion of the impurities in the metal thin film by using pure material and high vacuum process makes decrease the density of the grain boundary in the film due to holding the nucleation and advancement of the growth of the grains, in addition to decreasing the scattering by impurities themselves. The volume resistivity of the film at direct current (DC), and the optical transmission and reflection of the films were measured. Then the relaxation properties of free carrier drift by DC and optical electric field were evaluated as the relaxation time, as a figure of merit according to the density of the scattering sources. The new process using the ultra pure copper target gave the film with slower relaxation than that produced from a commercial grade purity target. The remedying of the electric quality of the film by using ultra pure material target was obvious even low heat treatment condition as the substrate temperature of 160 °C.

2. EXPERIMENTS AND THEORIES

2.1 Thin film preparations

The copper films were deposited on bare surfaces of optical polishing fused quartz substrates, in order to measuring film's resistivity and optical properties of the films as they are. In this case, the temperature of the substrate must be lower than 160 °C for avoiding thermal dispersion of copper atoms in the substrate. While, the low temperature process also permits the wiring in polymer or organic electric devices.

The copper target was 5mm-thicknes, 3inch-diameter and 99.999999% (8N) pure copper ingot provided by Nippon mining and metal co. ltd.. The setup of the ion beam sputtering (Elionix inc., EIS-220) was shown in Fig.1. The chamber was vacuumed till the pressure of $<1\text{x}10^{-4}$Pa before the deposition. The argon ion beam was emitted from ECR type ion-gun to the target with the fixed condition as: 2.45GHz and 100W microwave and 875Gs-magnetic flux density for large density plasma excitation, 2.4kV accelerating voltage, and 0.55sccm infusion of 99.9999%(6N) pure argon gas. Then, the pressure in the chamber was $3\text{x}10^{-3}$Pa, and the ion beam with the diameter at the target about 1-inch and the ion current of 10.5mA was emitted to the target with the incident angle of 60°. The sputtered copper atoms were deposited on the substrate that was faced parallel to the

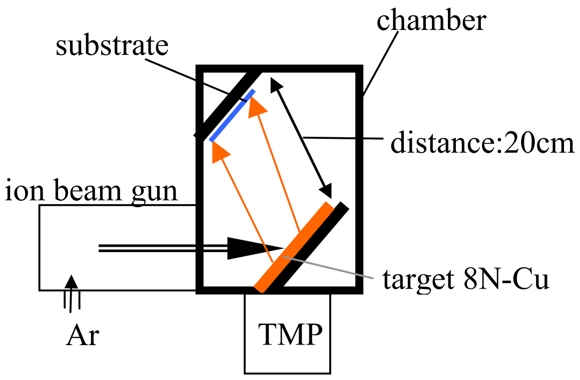

Fig.1 scheme of the copper thin film processing.

target surface, with the distance of 20cm. Temperature of the substrate was controlled by a heater in the substrate holder with a thermometer. In the conditions, the growth rate of the film thickness was 5.8 nm/min.

The copper thin film with the purity of 99.99% (4N) was also prepared to make sure of the effect of target purity by comparisons of the evaluation results.

2.2 Resistivity measurements

The sheet resistivity of film ρ_{sheet} was measured with 4-point probe method (MCP-T360, Dia Instruments Co. Ltd.) at the room temperature. The pins of the probe (MCP-TP06, Dia Instruments Co. Ltd.) were lined straightly with the distance of 1.5mm, and the current of the measurement was 10mA.

The volume resistivity ρ_{volume} was obtained from ρ_{sheet} and the film thickness d as

$$\rho_{volume} = \rho_{sheet} \times d\ , \qquad (1)$$

and d was measured with a contact probe surface profiler (KLA Tencor, alpha-step). The relaxation time at DC measurement τ_{DC} was defined as

$$\tau_{DC} = m\ /\ N\ e^2 \rho \approx 1/\omega_p^{\,2} \varepsilon_0 \rho\ , \qquad (2)$$

here m was the mass of an electron, N was the density of free electron in copper at room temperature, and e was the elementally electric charge. In this definition, the effective mass of free electron in the copper film is obscure, therefore in order to estimate absolute values of τ_{DC}, substitution of a presuming value as the rest mass of electron, or the mass in optical range (1.45~1.49 times the rest mass) should be considered [2].

2.3 Optical transmission and reflection spectrums measurements for the relaxation time evaluations

Opt-electrical properties of the copper thin films using the new process were investigated to make sure the relaxation properties of the free carrier drift in the film. The free electron in copper is strongly interacted with the incident light on the film, and the drift of the free electron is induced by the electromagnetic field of light evanesced within the skin depth.

Fiber optic cable spectrometer set was used for the measurement as shown in Fig.2. The white light (halogen lamp DH2000, Ocean Optics inc.) emitted on the sample film through the fiber, and reflected /transmitted light was collected by the fiber connecting to the spectrometer (HR2000, Ocean Optics inc.). Reflection spectrum was measured with 3-port contact multi fiber probe with the distance between the sample surface and fiber end of 1mm, and the specular reflectance standard (STAN-SSH, Ocean Optics inc.) was used for obtaining the reference signal. The transmission spectrum was measured with confront configured fibers, and the sample film was inserted between the fibers.

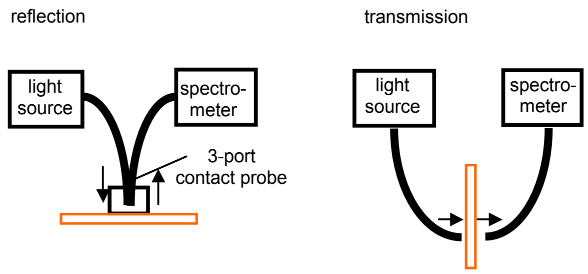

Fig.2 Measurement setup of optical properties.

The interaction between light and free electron is expressed as the dispersion formulas from the Drude model as

$$\varepsilon_f = 1 - \omega_p^{\,2}/(\omega^2 - i\omega/\tau)\ , \qquad (3)$$

where ω_p is plasma edge i.e. plasma resonance frequency of free electron which is determined with the density of free electron and the effective mass as eq.(2), but that can be obtained directly by spectrum measurements, and τ is the relaxation time in optical range. In the copper film, bound electrons on d-orbit affect the dispersion, and that is represented as ε_b, as

$$\varepsilon_{total} = \varepsilon_f + \varepsilon_b\ , \qquad (4)$$

and ε_{total} is the optical constant of bulk copper. Then plasma edge is shifted by the shield effect as

$$\omega_p' = (\omega_p^{\,2}/\varepsilon_b - 1/\tau^2)^{1/2}\ , \qquad (5)$$

thus $\lambda_p = 2\pi c/\omega_p'$ on copper is shifted from 115nm to 600nm. On the thin films, relaxation of carrier drift is promoted by the skin effect [1], and that is formed as,

$$1/\tau' = 1/\tau + 3/8 \times v_F/c \times \omega_p \times (1-p) \times f(k_p d)$$
$$f(k_p d) = (1+\cosh^2 k_p d)/(\cosh k_p d \times \sinh k_p d + k_p d) \quad (6)$$

where v_F is the Fermi velocity of the electron (1.5×10^6m/sec), c is velocity of light (3×10^8m/sec), p is the reflection coefficient of the electron on the surfaces (0 in our case), and d is the thickness of the film, respectively. As d is smaller, the effective relaxation time is shorter due to increasing the surface/volume ratio (size effect) as shown in Fig.3.

The optical transmission and reflection of the film are calculated using the dispersion of the dielectric constant represented by eq.(4), and the dispersion is modeled by the parameters of the electron as eq.(3)~(6). Sharp variations of the transmission and reflection are found at ω_p', so the difference of the carrier drift can be shown in the optical measurement around ω_p'. ε_b is indeed complex function in the case of copper, but in the analysis of the optical measurement, we treated ε_b as a constant (21.5) to simplify analysis model, as states of bound electron is not depended on film thickness or density of defects. The optical transfer matrix method was used for calculating the optical transmission and reflection on the thin film.

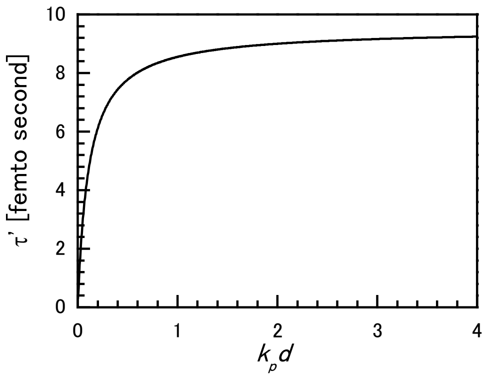

Fig.3 Size effect on the relaxation time τ'.

3. RESULTS AND DISCUSSIONS

3.1 Resistivity evaluations

Fig. 4 shows measurement results of the volume resistivity on the films with different thickness. The resistivity of the thin films was affected by scattering of carrier flow on atomic-order surface roughness, so the resistivity became larger as the film became thinner. The open triangular points were the films deposited with 8N target at room temperature. And the open circular points were the cases of 4N target, which was shown as the reference. The difference between them was vague, but the resistivity of 8N-film was smaller than that of 4N-film for range thinner than 100nm. Heat treatment assisted reducing grain boundaries according to the grain growth. The close triangular points and circular points were shown the films deposited with the substrate temperature of 160°C. The distinct improvements of decreasing resistivity were found especially for thinner range. 40~100% decreases of the resistivity were found for the range thinner than 100nm. The solid curve was the theoretical estimation of the resistivity using the Fuchs-Sondheimer model [3]. The resistivity of 8N-film was close to the theoretical limit, assumedly due to low impurities. These results indicate that the resistivity of the film was certainly decreased by using ultra-high purity target with the heat treatment at 160°C, which was inferentially due to less impurities and grain boundaries in the film.

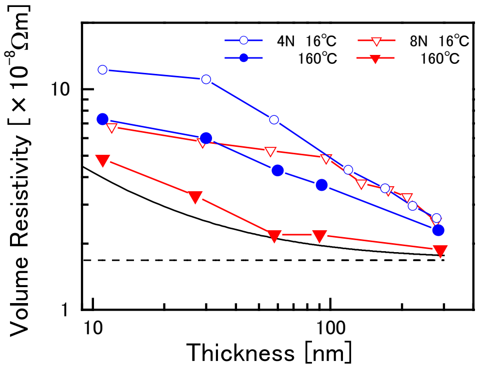

Fig.4 the volume resistivity on the films with different thickness.

3.2 Optical properties and the relaxation time evaluations.

Firstly, we describe the calculations of the optical transmission and reflection spectrum with varying τ'. Fig.5 (a)(b) show the results of the calculations on the thickness of 11nm and 29nm, and τ' varying for 0.5~2.5fs that is corresponded with the value of $k_p d$ <1 in Fig.3. Transmitting peaks and reflection edges were shown at the plasma edge of the wavelength of 600nm. The transmission peak became sharper and shifted slightly to longer wavelength side, and the reflection under the plasma edge wavelength (λ>600nm) became higher as τ' became longer. Fig.6 (a)(b) show the experimental results on 2 kinds of the thickness d of 10~12nm and 27~30nm, and 3 kinds of the process conditions as 8N target and 160°C, 8N target and room temperature, and 4N and room temperature. Each curve had a different shape each other though it was hard to distinguish by gazing. And the shapes of the spectrums by the calculation weren't fit on the experimental ones, thus estimation of absolute value on the relaxation of carrier drift was difficult by the fitting. However, they were helpful for understanding the essential features. The sharpest transmitting peak and highest reflection was found on the curve of 8N target and 160°C, which meant the film by the process had the longest relaxation time correlating to the low resistivity as eq.(2) and discussion in section 3-1.

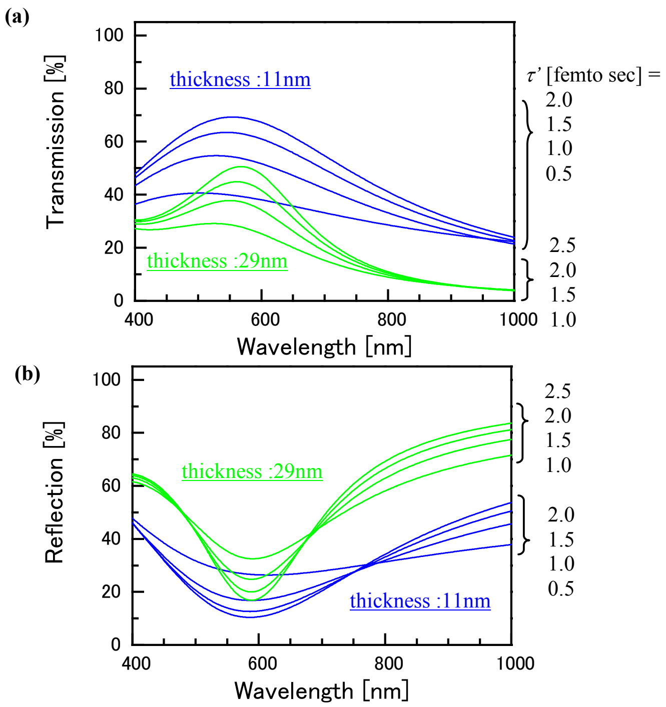

Fig.5 Calculated transmission and reflection spectrum on copper films.

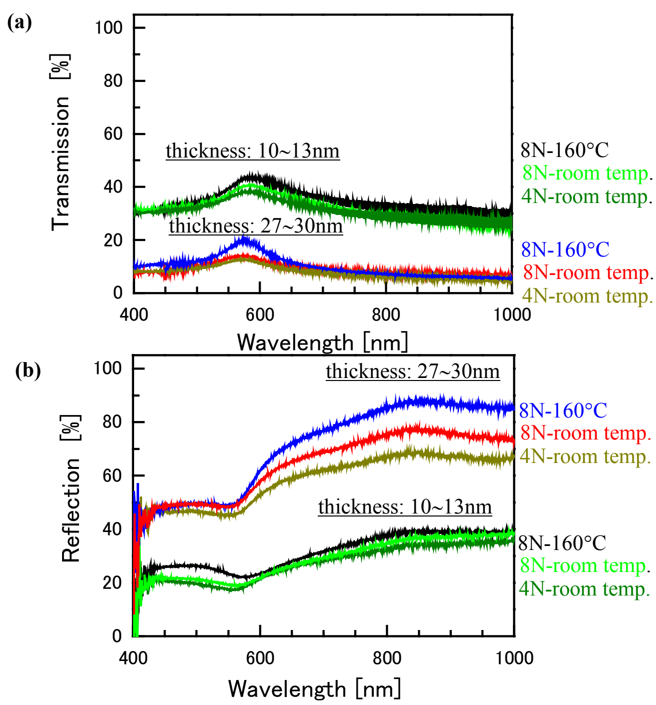

Fig.6 Measured transmission and reflection spectrum on the copper films.

The thicker curves in Fig.7 shows the reflection spectrum on the thickness of 285nm with process conditions of 8N target and 160°C and 4N target and room temperature, respectively. The thickness was much thicker than the skin depth in this range thus the size dependency was disappeared. The difference of the reflection was found near the plasma edge wavelength. The thinner curves were the calculated ones with τ' varying for 5~10fs. The edge of the reflection became steeper with τ' became longer. If τ' was estimated with the fitting of the curve at the edge, 9.5fs on 8N-160°C-film and 6.5fs on 4N-film, respectively. The estimated τ' on 8N-160°C-film was 40% longer duration of drifting relaxation than that of 4N-film or the previous reports [2].

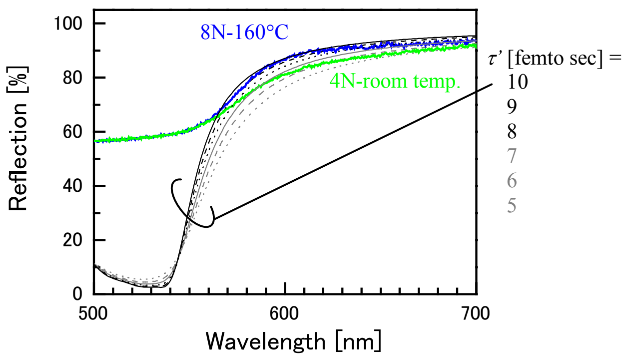

Fig.7 Reflection spectrum on copper surfaces.

4. CONCLUSION

Copper thin films were fabricated using ultra pure target under high vacuum and low temperature condition by ECR-ion beam sputtering method. Lower electric resistivity was found on the film according to longer duration of electric carrier drifting. We have never confirmed directly the difference of the density of atomic obstructions in carrier flow, i.e. the impurities and the grain size in the films by different purity target, however our investigations signify the efficacy of the thin film process for defects/impurity less copper thin film.

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