Transactions of the Materials Research Society of Japan 28 [4] 1303-1306 (2003)

Ellipsometry Analysis of Metal Nanoparticle Composites Fabricated by Negative Ion Implantation

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Negative ion implantation has enabled us to form self-assembled metal nanoparticles in insulating substrates. Nanoparticle morphology is greatly dependent on the implantation conditions. Ellipsometry is applied to analyze spatial distribution and dielectric properties of Cu nanoparticle composites fabricated by negative ion implantation. The depth profiles of a-SiO_2 samples become narrower and shallower with increasing dose rate. The depth profiles of MgO2.4(Al_2O_3) samples are close to a profile of deposited ions by the TRIM codes and almost independent of the dose rate. The ellipsometric results sensitively reveal difference of the depth profile and well agree with the cross-sectional TEM images. Effective depolarization coefficients of Cu nanoparticles exhibited the value of 0.4 to 0.6 by the extended Maxwell-Garnett theory. The effective dielectric shapes of Cu nanoparticles are cylindrical or ellipsoidal with their axes normal to the plane of the substrate and are affected by disperced Cu clusters close to the nanoparticle.

Key words: Ion implantation, Ellipsometry, Cu nanoparticle, Depth profile, Depolarization coefficient

1. INTRODUCTION

Metal nanoparticle composites consist of metal nanoparticles embedded in an insulator and have a high potential for optical applications because of a large photo-induced optical nonlinearity with picosecond response [1, 2]. The negative ion implantation at high currents has enabled us to form self-assembled metal nanoparticles in insulating substrates without applying post-irradiation annealing [3, 4]. The nanoparticles spontaneously grow by Ostwald ripening with a radiation-enhanced diffusion of Cu solutes during high-flux implantation. The nanoparticles are located around a projectile range near the surface with narrow distribution. Nanoparticle morphology in the composites is greatly dependent on the implantation conditions. According to cross-sectional TEM images, spherical Cu nanocrystals of 10-15 nm in diameter grow near the surface in amorphous SiO_2 [3]. On the other hand, nanoparticles in magnesium aluminate spinel remain below 5nm in diameter. MgO2.4(Al_2O_3) shows no long-range migration of the implants occurred because of good radiation resistance and phase stability [4]. Linear and nonlinear optical properties of the composites also depend on dose rate and are largely influenced by the morphology change [5]. It is extremely important process to estimate depth profile and optical properties of nanoparticles composites for optical applications. Optical ellipsometry is a nondestructive and capable method to analyze polarized status of reflected light from a sample surface and to evaluate optical properties and structure of multilayered thin-films and surface of a material.

In this paper, we present ellipsometry analysis of Cu nanoparticle composites fabricated by high-current negative ion implantation and discuss the depth profile and the effective depolarization coefficient of Cu nanoparticles in silica glass and magnesium aluminate spinel.

2. EXPERIMENTAL

Negative Cu ions of 60 keV were produced by a Cs-assisted plasma-sputter-type ion source with a cusp magnetic field. The details of the techniques have already been described elsewhere [6, 7]. The dose rate ranged from 1 to 100 $\mu A/cm^2$, achieving a total dose of 3×10^{16} ions/cm^2. Insulating substrates used were amorphous (a-)SiO_2 and magnesium aluminate spinel MgO2.4(Al_2O_3) single crystal of (100) plane. The diameter of the substrates was 15 mm and the thickness was 0.5 mm. A Cu mask with 6 mmϕ quadri-hole was screwed onto the substrate to avoid the local beam heating and charging if any. Depth profiles of 60 keV Cu were roughly estimated with the TRIM code [8]. The calculated projectile ranges for MgO2.4(Al_2O_3) and SiO_2 are 30 and 45 nm, respectively.

Ellipsometry measurements were made using a multi-angle spectroellipsometer with a rotating polarizer (SOPRA, GESP). The ellipsometry spectra were obtained in the range from 300 to 850 nm at incident angles of 55°, 60° and 65°. Optical parameters of the substrate were obtained from measurements with unimplanted samples.

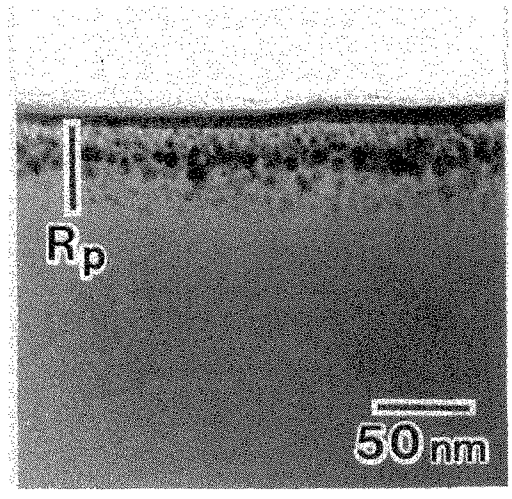

Fig.1 Cross-sectional TEM images of a-SiO2 implanted at 10 μA/cm2 with 60 keV.

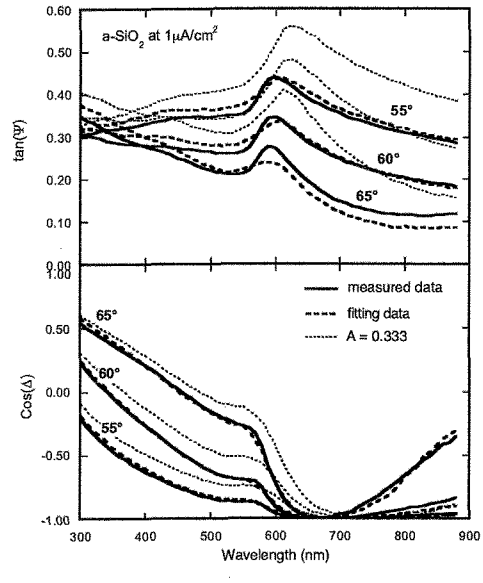

Fig.2 Ellipsometry spectra at various incident angles and fitting results. Dashed lines: fitting results, Dotted lines: calculated spectra with A = 0.333 corresponding to sphere shape.

3. RESULTS AND DISCUSSION

Figure 1 shows cross-sectional TEM images of a-SiO_2 implanted at 10 μA/cm^2 to 3 × 10^{16} ions/cm^2. The large spheres of Cu particles of about 10 nm in diameter are located within a narrow depth 30 nm near the surface. The depth location is shallower and narrower than the projectile range of the TRIM code as shown in fig. 2. The narrowing is caused by surface sputtering effects and a depth-directional driving force associated with radiation-induced electronic/nuclear excitation [3].

To derive optical properties and a depth profile by ellipsometry, a simple model of the composites is adopted. That is, Cu nanoparticles distribute as a Gaussian function near the projectile range and dielectric constants of nanoparticles include a size effect of the intraband transition [9]. The assumption of Gaussian is valid except a special case of the in-plane arrangement [3]. The sizes of nanoparticles in a-SiO_2 and MgO2.4(Al_2O_3) were 10 nm and 5 nm in average diameter, respectively [3, 4].

A general representation [10-12] of an effective dielectric constant for mixed materials is

$$\frac{<\varepsilon>-\varepsilon_h}{(1-A)\varepsilon_h + A<\varepsilon>} = \sum_i f_i \frac{\varepsilon_i - \varepsilon_h}{(1-A)\varepsilon_h + A\varepsilon_i}, \quad (1)$$

where $<\varepsilon>$ denotes the effective dielectric function, and ε_i and f_i are the dielectric function and volume fraction of the material i. The quantity ε_h is a host dielectric function that depends on mixing models. The Maxwell-Garnett expression, which is applied to nanoparticle composites, is obtain by choosing $\varepsilon_h = \varepsilon_a$, where ε_a is the dielectric constant of the host medium. The A is an effective depolarization coefficient and depends on the dielectric shape of inclusions. In the special case, the depolarization coefficient takes 0.333 for spheres and 0.5 for cylinders with their axes perpendicular to the electric field. Three Gaussian parameters (amplitude, σ, shift) and an effective depolarization coefficient were adopted as fitting parameters for the ellipsometry.

Ellipsometric spectra of Cu nanoparticle composite in a-SiO_2, which implanted at 1μA/cm^2, at various incident angles are shown with the fitting results in fig. 2. Calculated spectra with A = 0.333 (sphere shape) are also shown as references. A rapid change of the spectra around 580 nm corresponds to the surface plasmon resonance of Cu nanoparticles. The increase of A attenuates a surface plasmon resonance. The shape of spectrum tends to mainly depend on the Gaussian parameters and the values of tan Ψ and cos Δ tend to hinge on the effective depolarization coefficient.

Figure 3 shows dose rate dependence of depth profiles of Cu nanoparticles in a-SiO_2 and MgO2.4(Al_2O_3), derived by the ellipsometry analysis. The nanoparticles in a-SiO_2, implanted at 1μA/cm^2, distribute with the center at a depth of 37.2 nm. The distribution is located near the side of the surface rather than the projectile range of the TRIM-code. The centers of nanoparticle distribution shift to 29.1 and 16.5 nm with increasing dose rate to 10 and 30 μA/cm^2. The fitting σ of Gaussian distribution are 18.0, 14.4 and 14.6 nm at 1, 10 and 30 μA/cm^2, respectively. The depth profiles of a-SiO_2 become narrower and shallower with increasing dose rate. Nanoparticles in MgO2.4(Al_2O_3), synthesized at the dose rates of 10, 30 and 50 μA/cm^2, range with the center at 28.2, 32.9 and 34.0 nm deep and the σ of 12.5, 15.2 and 14.6 nm, respectively. The depth profiles of MgO2.4(Al_2O_3) samples are close to a profile of deposited ions by the TRIM codes and almost independent of the dose rate. The ellipsometric results sensitively reveal difference of the depth profile and well agree with the cross-sectional TEM images [3, 4]. The Gaussian areas of the depth profiles are also in good

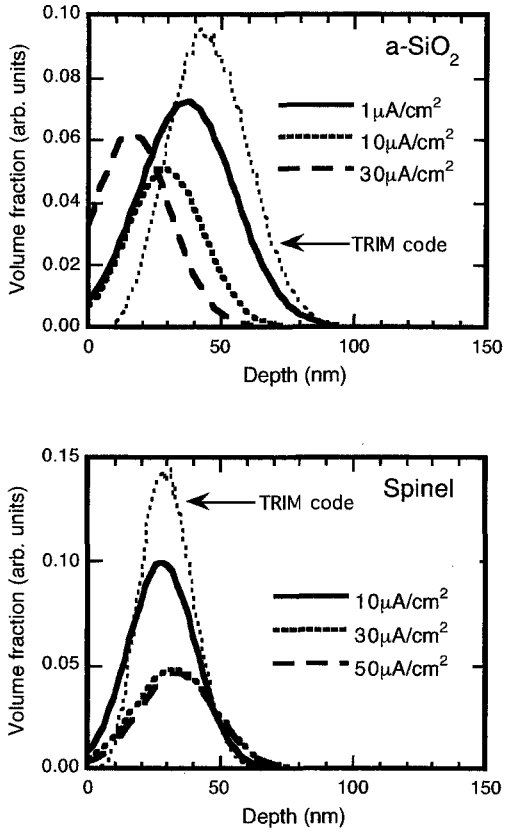

Fig.3 Depth profiles of Cu nanoparticle, fabricated at various dose rates, derived by ellipsometry analysis. A profile of deposited ions after the TRIM code is also depicted.

correlation with the optical absorbance, which depend on dose rate [5, 13]. The results show that the analysis is applicable to analyze depth profiles of nanoparticles fabricated by ion implantation.

The fitting effective depolarization coefficients *A* of Cu nanoparticles, synthesized in a-SiO_2 and MgO2.4(Al_2O_3) at various dose rates, exhibited the value of 0.4 to 0.6 as shown in fig. 4. The fitting results suggest dielectric shape of Cu nanoparticles is cylindrical or ellipsoidal with their axes normal to the plane of the substrate, but seem to disagree with physical spherical shape of the Cu nanoparticles observed by the cross-sectional TEM shape [3, 4]. A dielectric shape is susceptible to the electronic surroundings. Nanoparticles, fabiricated by ion implantation, have a distribution in direction of depth, and residual small clusters and solutes are located around large nanoparticles. It is considered that disperced Cu clusters close to a Cu nanoparticle lead to non-sphere dielectric shapes of the nanoparticle.

The increase of *A* also broadens a surface plasmon peak as shown in fig. 2. We have reported that a broad surface plasmon peak of as-implanted samples became clear and sharp after post-annealing, and that the optical

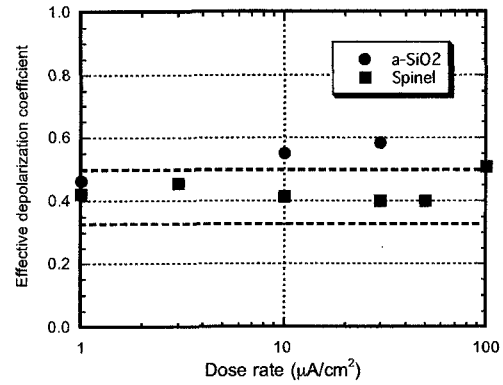

Fig.4 Effective depolarization coefficient of Cu nanoparticles in a-SiO_2 and MgO2.4(Al_2O_3), derived from ellipsometry.

absorption spectrum of annealing samples well agrees with the general Maxwell-Garnett theory with A = 0.333, [5]. Picosecond-order transient absorption, reflecting from energy transfers in a nanoparticle, of as-implanted samples decayed more slowly than that of annealed ones [5]. It is considered that the dielectric shape affects the attenuated plasmon peak and the slow transient response. For device applications, it might be necessary to control dielectric properties and spatial distribution of nanoparticles.

4 CONCLUSIONS

Depth profiles and dielectric properties of self-assembled Cu nanoparticles in silica glass and magnesium aluminate spinel were derived by ellipsometry analysis. The ellipsometric profiles were consistent with the cross-sectional TEM images and gave complementary information. The analysis is nondestructive and is applicable to analyze depth profiles of nanoparticles fabricated by ion implantation. The effective depolarization coefficients of Cu nanoparticles exhibited the value of 0.4 to 0.6 by the extended Maxwell-Garnett theory. The effective dielectric shapes of Cu nanoparticles are affected by disperced Cu clusters close to the nanoparticle.

ACKNOWLEDGEMENTS

A part of this study was financially supported by the Budget for Nuclear Research of the MEXT, based on the screening and counseling by the Atomic Energy Commission. The authors are grateful to Dr. H. Amekura, Mr. K. Kono, Dr. T. Suga, Ms. J. Lu and Mr. N. Ookubo for their assistance in the experiments.

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(Received December 20, 2002; Accepted January 31, 2003)