Synthesis of Cu Nanoparticles in Al₂O₃ by Ion Implantation and Subsequent Laser Annealing

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Abstract. Al₂O₃ samples with Cu nanoparticles synthesised by ion implantation at 40 keV, with a dose of 1×10¹⁷ ion/cm² and a current density from 2.5 to 12.5 µA/cm² were annealed using several pulses from a KrF excimer laser with a single pulse fluence of 0.3 J/cm². The copper depth distribution, formation and modification of metal nanoparticles under the ion implantation and laser treatment were studied by Rutherford backscattering (RBS), energy dispersive X-ray (EDX) analysis, atomic force microscopy (AFM) and optical spectroscopy. The metal nucleation, the change in particle size and the possibility for oxidation of the copper particles are examined in the framework of Mie theory.

INTRODUCTION

Composite materials representing dielectric matrices containing dispersed metal nanoparticles (MN) synthesized by ion implantation are promising for applications in optoelectronics [1]. However, there is one problem with this method, namely a wide size distribution of nanoparticles. One of the recent approaches to change the size distribution in implanted dielectrics is post-implantation laser annealing [2]. In particular, use of high-power excimer laser pulses to obtain new optical properties of dielectrics containing metal nanoparticles formed by implantation has been the subject of high interest for the last few years as it was reviewed [3]. It was shown that under certain conditions absorption of the excimer laser light by the composite stimulates surface melting and structural alterations. This effect was observed when the laser wavelength corresponded to the spectral absorption region of a dielectric substrate. One of the interesting, recently found features following the excimer laser treatment of implanted soda-lime silicate glass is a size reduction of synthesized metal nanoparticles. For silver nanoparticles formed by implantation in soda-lime silicate glass and treated with a KrF laser [3,4] it was suggested that the decrease of the nanoparticle size occurred as a result of melting of the glass substrate initiating melting of the metal nanoparticles.

In the present work the results on metal nanoparticle formation and alteration of Al₂O₃ by Cu⁺ ion implantation and consequent annealing using a pulsed KrF excimer laser are reported. The higher melting point (~ 2050 °C) and ultraviolet transparency of Al₂O₃ compared to soda-lime silicate glass allows the study of the modification of metal nanoparticles without melting of the dielectric substrate. The main feature of the current experiments is the use of a high-power laser with a wavelength where Al₂O₃ is transparent and thereafter the laser light is primarily absorbed by the metal particles.

EXPERIMENTAL

Al₂O₃ wafers were implanted with 40 keV Cu⁺ ions at a dose of 1×10¹⁷ ion/cm² and ion beam current densities from 2.5 to 12.5 µA/cm². The ion bombardment was carried out at room temperature. The implanted samples were studied by EDX spectroscopy on a scanning electron microscope (REMMA-202M) and by RBS using a beam of 2 MeV ⁴He⁺ ions. Pulsed laser treatment was done by a KrF excimer laser (ATLEX 210) with a wavelength of 248 nm and pulse length of 25 ns full width at half-maximum. Ten pulses of equal energy density (0.3 J/cm²) were accumulated in the same area of the sample at a repetition rate of 1 Hz.
The laser annealing was carried out in ambient atmosphere at room temperature. Optical spectra were recorded in the range from 200 to 800 nm. Topographic profiling of sample surfaces was performed with an AFM microscope working in the tapping mode.

As was shown earlier [3] the TRIM computation [5] of ion distributions is only roughly suitable for the cases of metal implantation with low energy into dielectrics. This algorithm ignores the strong surface sputtering and alterations of the ion range due to changes in the composition of the substrate. In the present work simulations for Cu+-ion implantation into Al2O3 were made using a dynamic computer code DYNA [3] based on binary collision approximations in intermixed layer formation. Target sputtering was also considered.

RESULTS AND DISCUSSION

Dynamic formation of a non-symmetrical depth distribution of implanted Cu+ ions in Al2O3 according to DYNA calculations is shown in Fig. 1. The peak position of the profiles moves closer to the implanted surface and the shape of the curves becomes asymmetrical when the dose is increased up to ~2.5x10^{15} ion/cm². As determined from DYNA calculations, increasing of the ion dose further up to 1x10^{16} ion/cm² does not change the ion distribution profiles. At higher values an increasing copper concentration exceeds the solubility limit in Al2O3 and causes growth of MN that immediately alters the range of the implanting ions and can not be properly estimated with the DYNA algorithm. As an example, Cu depth distributions in sapphire evaluated from experimental RBS spectra corresponding to a dose of 1x10^{17} ion/cm² at two current densities of 5 and 12 µA/cm² are presented in Fig. 2. It can be seen that the measured profiles are asymmetrical and have near-surface maxima with a tail extending into the sample, that is qualitatively similar to the calculated data, where it was shown that the diffusion coefficient dropped dramatically after metal particle formation. At higher value of ion current density a more strongly marked tail could be explained in the framework of thermo-stimulated diffusion of impurity caused by a fast rise of surface temperature under high-current ion beam irradiation. For lower ion current density, nanoparticles nucleated in the substrate act as effective traps for mobile Cu atoms preventing their diffusion into the sample. Unfortunately, RBS spectra and DYNA modeling allow only give the atomic concentration profiles without taking into account nanoparticle formation. Nevertheless, the nanoparticle distribution in the implanted insulator may also be predicted from the present data. It is obvious that during implantation the nucleation of nanoparticles and their size increase are proportional to the metal filling factor or, in other words, to the concentration profile of embedded Cu atoms. Consequently, larger metal nanoparticles are expected to be formed closer to the sample surface and smaller ones deeper in the modified region.

The formation of Cu nanoparticles at the sapphire surface is observed in AFM images, and one example corresponding to an ion current density of 7.5 µA/cm² is presented in Fig. 3. As can be seen, there are hemispherical hills on the surface with variations in dimensions up to 200 nm. It is known that there are no such protrusions on the unimplanted sample. These hills are supposed to be corresponding to the formation of nanoparticles [6]. The reason for the existence of the hills is assumed to be ion sputtering which leads to unequal ejection of atoms of different elements from the Al2O3 surface exposing the Cu nanoparticles synthesized in the sub-surface layer.

Lattice deformation and structural defects can occur due to the embedding of Cu atoms into the substrate and growth of small metallic particles. Radiation
defects in the $\text{Al}_2\text{O}_3$ lattice can decrease the transmittance especially in the ultraviolet region [1]. Nevertheless, as shown in the optical spectra of Fig. 4, despite the “stimulated” radiation absorbency the implanted substrates are transparent (up to 35 %) at wavelength of KrF excimer laser 248 nm compared to totally absorbing soda-lime silicate glass which was used for the laser annealing in previous works [2-4]. It should be mentioned also that the synthesized Cu nanoparticles absorb light in the ultraviolet themselves according to the electron interband transitions as in a bulk metal [7].

Measured optical reflectance spectra of Cu-implanted $\text{Al}_2\text{O}_3$ for various current densities are presented in Fig. 5 by thin lines. Wide reflectance bands appearing in the visible range are determined by the effect of the surface plasmon resonance of formed Cu nanoparticles [7]. For the lowest current density of 2.5 $\mu\text{A/cm}^2$ the reflectance peak is positioned at 610 nm with an intensity of 27 % implying the presence of small Cu particles. Increasing the ion current density shifts the reflectance peaks to longer wavelengths (up to 640 nm) and intensity reaches 41 % for 12.5 $\mu\text{A/cm}^2$. These spectra together with RBS data suggest that the ion implantation leads to metal nanoparticle formation in approximately the same region of 40-50 nm in depth for all samples and at higher current density the Cu nanoparticles are larger.

Changes in the reflectance spectra of the implanted samples after laser irradiation are shown in Fig. 5 by thick lines. The spectral selective plasmon band gives evidence for the presence of nanoparticles after annealing. For all samples the reflectance peak is reduced slightly in intensity and shifted to shorter wavelengths in comparison to the spectra of as-implanted sapphire. This shift is larger for $\text{Al}_2\text{O}_3$ implanted at higher current density. Thus, the samples with larger Cu particles are more sensitive to the laser treatment than ones with smaller nanoparticles synthesized at lower current density.

The spectra of plasmon excitations in small metal particles are well described by the Mie theory that explains the extinction as a function of the size of a particle and the permeability of its environment [7]. This approach can be also applied for analysis of the Cu nanoparticle reflectance. Extinction spectra of Cu nanoparticles embedded into $\text{Al}_2\text{O}_3$ as a function of particle size were calculated [8]. As it was shown for this composite, an increase of the metal particle diameter is accompanied with a shift of the spectral peak position to longer wavelengths. Thus, a small Cu particle in $\text{Al}_2\text{O}_3$ is characterized by a spectral band with maximum at shorter wavelengths than a larger one. Comparison of this calculation with experimental optical spectra in Fig. 5 assumes that laser annealing of the composites causes a decrease in size of the copper nanoparticles.
FIGURE 6. AFM image of Al₂O₃ surface implanted with Cu⁺ ions at ion current density of 7.5 µA/cm² after laser annealing. The X and Y scales are in nm, Z scale is 48 nm.

The assumption about a size reduction is in agreement with AFM measurements of the laser treated samples. As presented in Fig. 6, particles at the substrate surface become much smaller after laser annealing compared to those presented in Fig. 3 for as-implanted samples. Reduction of the sizes of Ag nanoparticles after laser annealing was also observed for implanted soda-lime silicate glass [2-4,9,10]. Modifications of nanoparticles in soda-lime silicate glass was explained by melting of a surface layer absorbing the laser light followed by heat transfer from the matrix to metal particles causing their melting. However, this model is not suited for the present experiment because of the transparency of Al₂O₃. Therefore, in order to interpret the observed decrease of the particle size, the direct absorption of laser light by nanoparticles which may initiate melting of the particles themselves has to be considered. As was found using RBS and EDX measurements, applied excimer laser treatment does not lead to a redistribution of copper into the depth of sample. Hence, synthesized nanoparticles are kept in the narrow near-surface layer which is very important from the practical point of view. The difference between the cases of Al₂O₃ and silicate glass can be also explained by the difference between very strong absorption in silicate glass and quite high transmittance of sapphire in the ultraviolet.

CONCLUSIONS

An Al₂O₃ matrix was used for formation of a metal/dielectric composite by high dose (1×10¹⁷ ion/cm²) Cu⁺ ion implantation at various ion current densities. The impurity depth distributions were analyzed using the DYNA code in comparison with RBS measurements. Synthesis of Cu nanoparticles in the implanted layer is found to occur due to the metal concentration exceeding the solubility limit in Al₂O₃. A rise of ion current density leads to a shift of the reflectance spectrum to longer wavelengths that corresponds to an increase of the metal particle sizes. Annealing of the implanted samples with excimer laser pulses causes both a decrease of the reflectance band intensity and a shift of the spectral maximum to shorter wavelengths.

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