CONF-9709116

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REI Conference, Knoxville, TN, 9/97
(NIMB)

**Fabrication of Copper and Gold Nanoclusters in MgO (100)
by MeV Ion Implantation**

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Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

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October 1997

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FABRICATION OF COPPER AND GOLD NANOCCLUSERS IN MgO (100) BY MeV ION IMPLANTATION.

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ABSTRACT

MeV ions of Au and Cu were implanted into single crystals of MgO (100) and the formation of metallic nanoclusters was observed by an indirect method of optical absorption spectrophotometry. Using Mei's theory we related the observed optical absorption band to the formation of nanoclusters and using Doyle's theory, as well as Rutherford Backscattering Spectrometry (RBS), we correlated the full width half maximum (FWHM) of the absorption bands to the estimated size of the metallic nanoclusters between 1-10 nm. These clusters were formed by implantation above the threshold fluence for cluster formation and by a combination of threshold fluence of the implanted species and thermal annealing. The changes in the estimated size of the nanoclusters, after annealing at temperatures ranging from 500°C to 1000°C, were observed using optical absorption spectrophotometry and calculated using Doyle's theory.

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INTRODUCTION

It has long been known that metallic colloids embedded in dielectrics produce colors associated with optical absorption at the surface plasmon resonance frequency [1-4]. These changes in the optical properties of insulating materials can be made to occur following the implantation of MeV metal ions. After heat treatment, small metal clusters form in the implanted layer and absorb light at the surface plasmon resonance frequency [5-9]. The nonlinear optical properties of the implanted layer is many orders of magnitude more than the host dielectric [10].

The thermal behavior of ion implanted material differs significantly from optical material prepared with a uniform distribution of colloidal material. Firstly, the host dielectric may be a single crystal, rather than a glass or ceramic. Secondly, the initial distribution of metal atoms is easily controlled by the energy and fluence of the incident ion beam. And there is no *a priori* restriction on the chemical affinity or stoichiometry of the implanted ions.

Subsequent thermal treatment controls the formation of nanocrystals of the metal. The metal atoms aggregate into single crystals of desired size perfectly aligned with the host crystal [10]. Because most of the crystal initially has no metal atoms, heating above a critical temperature causes the clustered atoms to disperse irreversibly. In the present paper we compare the thermal behavior of copper and gold colloids implanted near a (100) surface of MgO single crystals.

For clusters with diameters much smaller than the wavelength of light (λ), the theories of Mie [6] can be used to calculate the absorption coefficient of the composite:

$$\alpha = \frac{18\pi Q n_o^3}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2n_o^2)^2 + \epsilon_2^2} \quad (\text{cm}^{-1}), \quad (1)$$

where Q is the volume fraction occupied by the metallic particles, n_o is the refractive index of the host medium, and ϵ_1 and ϵ_2 are the real and imaginary parts of the frequency-dependent dielectric

constant of the bulk metal. Equation (1) has a maximum value at the surface plasmon resonance frequency (ω_p), where

$$\epsilon_1(\omega_p) + 2n_o^2 = 0. \quad (2)$$

In the above, $\epsilon_1 = n^2 - k^2$ where n and k are the optical constants of the bulk metal. Using the tabulated optical constants for gold and copper [11], ϵ_1 is obtained as a function of the photon wavelength. Knowing $n_o = 1.73$ for MgO, Equation (2) predicts a photon wavelength of 564 and 551 nm for the surface plasmon resonance frequency for colloidal Cu and Au in MgO, respectively. The average radius r of the metallic clusters can be calculated according to Doyle [7] from the absorption spectra using the equation

$$r = \frac{V_f}{\Delta\omega_{1/2}}, \quad (3)$$

where v_f is the Fermi velocity of metal ($v_f = 1.39 \times 10^8$ cm/sec for both gold and copper) and $\Delta\omega_{1/2} = 2\pi c \frac{\Delta\lambda}{\lambda_p}$ where $\Delta\lambda$ is the full width at half maximum (FWHM) wavelength and λ_p the peak wavelength, both determined from an optical absorption spectrum. λ_p depends on the element implanted and $\Delta\lambda$ is determined by the size of the nanoclusters.

EXPERIMENTAL PROCEDURES

Implantations were made into epi-polished 1x1 cm MgO (100) single crystals, a commercial product of Commercial Crystal Laboratories, Inc., using 2.0 MeV gold ions or 2.0 MeV copper ions at low fluxes to maintain the MgO crystals at room temperature. The expected penetration depths and standard deviations were 320 ± 50 nm for 2.0 MeV gold ions and 800 ± 125 nm for 2.0 MeV copper ions [4]. Separate MgO samples were implanted with copper ion fluences of 8×10^{16} , 1.9×10^{17} and 7×10^{17} cm⁻² and with gold fluences of 4×10^{16} , 8×10^{16} , 2×10^{17} and 4×10^{17} ions cm⁻².

Heat treatment of the samples was performed in air. Each gold implanted sample was treated sequentially for one hour at temperatures of 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C, cooling to room temperature after each for the optical measurements. The heat treatment of the gold implanted samples was repeated for additional periods for a total time of 20 hours at 1000°C. The copper implanted samples were heat treated at one hour only at 500°C.

RESULTS AND DISCUSSION

Figure 1 shows typical optical absorption spectra. The optical density as a function of wavelength is displayed for a single sample of MgO(100) crystal implanted with 2.0 MeV gold at a fluence of 2×10^{17} Au/cm². Spectra as implanted at room temperature and after heat treatment for one hour at several temperatures are shown. Evidence of a broad absorption band at about 580 nm appears before any heat treatment. That band shifts to lower wavelength with the first heat treatment. At increasing temperatures the band becomes more pronounced, narrows and shifts slightly to longer wavelengths.

Figure 2 shows three optical absorption spectra after further heat treatment of the same sample as shown in Figure 1 for 1, 10 and 20 hours at 1000°C and compares these with the spectrum of this sample as implanted before any heat treatment. The optical density of the absorption band increases significantly with heat treatment time only during the first 10 hours.

Figure 3 shows the average radius of the metal nanocrystals formed as a function of heat treatment time at 1000°C in two MgO samples with implantation fluences of (a) 8×10^{16} and (b) 2×10^{17} Au/cm². Like the peak value of the optical absorption the average radii also do not significantly change during heat treatment beyond 10 hours at 1000°C. Surprisingly, Figure 3 shows that the average radius of gold nanoclusters increases significantly more than the expected cube root of the fluence increase [7]. Coalescence of small clusters by a nearby larger one could

explain this phenomenon. The greater initial separation of nanoclusters in samples implanted with low fluence may permit less coalescence during thermal treatment.

Figure 4 shows the optical spectra of three MgO(100) crystals implanted with copper at room temperature with fluences of (a) 8×10^{16} , (b) 1.9×10^{17} and (c) 8×10^{17} Cu/cm². The optical absorption bands at 576 nm show that metal nanoclusters form during implantation at room temperature. Heat treatment of each sample at 500°C for one hour caused this absorption band to disappear as shown in Figure 4 (d) for the 8×10^{16} Cu/cm² sample. Evidently, such heat treatment causes irreversible dispersion of the Cu atoms from the implantation layer in the MgO crystal, a phenomenon shown also by silver implanted MgO, but only after heat treatment at temperatures above 1100°C [10]. Evidently the thermal stability of nanoclusters formed during implantation or by post bombardment thermal treatment is not related directly to the melting temperature of the bulk metals.

CONCLUSION

The implantation of metal ions into a single crystal of MgO(100), which is then submitted to careful heat treatment, creates a well defined layer of material with new optical properties. The optical absorption at the plasmon frequency of implanted gold may be used to calculate the average radius of the metal nanoclusters as a function of thermal treatment temperatures and times. Subsequent heat treatment of the gold implanted MgO causes metallic nanoclusters to grow to an equilibrium average radius that depends on the implantation fluence. An increase of the fluence of implanted gold causes an increase in the equilibrium radius of the gold nanoclusters. No such increase would be expected if the nucleation site density is proportional to the defect density caused by damage during implantation. In fact we observe an increase greater than the cube root fluence dependence expected for a constant density of initial nucleation sites. Possibly coalescence

of smaller nanoclusters with a single larger nanocluster occurs more with samples implanted with high fluences.

Copper atoms diffuse in MgO during room temperature implantation to form nanoclusters. Subsequent heat treatment at 500°C causes the copper atoms to disperse irreversibly into the host. In this respect, copper and gold behave strikingly different in MgO, even though their bulk melting temperatures are not very different.

ACKNOWLEDGMENTS

Research supported by the Center for Irradiation of Materials, Alabama A&M University, Alabama-EPSCoR-NSF Grant No. EHR-9108761/STI-9108761 and the Division of Materials Sciences, U. S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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FIGURE CAPTIONS

1. Optical absorption spectra of a single sample of gold implanted MgO(100) with a fluence of 2×10^{17} Au/cm² then thermally treated for equal one-hour intervals at successively higher temperatures.
2. Optical absorption spectra for the same sample as in Figure 1 after further thermal treatment at 1000°C for 1, 10 and 20 hours compared with the spectrum of the sample before any heat treatment.
3. The average radius of metallic gold nanoclusters in two samples of MgO (100), one implanted with (a) 8×10^{16} Au/cm² and the other with (b) 2×10^{17} Au/cm² after thermal treatment at 1000°C for 1, 10 and 20 hours. The ratio of the equilibrium radii attained after prolonged thermal treatment is larger than expected for the fluences shown.
4. Optical absorption spectra for three samples of MgO(100) implanted with 2.0 MeV copper ions at fluences of (a) 8×10^{16} , (b) 1.9×10^{17} and (c) 7×10^{17} Cu/cm². Thermal treatment of these samples at 500°C for one hour completely removes evidence of the plasmon absorption band as shown for the fluence of (d) 8×10^{16} Cu/cm².

Fig 1

2. MDT gldl 2.2×10^{-2}
MCDL gldl / An 3D 0.079

Optical absorption spectra for the same sample as in Figure 1 after further thermal treatment at 1000°C for 1, 10 and 20 hours compared with the spectrum of the sample before any heat treatment.

1.5 MeV copper implanted MgO

M98000691

Report Number (14) ORNL/CP--94847
CONF-9709116--

Publ. Date (11) 199710
Sponsor Code (18) DOE/ER, XF
UC Category (19) UC-400, DOE/ER

DOE