

ION BEAM-INDUCED CHANGES IN OPTICAL PROPERTIES OF MgO

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ABSTRACT

The implantation of Ag into MgO (100) single crystals, followed by thermal annealing at 1100°C, leads to dramatic changes in their optical properties. The changes in the optical properties are due to the presence of small Ag clusters which are formed in the annealed samples. The small Ag clusters are obtained by thermal annealing of the implanted MgO crystals between 600°C and 1100°C to investigate the changes in cluster sizes and to correlate with changes in their optical properties. Sample characterization is carried out using optical spectrophotometry to confirm the effective presence of Ag clusters and Rutherford Backscattering Spectrometry (RBS) to study the profile of Ag clusters.

INTRODUCTION

Ion implantation is the most successful and widespread surface modification technique in insulators and ceramic materials. An area which has drawn considerable attention is the use of implantation to cause changes in the optical properties of these materials [1][2]. One way to cause dramatic changes in the optical properties is through the formation of small metallic clusters which absorb light at the surface plasmon resonance frequency [3-5].

With regard to the phase formation in MgO implanted with a high dose (more than 10^{16} ions/cm²) of metallic ions, three cases have been distinguished [6] a) the alkaline ions [7] (Li, Na, K, Rb), which form metallic clusters, b) Ag and Au [8], which form metallic precipitates and binary alloys with magnesium, and c) Fe, which forms oxides and spinel ferrites [9].

In the present study, we have found that the implantation of Ag into MgO (100) single crystals, followed by thermal annealing at 1100°C, results in the formation of Ag clusters. These small metallic clusters are identified by optical absorption and Rutherford Backscattering Spectrometry (RBS). In addition, we have investigated the effects of thermal annealing on small metallic cluster sizes and correlated with changes in optical properties. The positions of the maximum and the full width at half maximum (FWHM) of the optical absorption band are related to the sizes of the small metallic clusters. Toward this objective, MgO single crystals were implanted with 1.5 MeV Ag and then subjected to thermal annealing at 600°C, 800°C, 1000°C and 1100°C, each sample for 30 minutes.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples of approximately 10 x 10 x 0.5 mm³ of MgO (100) single crystals were implanted with Ag⁺ ions using a 1.7 MV General Ionex Tandem ion accelerator at Oak Ridge National Laboratory. The beam energy was 1.5 MeV and the current density was maintained rather low ($\sim 1 \mu\text{A cm}^{-2}$) in order to restrict thermal effects during implantation. The theoretical

range from the TRIM calculation [10] for 1.5 MeV silver ions implanted in MgO gives a projected depth $\Delta x = 0.45 \mu m$. The ion beam scan area was $10 \times 10 \text{ mm}^2$. To produce small clusters of silver in MgO crystals, each implanted sample was heated in air to 1100°C in increments of 100°C from 600°C , with a 30 minute dwell time at each annealing.

Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering analysis performed using 3.5 MeV particles at RT gives information on the depth concentration profile of implanted particles in crystals. The analyzed surface is about 2 mm^2 . Backscattered particles are detected with a surface barrier detector located at an angle of 170° .

Optical Absorption Measurements

Optical absorption measurements were performed at room temperature using a Cary 13E spectrophotometer capable of measuring absorption in UV and visible portions of the spectrum (i.e., from 190 to 900 nm). For all these measurements, the unimplanted part of the sample was used as a reference.

RESULTS AND DISCUSSION

Theoretical Considerations

It has long been known that small metallic particles or colloids embedded in dielectrics produce beautiful colors associated with optical absorption at the surface plasmon resonance frequency [11-13]. For clusters with diameters much smaller than the wavelength of light (λ), the theories of Mie [3] can be used to calculate the absorption coefficient (cm^{-1}) of the composite:

$$\alpha = \frac{18\pi Q n_0^3}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2n_0^2)^2 + \epsilon_2^2} \quad (1)$$

where Q is the volume fraction occupied by the metallic particles, n_0 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) is a Lorentzian function with a maximum value at the surface plasmon resonance frequency (ω_p), where

$$\epsilon_1(\omega_p) + 2n_0^2 = 0 \quad (2)$$

In the above, $\epsilon_1 = n^2 - \kappa^2$ where n and κ are the optical constants of the bulk metal. Using the tabulated [14] optical constants for Ag, the value of ϵ_1 for silver has been plotted as a function of the photon wavelength (Fig. 1). Since we know $n_0 = 1.73$ for MgO, Equation (2) predicts a photon wavelength of 430 nm for the surface plasmon resonance frequency for colloidal Ag in MgO. On the other hand, the average radius of the metallic clusters, r , will be estimated from the absorption spectrum and using Doyle theory [4], according to 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 silver [8]) and $\Delta\omega_{1/2}$ is the full width at half maximum (FWHM) of the absorption band due to the plasmon resonance of silver particles. The value of the FWHM is derived from the absorption band ($\Delta\omega_{1/2} = 2\pi c \frac{\Delta\lambda}{\lambda_p}$) where $\Delta\lambda$ is the full width at half maximum wavelength of the plasmon band and λ_p represents the peak wavelength of the plasmon band).

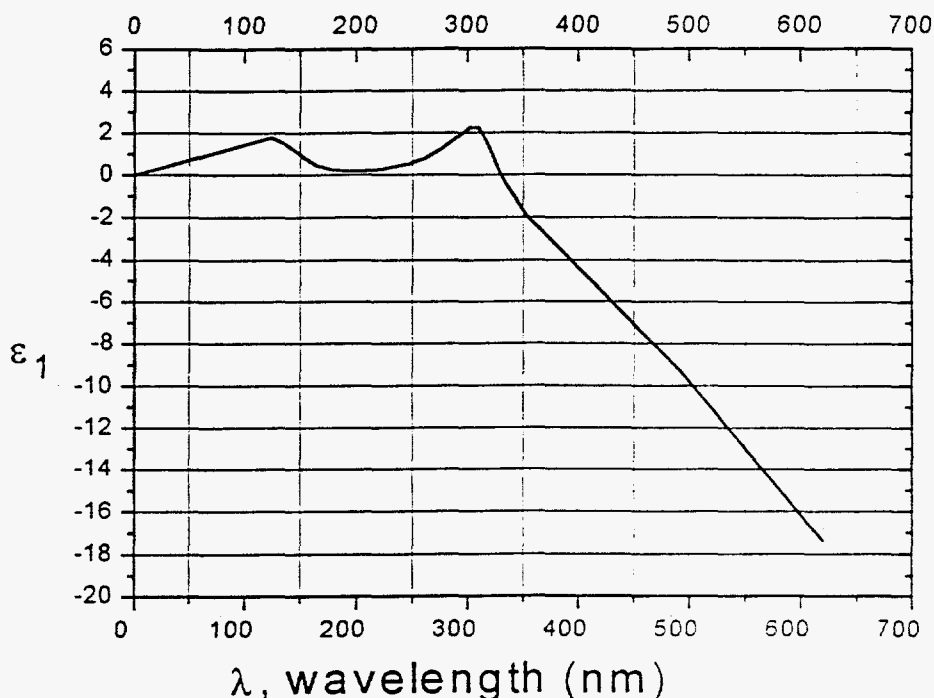


Fig.1. Value of ϵ_1 for bulk Ag as a function of photon wavelength (nm)

As implanted MgO

The implantation at room temperature of silver ions into MgO for 6.0×10^{16} and 1.2×10^{17} Ag^+/cm^2 doses produced defects in the oxygen and magnesium sublattices. These defects are identified by optical absorption measurement. Figure 2 shows the spectrum of the as implanted MgO. Two main absorption bands are observed at 250 nm in relation to F^+ and F -centers (oxygen vacancies with one or two trapped electrons) and at 575 nm corresponding respectively to absorption from V-type centers (magnesium vacancies) generated through nuclear elastic collisions.

Effect of heat-treatment on the Ag colloid particles implanted MgO

Absorption spectra have been studied following 30 min anneals between 600°C and 1100°C in order to determine the modifications induced in implanted species. For a sample implanted with 1.2×10^{17} Ag^+ ions/ cm^2 and subsequently isochronally annealed for 30 min, Fig. 3 shows an absorption at 410 nm after 600°C . The position of this band does not change or changes only a little for annealing temperature between 600°C and 800°C , however, the band optical density increases.

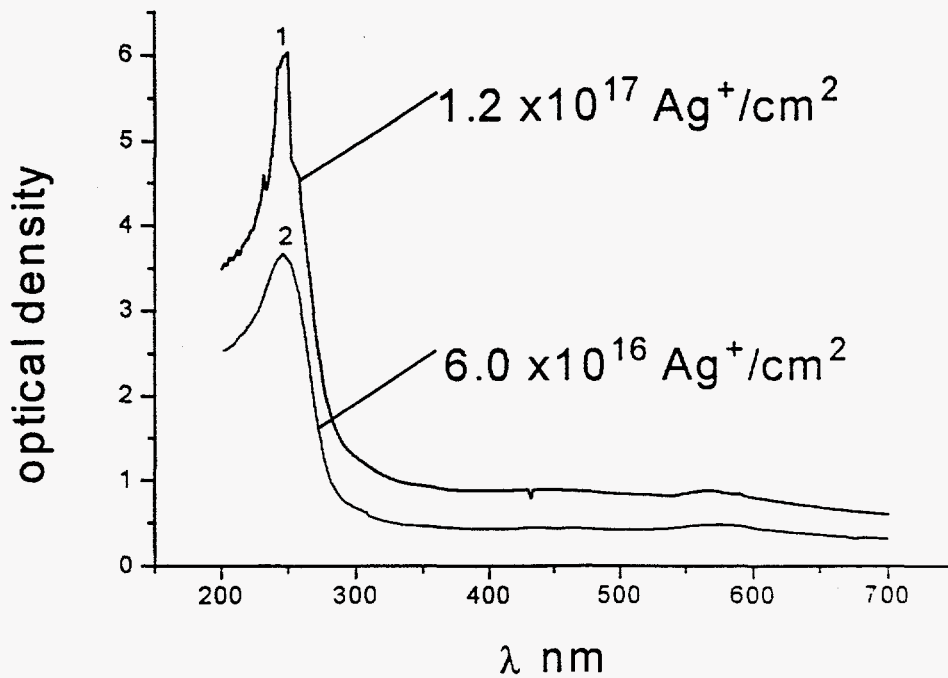


Fig. 2. Optical absorption spectra of MgO crystals implanted with 1.5 MeV Ag at room temperature

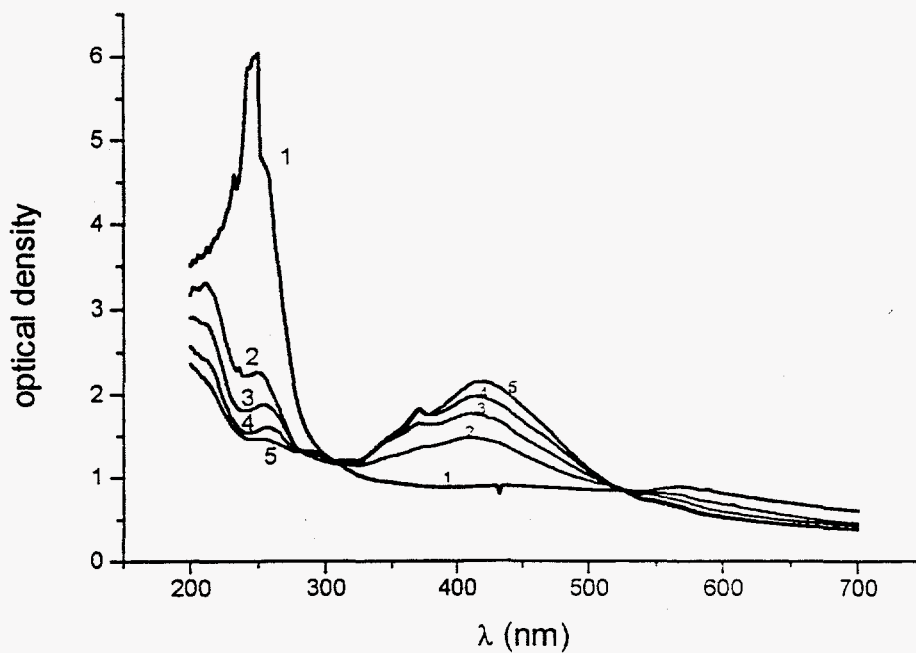


Fig. 3. Optical density as a function of wavelength for a MgO sample implanted with 1.2×10^{17} $1.5 \text{ MeV Ag}^+/\text{cm}^2$: 1: before annealing; 2, 3, 4 and 5 annealed for 30 min at 600, 800, 1000 and 1100°C.

For annealing temperatures higher than 800°C, the band maximum shifts to longer wavelengths and reaches 420 nm at 1100°C. The sample is brown in this case. This measured value of 420 nm is in good agreement with a photon wavelength of 430 nm deduced from Equation (2) for the surface plasmon resonance frequency for colloidal Ag in MgO.

Fig.3 shows that the spectrum also has an F-center band and a V-type center band after annealing. Only the optical density decreases. Additionally, a small sharp band located at 360 nm appears after annealing at 800°C. The 360 nm bands are F-aggregate centers [15].

The shift of the absorption maximum to longer wavelengths accompanied by the increase in absorption and a narrowing of the absorption band may be related to the growth of Ag colloids during annealing. The particle sizes deduced from Equation (3) and Fig.3 show that for annealing up to 1100°C the radii of the silver precipitates vary between 0.8 and 3 nm. However, positive identification of the precipitates and their size distribution can only be obtained by TEM measurements. These are in progress and will be reported in the future.

Rutherford backscattering spectroscopy-channeling results indicate that the precipitates form without the recovery of implantation-produced extended defects in the MgO lattice. Additionally, no long-range diffusion of silver is observed after annealing at 1100°C (Fig.4).

CONCLUSION

Ion implantation of Ag into MgO followed by thermal annealing at 1100°C forms crystalline Ag clusters (average size ~3nm). These clusters produce a strong optical absorption band at 420 nm due to surface plasmon resonance absorption, which leads to a brown color in the implanted region. Absorption spectrophotometer and RBS results indicate that the Ag clusters form without the recovery of implantation produced extended defects in the MgO lattice.

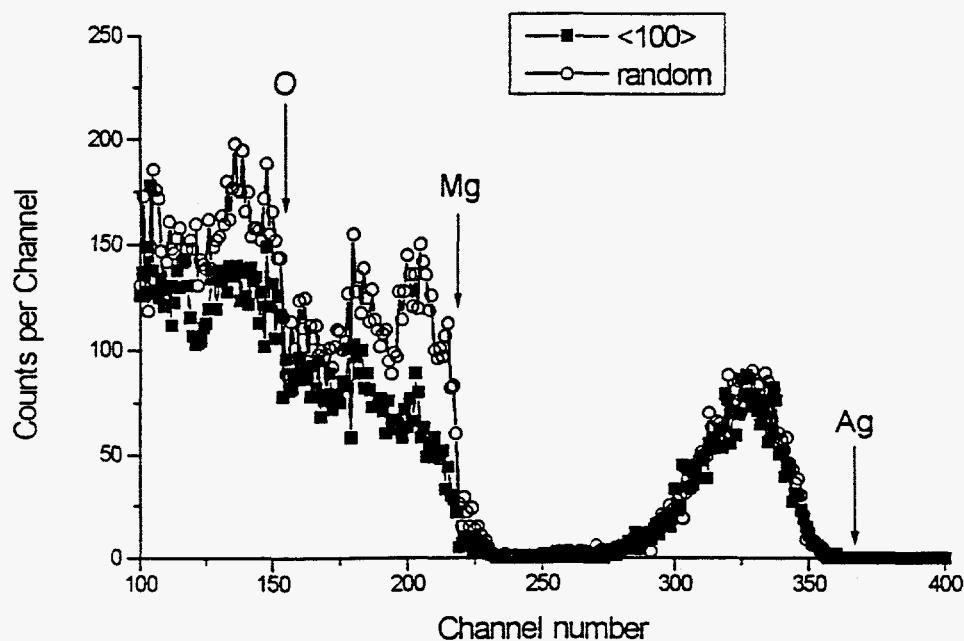


Fig.4. RBS ion channeling measurements in Ag (1.5 MeV, $1.2 \times 10^{17}/\text{cm}^2$, RT) implanted (100) MgO. Arrow with labels indicates the channel number for surface scattering from Ag, Mg and O.

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