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Effects of atomic collisions on rubidium clusters embedded into MgO crystals

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Résumé. — Des monocristaux de MgO, préimplantés avec des ions rubidium et ensuite recuits, contiennent des petits précipités de rubidium bien caractérisés par mesures d'absorption optique et microscopie électronique en transmission. Des mesures d'absorption optique ont montré que durant la réimplantation avec des ions Rb^+ le nombre de précipités diminue avec la dose : la phase précipitée a totalement disparue pour une dose égale à 7×10^{14} ions. cm^{-2} . Ces effets semblent être associés à un processus de collisions atomiques.

Abstract. — MgO single crystals, preimplanted with rubidium ions and subsequently annealed, contain small rubidium precipitates which have been well characterized by optical absorption measurements and transmission electron microscopy. Optical absorption measurements have shown that during the reimplantation with Rb^+ ions the number of precipitates decreases with the fluence : the precipitated phase has completely disappeared for a fluence of 7×10^{14} ions. cm^{-2} . These effects seem to be associated with an atomic collision process.

1. Introduction.

Optical absorption of MgO, implanted with alkali ions [1-3] shows two absorption bands located at 250 nm and 575 nm, which correspond to anionic vacancies (F type centres) and cationic vacancies (V type centres) respectively. Even for high fluences the optical spectra do not reveal the presence of alkali atoms.

Subsequent annealing performed on these samples lead to the disappearing of intrinsic point defects (F and V type centres) as also the aggregation of a part of the implanted atoms. Then an optical absorption band due to plasma oscillation of free electrons in metallic precipitates of alkali metal embedded in the MgO matrix is observed in the spectra.

In this paper, we report on the evolution of MgO crystals implanted with Rb^+ ions. The purpose of this work is to investigate the effects of ion beam on small metallic precipitates of rubidium embedded into an insulating matrix MgO. Fortunately, the optical absorption due to metallic precipitates depends on the number of precipitated atoms [4], thus, the evolution of this band is directly connected with the evolution of the precipitated phase.

As the maximum energy transferred in a nuclear collision is obtained when projectiles and target atoms have the same mass, the implantations have been performed with rubidium ions.

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2. Experimental procedure.

MgO crystals (4N purity) cleaved into (100) platelets of dimensions $12 \times 12 \times 0.3 \text{ mm}^3$ were obtained from W. C. Spicer Ltd. Implantations were performed, using a Balzers implantor for low energies ($\leq 200 \text{ keV}$), and a 2.5 MeV Van de Graaff accelerator for high energies. The bombarded target area was 1 cm^2 . The crystals implanted at high energies were annealed in air whereas the other ones were annealed under vacuum in order to prevent oxidation of aggregates. The optical absorption spectra were recorded using a Cary 17 double beam spectrophotometer. For *in situ* analysis during implantation a Beckman DK 2A spectrophotometer was used. Classical transmission electron microscopy (T.E.M.) observations were carried out with a 100 keV Philips EM 300.

3. Experimental results.

3.1 THERMAL EVOLUTION OF MgO CRYSTALS IMPLANTED WITH A HIGH FLUENCE OF Rb^+ IONS. — Figure 1 shows the optical absorption spectrum of a MgO crystal implanted at low energy (170 keV) with Rb^+ ions. As expected, this spectrum only exhibits the two bands, at 250 and 575 nm, due to intrinsic defects (F and V type centres).

Thermal annealings performed on this sample lead to the decrease of these band amplitudes. After a 950 K anneal these bands have completely disappeared and a broad band located at about 850 nm appears in the spectrum. According to the Doyle theory [4], this optical absorption band should be due to plasma oscillations of free electrons in small rubidium precipitates embedded into the MgO matrix. The energy at which this absorption occurs is given by :

$$\hbar\omega = \hbar\omega_p(1 + 2n_0^2)^{-1/2}$$

where $\hbar\omega_p$ is the plasmon energy of free electrons in the bulk metal (3.65 eV for rubidium) and n_0

Fig. 1. — Optical absorption spectra of MgO implanted with $2 \times 10^{16} \text{ cm}^{-2}$ Rb^+ ions of 170 keV energy ; (a) as implanted, (b) annealed under vacuum for 15 min at 1 023 K.

the refractive index of the MgO matrix ($n_0 = 1.73$). Then the calculated energy position of this absorption band is 1.38 eV ($\lambda \simeq 900$ nm) which is very close to the experimental value : 1.46 eV ($\lambda \simeq 850$ nm). The amplitude of this band increases with increasing temperature and its maximum shifts towards larger wavelengths. This evolution seems to be characteristic of the precipitation of implanted atoms into small metallic clusters [5, 6]. As expected, after anneal at 1 023 K, the optical absorption band shifts towards larger wavelength : 1 030 nm (Fig. 1).

The size distribution of the precipitates cannot be deduced from the optical absorption band. However, when the size of precipitates is small compared with the mean free path of electrons in the bulk metal, assuming a sharp size distribution around the mean radius $\bar{r}$, the full width at half maximum of the absorption band $\Delta E_{1/2}$ is related to the mean radius by the formula [4] :

$$\Delta E_{1/2} = h \frac{v_F}{\bar{r}}$$

where h is the Planck constant and v_F the Fermi velocity of electrons.

Considering the experimental value ($\Delta E_{1/2} = 0.61$ eV) deduced from the optical absorption band and the Fermi velocity ($v_F = 0.81 \times 10^6$ m.s⁻¹), the mean radius of precipitates $\bar{r}$ is about 5.5 nm.

These precipitates of rubidium in MgO lattice have been clearly characterized using transmission electron microscopy. Figure 2 shows a large precipitate of rubidium and the corresponding diffraction pattern indicating precipitate reflections.

3.2 EFFECTS OF ATOMIC COLLISION IN MgO CRYSTALS CONTAINING RUBIDIUM PRECIPITATES. —

The MgO sample was implanted with 5×10^{16} cm⁻² 2 MeV Rb⁺ ions. The electronic and nuclear energy losses of 2 MeV Rb⁺ ions in MgO, calculated from the L.S.S. theory [7] are reported in figure 3a. The range-energy relation, deduced from these two curves is nearly linear for energies lower than 2 MeV (Fig. 3a). As shown in this figure, the mean projected range R_p of 2 MeV rubidium ions in MgO is about 670 nm. The range straggling ΔR_p , calculated from the Dearnaley *et al.* tables [8] is about 135 nm. Assuming a Gaussian distribution in depth for the implanted particles, we have plotted in figure 3b the concentration of rubidium atoms *versus* the depth for a fluence of 5×10^{16} Rb⁺.cm⁻². The maximum concentration is about 1.6×10^{21} Rb⁺.cm⁻³, which corresponds to approximately 3 foreign atoms per 100 Mg or O atoms.

The optical absorption spectrum of this sample annealed for 15 min at 1 173 K, exhibits a band at 850 nm (1.46 eV) associated with rubidium precipitates and a bump at a shorter wavelength : 560 nm (2.21 eV) (Fig. 4). A similar bump together with the principal optical absorption band associated with metallic precipitates was observed in the case of MgO crystals implanted with Li⁺, Na⁺ and K⁺ and subsequently annealed [1, 9], and also in additively coloured alkali halides [10-12].

Fig. 2. — MgO implanted with 4×10^{16} cm⁻² 150 keV Rb⁺ ions and subsequently vacuum annealed for 15 min at 1 073 K. (a) Diffraction pattern on a large precipitate : (113) Rb ; (b) bright field image of the Rb precipitate ; (c) dark field image of the Rb precipitate using (110)* precipitate reflection.

Fig. 3. — (a) Theoretical results of L.S.S. for the slowing down of 2 MeV Rb^+ ions incident on a MgO target : stopping power ($-\text{d}E/\text{d}R$) for electronic (Δ) and nuclear ($\blacktriangle$) processes for the « average » particle; ($\blacklozenge$) range energy relation. (b) Distribution of the concentration C of Rb atoms versus the depth R for $5 \times 10^{16} \text{ cm}^{-2}$ Rb^+ ions of 2 MeV energy.

Fig. 4. — Optical absorption spectra of MgO implanted with $5 \times 10^{16} \text{ cm}^{-2}$ Rb^+ ions of 2 MeV energy annealed for 15 min at 1 173 K : (a) as annealed; (b) $5 \times 10^{12} \text{ Rb}^+ \text{ cm}^{-2}$ reimplantation; (c) $4.5 \times 10^{13} \text{ Rb}^+ \text{ cm}^{-2}$ reimplantation; (d) $7 \times 10^{14} \text{ Rb}^+ \text{ cm}^{-2}$ reimplantation.

The mean size of rubidium precipitates, deduced from the principal optical absorption band, is about 10 nm (Fig. 4).

This crystal was implanted, at a low dose rate (5×10^{11} ions $\cdot$ cm $^{-2}$ s $^{-1}$), with the same 2 MeV Rb $^{+}$ ions and the optical absorption spectra were recorded *in situ* after each dose. Figure 4 shows the evolution of the optical absorption spectrum of this sample. The amplitude of the 850 nm (1.46 eV) optical absorption band, due to Rb precipitates, decreases with the fluence. Up to 7×10^{14} Rb $^{+}$ cm $^{-2}$, this band fully vanished. Simultaneously to this evolution a band at 250 nm appears and the bump near 560 nm increases. The 250 nm absorption band is associated with F type centres; its amplitude increases fastly with the fluence. Concerning the absorption spectra evolution near 560 nm, it results from the contribution of two previously discussed bands, one corresponding to the bump at 560 nm and the other one at 575 nm associated with V type centres. As the amplitude of the principal optical absorption band (850 nm) decreases during bombardment, the amplitude of the bump associated with this band should decrease. On the contrary the amplitude increase of the bump (560 nm) observed on the spectra, simultaneously with the one of the band associated with the F type centres suggests that the contribution of V type centres to the evolution of this bump is preponderant.

The main result of this experiment is the evolution of the principal optical absorption band (850 nm) *versus* the fluence. As the area under the optical absorption band associated with precipitates is proportional to the number of Rb atoms precipitated [4, 6], the decrease of this area (Fig. 4) indicates a destruction of Rb precipitates during bombardment. The same evolution was observed in MgO crystals containing sodium aggregates implanted with Na $^{+}$ ions, and the destruction of Na precipitates confirmed by T.E.M. observations [13]. However, the decrease of the absorption band area due to metallic precipitates was of 40 % for 4.5×10^{13} Rb $^{+}$ $\cdot$ cm $^{-2}$ whereas it was only of 30 % for 3×10^{14} Na $^{+}$ $\cdot$ cm $^{-2}$. The cross section relative to the destruction of precipitates is thus higher for the heaviest ion (Rb $^{+}$) showing the preponderant effect of atomic collisions.

4. Discussion and conclusion.

Small metallic precipitates embedded into an insulating matrix (MgO) can be destroyed by irradiation with energetic particles. Two processes can produce this aggregate destruction : ionization and elastic collisions. In the region containing the precipitates, the linear nuclear and electronic energy losses of Rb $^{+}$ ions are high (2.8 keV $\cdot$ nm $^{-1}$ and 0.8 keV $\cdot$ nm $^{-1}$ respectively). Therefore the two processes could be responsible for this destruction.

In order to determine which one of these processes is preponderant, we have bombarded a MgO crystal containing Rb precipitates with 2 MeV protons. With such particles, the energy losses, *in the region containing the precipitates*, are mainly electronic. After irradiation with 9×10^{16} protons $\cdot$ cm $^{-2}$ the precipitates are not destroyed : no modification occurs in the optical absorption band associated with rubidium aggregates. The linear electronic energy loss of protons in the region containing the precipitates is about 0.04 keV $\cdot$ nm $^{-1}$. Assuming an homogeneous dissipated energy in the crystal volume containing the aggregates the energy dissipated by electronic process in this region is approximately 3.6×10^{22} keV $\cdot$ cm $^{-3}$ for 9×10^{16} protons $\cdot$ cm $^{-2}$ of 2 MeV energy. This value is higher than the one obtained for 7×10^{14} Rb $^{+}$ cm $^{-2}$ of 2 MeV energy which is about 5.6×10^{21} keV $\cdot$ cm $^{-3}$. These results, clearly indicate that the ionization process is not responsible for the metallic precipitate destruction. They are in agreement with the observations of defect production in MgO and metals [8, 14]. In these materials, defects are not created by an ionization process.

In conclusion, considering the effects of Rb $^{+}$ ion bombardment on small Rb precipitates embedded into MgO, the precipitate destruction seems to be closely related to the nuclear energy losses of the particles in the region containing the aggregates and then to an atomic collision process.

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