

Ion irradiation effects on the formation of metal nanoparticles in crystals

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Abstract. Metal nanoparticles (MNP) were synthesized by room temperature ion implantation of high fluences (from 6×10^{16} to 5×10^{17} cm⁻²) of 150 keV Ag and 15 -22 MeV Au ions into Al₂O₃ and MgO single crystals. Optical absorption (OA) spectra show surface plasmon resonance (SPR) bands characteristic of the implanted metal ions. Upon annealing (300°-1200°C) the optical response of the metal nanostructures changes, related directly to their morphology, shape and size. High resolution transmission electron micrographs indicate that the particles are often crystalline. The implanted ions profiles were obtained from 1.6 MeV He⁺ Rutherford Backscattering (RBS) for the silver implanted substrates and High Resolution Transmission Electron Microscopy (HRTEM), revealed buried layers of implanted ions in the form of MNP.

1. Introduction

A study of properties of colloidal small particles has a long history and there is a large body of theoretical [14] – [19] and experimental work [1] – [13], [20] - [24] in this field of study. Metal nanoparticles can be produced by various methods e.g. chemical vapour deposition (CVD) and among them is ion implantation. Ion implantation produces NP of varying sizes contrary to CVD that offers particles of uniform sizes. Usually metal NPs don't form during irradiation and annealing is required to precipitate implanted metal ions into colloidal particles. Formation of NPs from implanted material requires bombarding the substrate with high fluences of an order 10^{17} ions/cm² depending on the ions used.

2. Experimental details

We have implanted Al₂O₃ and MgO single crystals from MTI and Crystec of different orientations using 150 keV Ag⁺ and C⁺ ions using 200-20A2F Ion Implanter with the Freeman type ion source.

15 MeV Au³⁺ was performed on a Van de Graff tandem accelerator. All implantations were done with no temperature control. A fluence of 3×10^{17} ions/cm² was used for carbon implantation. Au implants were done with $\sim 1 \times 10^{17}$ cm⁻² fluences and silver with a range of doses from 2.9×10^{16} to 5×10^{17} ions/cm².

Annealing was carried out in a Carbolite tube furnace for 1h in 100°C intervals from 300 up to 1200 °C in Ar + 4% H atmosphere and allowed to cool to ambient temperatures. After each annealing step, optical absorption was measured on Varian Cary 500 UV – VIS – IR double beam spectrometer with a non irradiated sample in the reference beam.

RBS spectra were obtained on the van der Graff accelerator using 1.6 - 2 MeV He⁺ beams with Si barrier detector at 165° in IBM geometry.

HRTEM specimens were prepared from crystalline sapphire flakes of the average thickness of 200 nm and diameter 3 – 10 μm, deposited and implanted on TEM carbon film coated grids and analyzed on 400 kV Tecnai F20.

3. Results and discussion

Annealing from 300° to 1100° has removed F- type centres absorption bands from the OA spectra in both materials. Colour centres aggregate upon heat treatment producing optical absorption bands in the visible range of spectrum with peak positions, which correspond to SPR bands of the implanted ions.

In Au³⁺ 15MeV implanted sapphire crystals a band appears at 530 nm (2.3 eV) after annealing at 1000°C. The peak reaches its maximum after 1100°C annealing and the sample acquire pink colour. The peak position is associated SPR of the Au MNP absorption band. (figure 1)

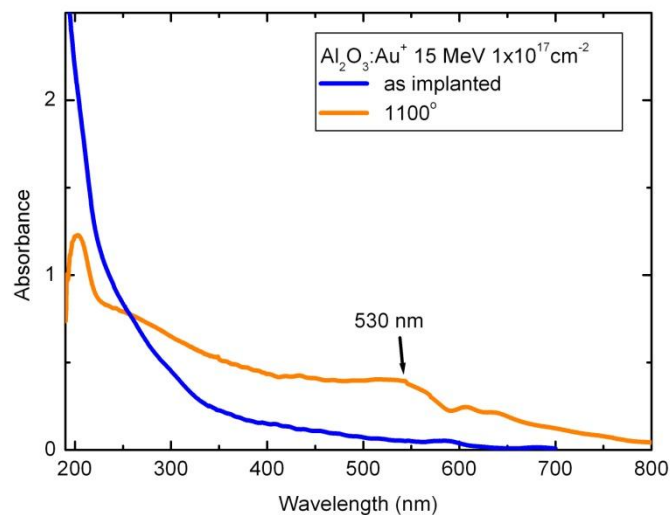


Figure 1. 15 MeV gold implanted sapphire 1×10^{17} ions/cm² as implanted and after annealing and 1100°C in reducing atmosphere.

Al₂O₃ implanted with high fluence of silver ions show a peak at 426 nm (2.9 eV) (figure 2) in as implanted samples, attributed to SPR absorption by silver nanoparticles. Similar behaviour is observed in MgO crystals implanted with Ag⁺ ions

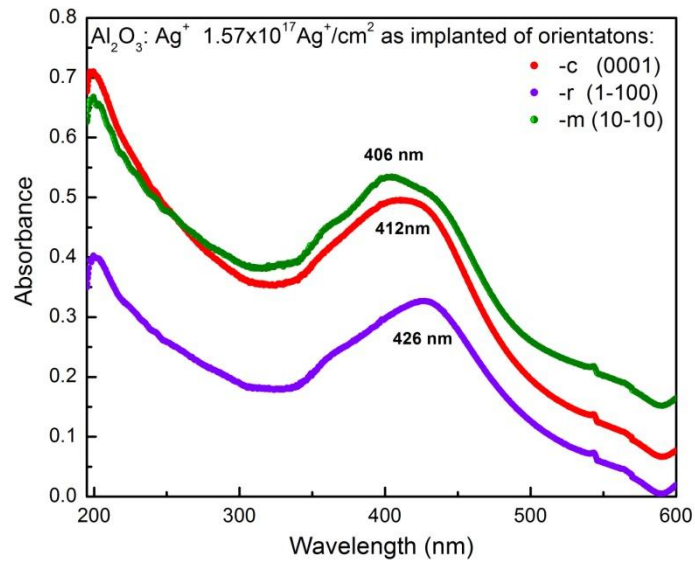


Figure 2. Al₂O₃ with different crystal orientations implanted with high fluence 1.57×10^{17} ions/cm² of silver ions. Peaks at 412 nm and 426 nm are due to the presence of colloidal silver. Spectra were measured in RT from as implanted material.

For lower Ag fluences 2.9×10^{16} Ag ions/cm² in MgO, the band formed only after 1100° C annealing (figure 3).

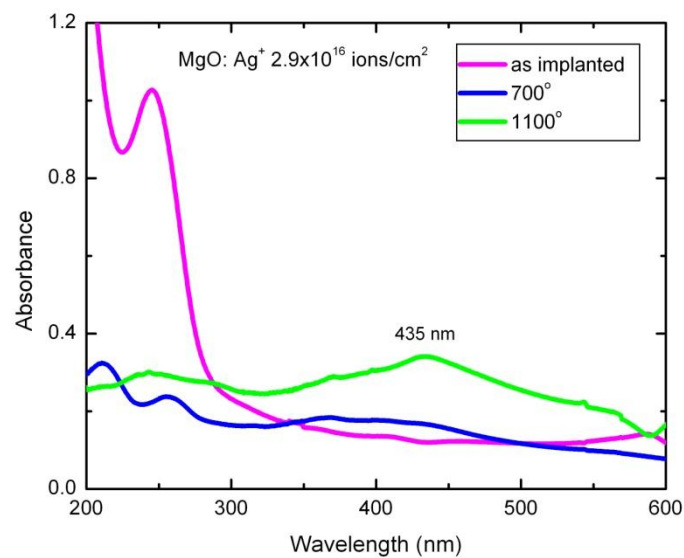


Figure 3. MgO Implanted with 2.9×10^{16} Ag ions/cm² and annealed. SPR band appears after 900°C annealing and has max intensity after 1100°C anneal.

In the $3 \times 10^{17} \text{ cm}^{-2} \text{ C}^+$ implanted sapphire samples the 245 - 260 nm band develops after annealing in forming gas at $700^\circ - 900^\circ \text{ C}$ depending on the sapphire orientation. After the band intensity reaches maximum its position shifts gradually to shorter wavelengths with decreasing intensity. The band origin is possibly due to Mie scattering from carbon nanoparticles [19].

High Resolution TEM micrographs of silver implanted samples indicate the presence of Ag crystalline nanoparticles, whose sizes vary from 3 to 7 nm for as implanted specimens. SAD pattern of implanted sapphire substrate shows that the crystalline structure was preserved. The depth profile obtained from RBS measurement has a maximum at 41 nm, in agreement with SRIM calculations [22].

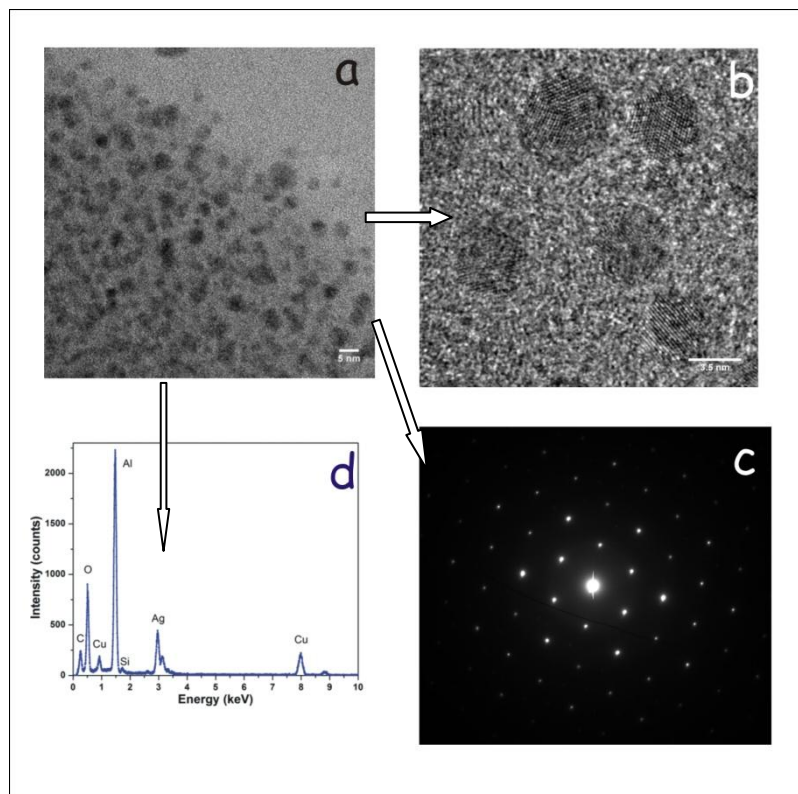


Figure 4. (a) Sapphire substrate with silver nanoparticles after RT ion implantation at high fluence $1 \times 10^{17} \text{ ions/cm}^2$. (b) SAD electron diffraction pattern of sapphire substrate after RT Ag⁺ ion implantation show the crystalline structure. (c) Sapphire implanted with silver ions show the presence of Ag crystalline nanoparticles. The particles with visible lattice fringes are on the carbon support film. (d) EDS spectrum of a silver NP on the implanted sapphire substrate.

4. References

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