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Creation of noble metal nanoclusters in bismuth tellurite

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Abstract

Single crystalline samples of bismuth tellurite were implanted with 800 keV $Au^+$and 450 keV Ag^+ions to fluences between 5×10^{15} and 2.5×10^{16} cm^{-2} at room temperature. The samples were annealed at temperatures of 600 °C for Au, 450 °C for Ag and 500 °C for Au/Ag implanted crystals. Strong optical absorption maxima at about 630 nm yielding Au-implanted samples and at about 570 nm for Ag-implanted samples indicate the formation of noble metal clusters. For Au and Ag co-implanted samples the optical absorption spectrum shows a complex structure with a main maximum around 600 nm which is tentatively associated with mixed Au/Ag clusters. The average cluster radii were calculated to be in the range of 2–10 nm depending on the implanted ion species.

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1. Introduction

Bismuth tellurite (Bi_2TeO_5) is a new material with interesting optical properties for applications in optoelectronic components and lasers [1,2]. The formation of metallic nanoclusters in transparent materials is, due to their unique nonlinear-optical properties, of high technological interest. In a previous work we have demonstrated the creation of Au clusters in this material by ion implantation and subsequent annealing and the dependence of their properties on annealing temperature and ambience [3,4]. The present paper extends the research to the formation of Ag nanoclusters and the effects of co-implantation of Au and Ag on the formation and composition of these particles. Also the influence of the implantated dose on the optical properties of the material is investigated.

2. Experimental details

Bi_2TeO_5 single crystals grown at the Research Laboratory for Crystal Physics in Budapest were cleaved along the (1 0 0) cleavage plane. Implantations with Au an Ag ions were performed at room temperature at the 3.5 MV Tandem accelerator

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and the 400 kV ion implanter of the ion beam laboratory in Porto Alegre. The implantation energies of 800 keV for Au^{2+} and 475 keV for Ag^{+}ensured that the profiles of the implanted ion species are very similar. During the Au- and Ag-implantations beam current densities were limited to $\approx$10 nA/cm^2 in both cases. The projected range and straggling were calculated by SRIM2000 [5] to be 1940 and 760 Å for Au and 1930 and 850 Å for Ag, respectively. The implantation doses range from 5×10^{15} to 2.5×10^{16} cm^{-2}. Besides singly Au- and Ag-implanted samples also Au–Ag co-implantations (Au-implantation first) were performed with doses of 1×10^{16} cm^{-2} for each ion species.

Annealings with a duration of 2 h were performed in a conventional furnace under vacuum at temperatures ranging from 450 to 600 °C. The optical absorption spectra of annealed samples were recorded for the visible spectral range (400–800 nm) using a CARY 5G spectrophotometer.

The damage introduced during the ion implantations and its evolution during the annealing procedures was monitored by Rutherford backscattering (RBS) measurements performed under channeling conditions using a 2.0 MeV He^{+}beam at the 3.1 MV van-de-Graaff accelerator facility at Sacavém. The backscattered ions were detected using silicon surface barrier detectors located at 160° and 180° (annular detector) with respect to the beam.

3. Results and discussion

Fig. 1 shows the 2.0 MeV RBS/channeling spectra of Bi_2TeO_5 implanted with 2.5×10^{16} cm^{-2} Au (as-implanted and annealed at 600 °C) as well as for implantation with 1×10^{16} cm^{-2} Ag (annealed at 450 °C). The spectra for aligned incidence were obtained for the ⟨100⟩ axis of bismuth tellurite. A comparison of the as-implanted spectra for random and aligned incidence clearly indicates the complete amorphization of a 2000 Å thick layer at the surface of the sample. A complete amorphization of the implanted layer was also observed for all other investigated implantation doses and species.

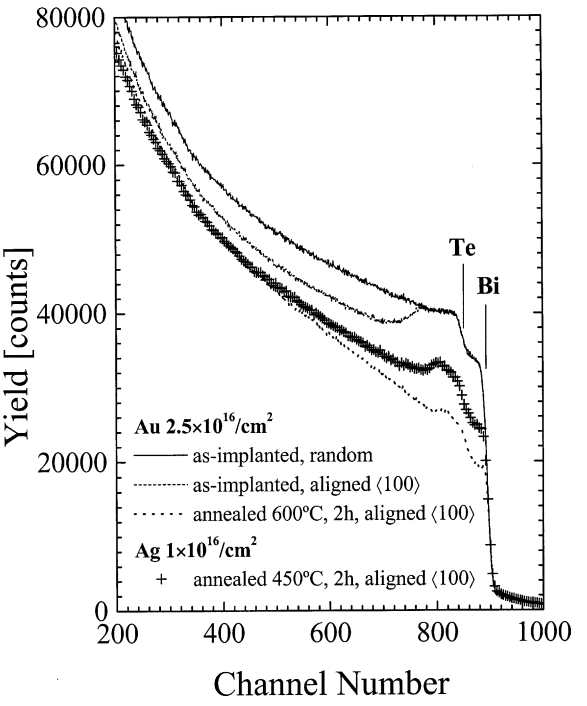

Fig. 1. 2.0 MeV He^{+} RBS/channeling spectra (⟨100⟩) for Bi_2TeO_5 samples implanted with 2.5×10^{16} cm^{-2} Au or 1×10^{16} cm^{-2} Ag in the as-implanted state and after annealing.

Due to the high atomic fraction of Bi in the crystal the RBS signals corresponding to the implanted ions cannot be discerned. For both implanted species annealing significantly reduces the thickness of the damaged layers and a partial recovery of the crystal is achieved. In the case of the Ag-implanted samples the lattice recovery is, due to the lower annealing temperature (450 °C), less pronounced than in the Au-implanted.

Annealing at a temperature of 600 °C for 2 h causes the Au-implanted samples to darken and display a blue–green color associated with the creation of Au nanoclusters. The intensity of the coloration increases with implantation dose. In contrast, Ag-implanted samples annealed at this temperature become completely transparent indicating that the silver has either been completely distributed in the crystal by diffusion or has left the sample due to evaporation. On the other hand, heat treatments of Ag-implanted crystals performed at 450 °C yield a pink coloration that also

intensifies with increasing fluence. These results show that silver has a much higher mobility in bismuth tellurite than observed for Au [3]. The Au/Ag co-implanted sample, which was annealed at 500 °C in order to avoid excessive diffusion of Ag on the one hand and assure sufficient mobility of Au on the other hand exhibits a violet hue.

Fig. 2 depicts the optical absorption spectra of a virgin and noble metal implanted Bi_2TeO_5 crystals after annealing in the visible spectral range (400–800 nm). The Au-implanted crystals with implantation doses of 1 and 2.5×10^{16} cm^{-2} annealed at 600 °C, respectively show a clear peak in the region of 630 nm. For the highest implantation dose a higher absorption and a larger half-width of the peak is observed. In contrast, for the lowest Au-implantation dose no peak can be detected although the samples show a weak blue–green coloration. The absorption maxima for the samples implanted with Ag and annealed at 450 °C are located around 570 nm and show no variation in their width. Again the absorption increases with implantation dose.

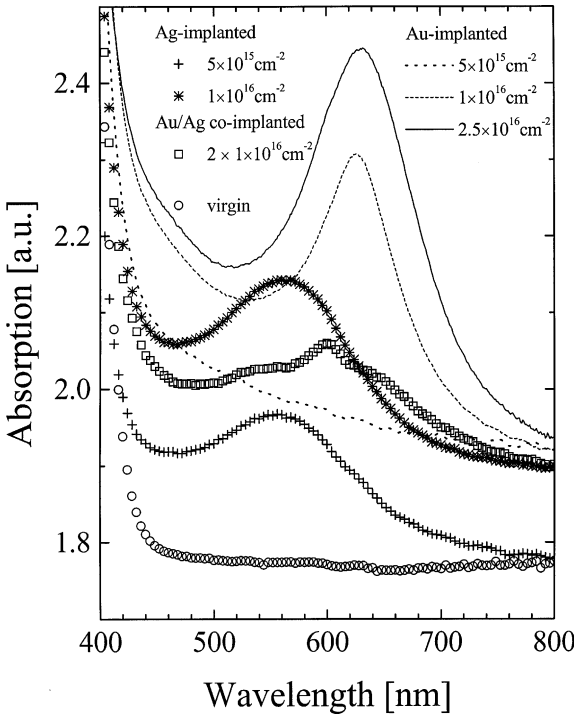

Fig. 2. Optical absorption spectra in the visible spectral range for virgin Bi_2TeO_5 and after Au, Ag and Au/Ag co-implantation and annealing for 2 h in vacuum.

The Au/Ag co-implanted sample annealing at 500 °C exhibits a more complex absorption structure. From the best fit to the absorption spectrum a main peak is found at about 600 nm, 30 nm from the absorption maxima of Au and Ag and two other maxima at about 550 and 640 nm. These findings point to the existence of three main types of clusters that may be associated with Au/Ag mixed clusters for the main peak and pure Ag or Au clusters for the additional peaks.

Assuming that a major fraction of the implanted noble metal ions is incorporated into clusters and that the mean free path of the free electrons in the gold and silver are larger than the size of the clusters the average radius R of the clusters can be estimated to be [6]

$$R = \frac{V_F}{\Delta\omega_{1/2}}, \tag{1}$$

where V_F is the Fermi velocity of the metal and $\Delta\omega_{1/2}$ the half width of the absorption peak. For the absorption spectra of the samples annealed at 450 and 600 °C the shape and height of the absorption peaks allow to determine these parameters. Table 1 lists the positions of the absorption peaks, their half widths and the values of the cluster radii derived using Eq. (1). The results show that the average cluster size induced by implantation of 2.5×10^{16} cm^{-2} Au is smaller than for 1×10^{16} cm^{-2} Au. Both effects, cluster growth and shrinking with implantation dose, have been regularly observed for noble metal cluster formation in insulators (e.g. [8]). Increasing the ion implantation dose can lead either to the growth of more clusters with smaller size due to the larger number of nucleation centers existing or to the growth of larger clusters due to the higher metal concentration achieved. Which effect is governing in a certain case depends mainly on the annealing temperature. The Ag-implanted samples show smaller cluster radii that are comparable to those obtained by annealing of Au-implanted samples at a similar temperature [3]. The red shift of the absorption peaks observed in the singly implanted crystals is due to the increase in the volume fraction occupied by the noble metal clusters [7].

Table 1
The wavelength of the optical absorption maximum, its half-width and the average cluster radii derived for different implants and fluences

Implanted ion	Annealing temperature	Dose (10^{15} cm^{-2})	Absorption peak position (nm)	$\Delta\omega_{1/2}$ (10^{14} Hz)	Average cluster radius (nm)
Au	600 °C	5	–	–	–
		10	628	3.0	4.6
		25	633	4.1	3.4
Ag	450 °C	5	564	5.5	2.5
		10	570	5.6	2.5
Au + Ag	500 °C	2×10	553	7.9	1.8
			599	1.4	9.8
			642	2.3	6.0

For the Au/Ag co-implanted clusters the Fermi velocity was assumed to be the average of those of Au (1.39×10^6 m/s) and Ag (1.40×10^6 m/s). The average cluster size calculated for the main peak, which was tentatively be associated with mixed Au/Ag clusters, is much larger than for any of the singly implanted cases. A possible creation mechanism is the growth of Au nanoclusters by indiffusion of the more mobile Ag which would also explain the smaller size of the Ag clusters associated with the peak at about 550 nm.

4. Conclusions

The formation of noble metal nanoclusters in bismuth tellurite samples implanted with 800 keV $Au^+$and 450 keV Ag^+ions was observed in singly and co-implanted samples by the use of optical absorption measurements in the visible spectral range. In the co-implanted case indications for the occurrence of mixed Au/Ag clusters were found. Variation of the implanted dose ratio of the two ion species and of annealing conditions may open a path to taylor of the optical properties of nanoclusters in this material.

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