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Electrical transport studies of Ag nanoclusters embedded in glass matrix

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Abstract

Silver nanoclusters embedded in glass matrices have been obtained by the combined use of ion exchange and subsequent ion implantation. XRD and UV-visible spectro-photometric analysis have confirmed the formation of Ag nano-clusters in the ion-irradiated samples. Temperature-dependent resistivity measurements of the irradiated samples have been found to follow $\rho(T) \propto \exp\sqrt{(T_0/T)}$ in the temperature range of 80–280 K. The observed behaviour of $\rho(T)$ is consistent with charge transport due to hopping between isolated, conducting islands. The separation distance between the conducting islands has been found to be a function of fluence.

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1. Introduction

The physics of metal clusters having nanodimensions embedded in dielectrics has attracted considerable attention in recent years because of their novel properties and their potential applications in non-linear optics [1,2]. The non-linear response of glasses may be enhanced by several orders of magnitude by introducing small metal or semiconductor clusters and thus, nanocrystal doped planar wave guides may be used in all-optical switching components.

The DC electrical transport of granular systems has been a subject of intensive experimental and theoretical studies for more than three decades. The electrical transport mechanism for granular systems of metallic nanoclusters embedded in dielectrics is of fundamental interest [3–5]. Many experimental studies [6–10] on granular systems show a temperature dependence of resistivity as

$$\rho(T) \propto \exp\sqrt{(T_0/T)} \tag{1}$$

Sheng et al. [3], using an optimal percolation path, have derived such a formula for granular metals by considering the effect of charging energy $E_c = E_c(d, s)$ on the conductance of paths linking grains of separation s and diameter d. They make the assumption that s and d are correlated in such a way that the ratio s/d is essentially constant throughout the specimen. Later, Simanek [4] using the percolation method derived Eq. (1) without

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assuming any correlation between d and s. Further, he has also taken into account the contribution to the activation energy from the energy level splitting due to the finite size of the grains, apart from the usual electrostatic charging energy, E_c. Later on Sheng and Klafter [9], have shown the role of 'site energy' in introducing correlated Coulomb gap.

In this paper, we report temperature-dependent resistivity studies of Ag nanoclusters in a glass matrix formed by ion exchange and subsequent ion irradiation. We have analysed our experimental results in the light of existing models of hopping transport in granular systems. The presence of Ag clusters has been probed using glancing angle X-ray diffraction (GIXRD) and ultra-violet-visible (UV-Vis) spectro-photometric studies.

2. Experimental details

Ion exchange is a well-known method for introducing ions such as Ag^+ or K^+ into Soda glass. The composition of the glass used in the present experiment is Si–21.49%, Na–7.1%, Ca–5.78% Mg–0.34% and Al–0.15% by weight. Ag^+–Na^+ ion exchange was performed by dipping soda lime glasses in a molten salt bath of $AgNO_3$ (0.2 N) in $NaNO_3$ for a few minutes. The bath was stirred to assure uniform concentration of Ag and the exchange temperature was in the range of 320–350°C. These samples were irradiated with 100 keV helium ions for various fluences in the range of 2×10^{17}–1×10^{18} ions/cm^2. Implantations were carried out at room temperature at a pressure of 5×10^{-7} mbar. The samples were irradiated with current density lower than 2 μA/cm^2 to avoid heating effects.

Glancing incidence X-ray diffraction (GIXRD) studies were performed using Cu K_α radiation with an incidence angle of 0.3°. Optical absorption spectra were recorded in the wavelength region of 1000–300 nm, by using a Shimadzu ultraviolet-visible-near infra-red (UV-VIS-NIR) dual beam spectrometer. Temperature-dependent resistivity studies have been performed in the irradiated samples in the temperature range of 80–280 K.

3. Results and discussion

3.1. Crystallographic structural studies

GIXRD studies confirmed the formation of silver nanocluster during ion irradiation. Fig. 1 shows the GIXRD pattern of pristine ion-exchanged and irradiated samples at various fluences. No signature of Ag in the pristine sample has been observed in the GIRXD analysis [Fig. 1 curve (a)]. However, signature of Ag has been observed in the irradiated samples. Curves (b)–(d) in Fig. 1 show four peaks at 2θ values of 38.2°, 44.5°, 64.5° and 77.7° corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of silver, respectively. Peaks are broadened due to the nanocrystalline nature of Ag. The average particle diameter was calculated using Scherrer's formula

$$d = 0.9\lambda/\mathrm{FWHM}^*\cos 2\theta(\mathrm{peak}), \quad (2)$$

where λ is the wavelength of X-radiation (Cu $K_\alpha = 1.540$ Å), FWHM* is the full width at half-maximum of XRD peak in radians corresponding to the peak at 2θ. The average size of the Ag clusters for all the fluences was found to be around ≈ 10 nm.

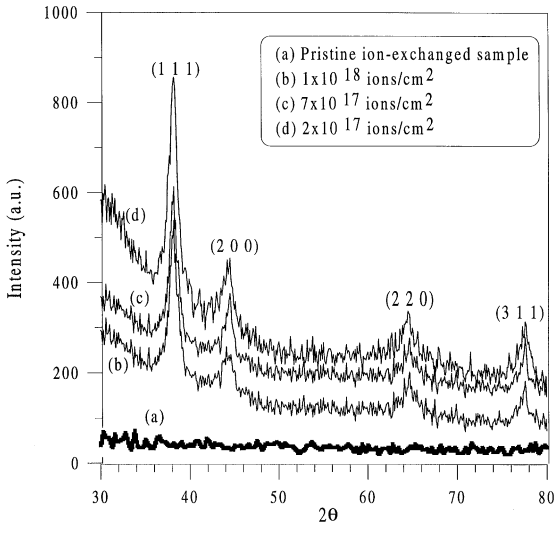

Fig. 1. XRD spectra of the ion exchanged and irradiated samples at various fluences.

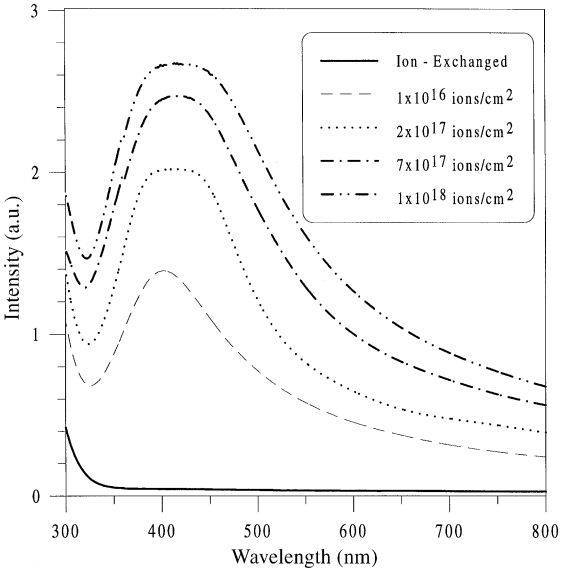

Fig. 2. Optical absorption spectra of ion exchanged and irradiated samples at various fluences.

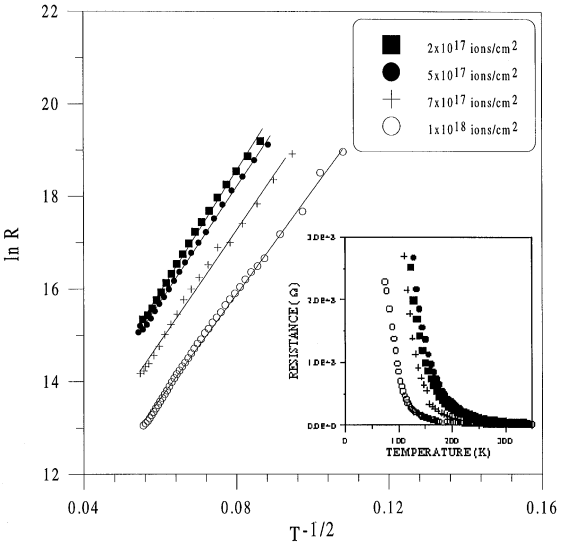

Fig. 3. Plot of ln R versus $T^{-1/2}$ at various fluences. The inset shows resistance versus temperature plot.

3.2. Optical absorption studies

The optical absorption spectra of Ag exchanged samples and irradiated samples with helium ions at different fluences are shown in Fig. 2. The samples display an optical absorption band peaked at about 410 nm (~ 3 eV), typical of absorption at metallic Ag nanoclusters, due to the surface plasmon resonance (SPR) [10]. This absorption band is consistent with the reported value for Ag nanoclusters [2,10,11]. Fig. 2 also shows that the peak intensity increases with the helium fluence, without any significant modification in the corresponding maximum wavelength position. It is also known that the volume fraction of the clusters is proportional to the area under optical absorption curve. For grain sizes smaller than the optical wavelength, the optical absorption coefficient [12] can be expressed as

$$K\,(\mathrm{cm}^{-1}) = 18\pi Q n_{\mathrm{d}}^{3/2}/\lambda[\varepsilon_2/(\varepsilon_1 + 2n_{\mathrm{d}}^2)^2 + \varepsilon_2], \quad (3)$$

where Q is the volume fraction occupied by the metallic particles, n_{d} is the refractive index of the host medium, ε_1 and ε_2 are the real and imaginary parts of the dielectric constant of the bulk metal and λ is the optical wavelength corresponding to SPR peak. From Eq. (3) the volume fraction of the Ag particles is calculated and found to be increasing from 9.84% to 13% at fluences of 2×10^{17}–1×10^{18} ions/cm^2.

3.3. Electrical transport studies

Temperature-dependent DC transport properties of irradiated samples in the range of 80–280 K show an increase in resistance with decreasing temperature, indicating semiconductor-like (non metallic) behaviour (inset of Fig. 3). The DC resistivity of embedded metal clusters in insulating matrix is reported to follow the temperature dependence described by Eq. (1). This expression is derived for thermally activated hopping conduction of charge carriers in discontinuous metal islands embedded in an insulating matrix. Fig. 3 shows the ln(R) versus $T^{-1/2}$ plot for the samples irradiated at fluences in the range of 2×10^{17}–1×10^{18} ions/cm^2, showing a good fit to the experimental data.

In deriving Eq. (1), Simanek [4] assumed the concept of the activation energy containing two parts, viz., E_{c} the usual electrostatic energy for intergrain hopping and E_{d} the intragrain hopping

due to the energy level splitting of grains with finite size. For metallic grains of size d with infinite potential barrier, the energy of dimensional quantization is expressed [6] as

$$E_d = (h/2\pi)^2 \varphi_{l,n}^2/2md^2, \quad (4)$$

where m is the electron mass and $\varphi_{l,n}$ is the universal set of numbers dependent on the momentum l and the principal quantum number n, but independent of d. In the present study, restricting our consideration to the lowest level ($l = 0$, $n = 1$) in each grain, we obtain $E_d = 0.0038\,\text{eV}$ and $E_c = 0.0544\,\text{eV}$ and hence variation due to E_d can be neglected.

Further in the present experiments, Ag nanoclusters are formed by irradiation-induced agglomeration of Ag atoms introduced into the glass matrix by ionexchange. Since the concentration of Ag in the ion-exchanged glass was uniform prior to irradiation, it is expected that s/d will be constant throughout the sample following the argument of Sheng et al [3]. Thus, the model proposed by Sheng et al. [3] is applicable for the present study.

According to the model proposed by Sheng et al. [3], the characteristic temperature of the conductivity, T_0 is given by

$$T_0 = 4\chi s E_c/k_B, \quad (5)$$

where k_B is the Boltzmann's constant and $\chi = [2m^*\varphi/(h/2\pi)^2]^{1/2}$ is the effective inverse tunneling width. Here, m^* is the effective mass of the charge carrier, is φ the energy barrier over which the charge must hop, h is Planck's constant and

$$E_c = 2q^2 s/[\kappa d^2(1/2 + s/d)], \quad (6)$$

where E_c is the electrostatic energy needed to remove a charge from a neutral particle and place it on another particle. κ is the permittivity of the insulating material and q is the electronic charge. T_0 can be obtained from the slope of the temperature-dependent resistivity plot. The s/d value can be calculated from Eqs. (5) and (6) by taking the value of φ, the barrier energy for the insulating matrix of glass to be 4 eV from optical measurement and d, the average size of the Ag cluster from GIXRD analysis ($\approx 10\,\text{nm}$). The fluence, T_0, s/d and s values are tabulated in Table 1.

Table 1
Calculated parameters

Fluence (ions/cm^2)	T_0 (K)	s/d	s (nm)
2×10^{17}	16952	0.05877	0.5877
5×10^{17}	15178	0.05561	0.5561
7×10^{17}	13829	0.05308	0.5308
1×10^{18}	2780	0.05102	0.5102

Decreasing value of T_0 (and therefore s/d as obvious from Eqs. (5) and (6) with increasing ion fluence (Table 1) indicates reduction in separation between Ag clusters as d does not change with fluence. This indicates increase in cluster density with increasing fluence which is also substantiated by the optical absorption studies where the peak intensity of SPR scales up with fluence as an indication of increasing cluster density [11].

4. Conclusion

In summary, we conclude that Ag cluster with an average size of $\sim 10\,\text{nm}$ was grown with ion irradiation on Ag^+-exchanged glass. Temperature-dependent DC transport properties of Ag clusters show activated tunneling mechanism to play a major role. The detailed analysis of the temperature-dependent transport properties shows the increase in cluster density with increasing fluence.

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