Shape deformation of embedded metal nanoparticles by swift heavy ion irradiation

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ABSTRACT

Swift heavy ions (SHI) induce high densities of electronic excitations in narrow cylindrical volumes around their path. These excitations have been used to manipulate the size and shape of noble metal nanoparticles embedded in silica matrix. Films containing noble metal nanoparticles were prepared by magnetron co-sputtering techniques. SHI irradiation of films resulted in the formation of prolate Ag nanoparticles with major axis along the ion beam direction. It has been observed that the nanoparticles smaller than the track size dissolve and other grow at their expense, while the nanoparticles larger than track size show deformation with major axis along the ion beam direction. The aspect ratio of elongated nanoparticles is found to be the function of electronic energy loss and ion fluence. Present report will focus on the role of size and volume fraction on the shape deformation of noble metal nanoparticles by electronic excitation induced by SHI irradiation. The detailed results concerning irradiation effects in silica–metal composites for dissolution, growth and shape deformation will be discussed in the framework of thermal spike model.

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1. Introduction

The confinement of light is a very important and current challenge for nano-dimensional integrated optical devices, near-field optics and nanophotonics. Noble metal nanoparticles are attractive in this field because of their surface plasmon resonance (SPR), which couples with electromagnetic fields and leads to interesting properties such as a transmission in a selected wavelength range [1], a nonlinear optical response [2], and a highly localized field enhancement [3,4]. Therefore, noble metal particles have great potentials as elements of biosensor [5], nanophotonic devices [6,7], and plasmonic devices [8]. These with anisotropic shapes are interesting because their polarizability depends on the filed orientation. For large aspect ratios, plasmon band may shift well into the infrared along the major axis, making the particles useful for telecommunication applications. In addition, anisotropic particles show a reduced plasmon resonance time and longer dephasing time as compared to spherical particles. The particle size, shape or spatial distribution can be modified by thermal annealing [9], ion irradiation [10–12] and laser treatment [9,13,14]. Swift heavy ion (SHI) irradiation of amorphous materials leads to an anisotropic deformation, known under the name of hammering.

In a study of SHI effects on silica colloidal particles encapsulating cores of Au (with smaller sizes), it has been found that the silica shells expanded perpendicular to the ion beam direction and compressed parallel to the beam, becoming oblate ellipsoids. On the contrary, the Au core underwent an elongation parallel to the ion beam by a creep process, because they are heated and compress by the matrix at same time [15]. In another study on ion-exchanged glasses containing Ag nanoparticles with a filling factor of a few % and sizes of 5–10 nm, SHI induced an alignment of the particles [16]. In the present paper we are reporting a change in shape from spherical to ellipsoidal by electronic excitations induced by heavy ion irradiation at lower ion fluences. This is the detailed report using transmission electron microscopy (TEM) on the elongation of silver nanoparticles in contradiction to the work of Penninkhof et al. [17] that embedded silver particles cannot be elongated like Au nanoparticles [17,18], but in accordance with work of Oliver et al. [19].

2. Experimental details

Silica films containing silver nanoparticles with a volume fraction of 3–6 at.% were grown by magnetron co-sputtering on silicon substrates. The as-deposited films were annealed at 950 °C for 1 h under Ar + H₂ (5%) in a continuous flow tubular furnace for growing particles without oxidation. Annealed samples were irradiated,

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using 15UD Tandem Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi, with 120 MeV Au ions in high vacuum chamber with a base pressure of 3.2×10^{-6} torr. The beam current was kept constant ~0.5 pna (particle nano ampere) during the irradiation. These ions loose 13.91 and 33.53 keV/nm in electronic excitations in silica and silver, respectively, as determined from SRIM code. The samples were irradiated with an ion beam 45° off normal at fluence of 3×10^{13} ions/cm². Cross sectional TEM investigations were carried out using JEOL 2010 UHRTEM facility at Institute of Physics, Bhubaneswar.

3. Results

Fig. 1(a) shows the TEM micrograph of silver nanoparticles after annealing at 950 °C and the corresponding histogram of sizes is shown in Fig. 1(b). They clearly reveal that the particles are spherical with a narrow size distribution of particles. The mean particle size and size straggling calculated by fitting the data with a Gaussian distribution are (9.6 ± 1.5)nm. The inset of Fig. 1(a) also shows a high-resolution micrograph of a particle, evidencing its crystallinity and the measured lattice parameter, of 0.206 nm, corresponds to the (002) spacing of fcc Ag. A change from spherical to ellipsoidal shape of the silver nanoparticles is observed after irradi-
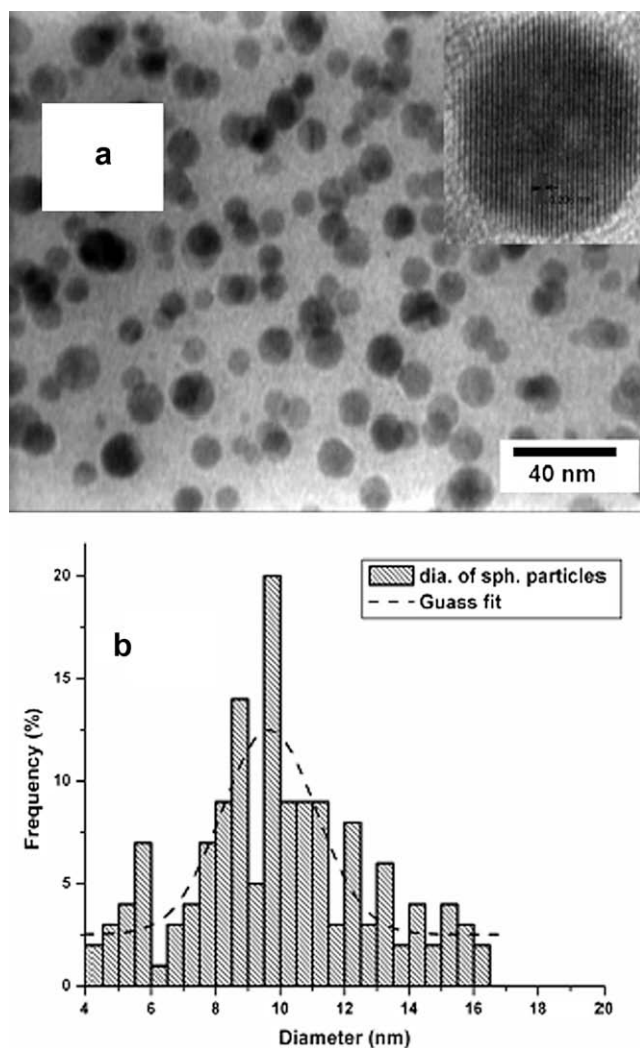
Fig. 1. (a) Cross sectional TEM micrograph of pristine silica film containing silver nanoparticles (Inset shows the HRTEM image of one nanoparticle). (b) Histogram of particles size distribution. Dashed line shows the Gaussian fit to size distribution.

ation, with the long axis of the ellipsoids aligned along the ion beam direction, as shown in Fig. 2(a) for the irradiation fluence of 3×10^{13} ions/cm². The high-resolution TEM micrograph of Fig. 2(b) shows that the particles remain crystalline with a lattice parameter of about 0.212 nm (the arrow in the image indicates the direction of ion beam, perpendicular to the film surface). The mean particle size for this fluence of 120 MeV Au ions is 13.9 ± 1.7 nm along the major axis and 9.4 ± 1.7 nm along the minor axis, as determined from histograms of size shown in Figs. 2(c) and (d), and their average aspect ratio is about 1.47. Further, the comparison of histograms in Figs. 1 and 2 also puts into evidence that the smallest particles disappear after ion irradiation, while the mean size of nanoparticles increases. This result seems to indicate that the electronic excitations induce the dissolution of nanoparticles smaller than the ion track in silica (of which diameter will be specified latter) whereas larger ones grow and get elongated along the beam direction in accordance with previous works on other systems [18–22].

4. Discussion

The mechanism of the observed shape changes can be explained by the high density of electronic excitations induced by SHI, of which energy is transmitted to the lattice by several processes [23]: Coulomb explosions [24,25], thermal spikes [26,27] and hammering [28,29]. The preponderance of each one depends on the electronic structure and is a subject of discussion, especially in the case of composite systems. Coulomb explosions occur mainly in insulators, due to the ejection of secondary electrons with high energies out of the core of each ion track (cylindrical volume with a radius of a few nm). However, most of the authors consider that the agitation of target atoms by electron phonon coupling is more significant, as it lasts for a longer time than electrical perturbations and takes place in targets of any nature [27]. The calculations of thermal exchanges between the electronic and atomic systems during these pseudo-thermal spikes have been used to explain the differences of radiation resistance of metal, semiconductors and ionic insulators [30]. The solution of equations for targets made of a matrix embedding an isolated particle is expected to put into evidence a phenomenon of transient overheating of the particle, if it is a better conductor of heat than the matrix.

4.1. Simulations

Simulations of thermal spikes for a system with a single particle at the origin at coordinates (of cylindrical type r, y as shown in Fig. 3) were performed by solving the following coupled differential equations, which describes the temperature evolution in the electronic and atomic subsystems of the materials [26,31]:

$$C_e \rho \frac{\partial T_e(\vec{r}, t)}{\partial t} = \vec{\nabla} \cdot (K_e \nabla T_e(\vec{r}, t)) - g(T_e - T_a) + A(\vec{r}, t),$$

$$C_a \rho \frac{\partial T_a(\vec{r}, t)}{\partial t} = \vec{\nabla} \cdot (K_a \nabla T_a(\vec{r}, t)) + g(T_e - T_a),$$

where C_e, K_e and T_e are the specific heat, thermal conductivity and temperature of electronic subsystem, while C_a, K_a and T_a are the specific heat, thermal conductivity and temperature of the atomic subsystem. ρ is the mass density of the lattice and g is the electron–phonon coupling constant. $A(r,t)$ is the energy density per unit time provided by the incident ions to the electronic subsystem at radius r and time t. Heat transfers from the electrons to the lattice via electron–phonon coupling and propagates simultaneously in the different subsystems.

Fig. 3(a) shows the temporal profile of temperature at the center of silver metal particles with different sizes of 2–30 nm