Thin Solid Films 527 (2013) 186–192

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Elongation of gold nanoparticles by swift heavy ion irradiation: Surface plasmon resonance shift dependence on the electronic stopping power

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ARTICLE INFO

Article history:
Received 3 August 2011
Received in revised form 27 October 2012
Accepted 7 December 2012
Available online 19 December 2012

Keywords:
Nanoparticle
Shape transformation
Shift heavy ion irradiation
Surface plasmon resonance
Ion track

ABSTRACT

Gold nanoparticles embedded in a silica matrix were irradiated with 2 to 40 MeV Cu or Si ions at fluences ranging from 1×10^{13} to 4×10^{15} ions/cm^2, and their deformation from spheres to prolate ellipsoids with major axis parallel to the ion beam was studied using *P* and *S* polarized light. For fixed ion energy, the longitudinal surface plasmon resonance (SPR) at 520 nm is red-shifted with an increase of the ion fluence up to a certain value where it reaches a plateau indicating that a maximum aspect ratio is obtained. This saturation in the wavelength shift was found to depend on the ion energy and reaches a maximum of 40 nm. The SPR shift was also used to measure the electronic stopping power dependent deformation rate and to deduce the electronic stopping power threshold of (1.9 ± 1.3) keV/nm required for shape transformation of the embedded gold nanoparticles. Ion track diameters of 0.18 to 1.4 nm were inferred from the fluence dependence of the SPR shift. Analysis by transmission electron microscopy shows that large ($d>10$ nm) particles are more elongated than smaller ones. Our data are consistent with a mechanism of gold nanoparticle elongation requiring both the silica matrix and the nanoparticles to melt following the passage of the swift heavy ion and with elongation being due to the relief of stress in the gold nanoparticle which had built up as a consequence of the deformation of the surrounding silica matrix.

1. Introduction

Ion irradiation produces many effects on condensed matter such as anisotropic deformation at constant volume of single colloidal particles [1,2] and glass foils [3,4], wafer curvature of thin films constrained on substrates [5–7], densification [6] and phase transformation [8]. Among these examples, we investigated previously the spherical gold–silica core–shell colloid system [9]. The silica shells were shown to transform into oblate ellipsoids with its minor axis parallel to the ion beam whereas the gold cores deformed into prolate ellipsoids with its major axis parallel to the ion beam. Simply put, the silica shell shrinks in the direction of the ion beam whereas the gold core elongates. In order to go beyond an incomplete description of this process, we have prepared and investigated Au nanoparticles embedded in silica films [10–12] as it was shown that Au particles deform more efficiently if the surrounding silica shell is thick [9] and not at all when surrounded by a non-deforming crystalline matrix such as AlAs [13]. The mechanism responsible for the deformation of the nanoparticles has not been uniquely identified, but it appears that both anisotropic deformation of the surrounding matrix [1,9,14,15] and melting of the nanoparticle play an essential role [15–18]. The electronic, magnetic, and optical properties of metallic nanoparticles embedded in a dielectric matrix are very interesting and depend strongly on the nanoparticle size, shape, orientation, interparticle distance, and environment [10,12]. The fabrication, modification, and characterization of these heterogeneous nanocomposite materials is an active field of research motivated by the potential applications in optical and optoelectronic devices [19,20], biosensing [21], and in medical applications [22].

When ions are slowed down in condensed matter they deposit a vast amount of energy within a small material volume, during a short time. This energy is lost via two distinct mechanisms: i) elastically by scattering of the projectile on the target nuclei, and ii) inelastically by ionization and electronic excitation of target atoms [3,23]. Both mechanisms strongly depend on the kinetic energy of the incident ion. For high energy heavy ions, electronic interactions dominate and the ion loses energy at a rate of a few to a few tens of keV per nm. During a short period of time, the system within a small localized region around the ion trajectory is far from equilibrium due to a high density of highly excited electrons. These electrons are initially accelerated towards the center of the ion track and will either undergo scattering or overshoot the track center and end up moving outward while an energy transfer to the atomic network takes place. This energy transfer was explained by two models: the thermal spike model [24–26] and the ion spike model, also known as Coulomb explosion [27,28]. In the first model, the energy is thermalized by electron–phonon coupling and leads to the increase of local temperature. In the second one, kinetic energy of electrons allows them to move far from the ion track leaving behind a cylinder of positively charged ions. The mutual electric repulsive forces between the positive ions lead to ionic Coulomb explosion. Hybrid

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0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2012.12.007

models have also been proposed [29,30] and validated by simulations [31].

The deposited energy during ion irradiation can affect the crystalline structure, the morphology and other properties of irradiated materials. In particular, amorphous targets can suffer macroscopic deformation, known as anisotropic growth or ion hammering, whereby a thin film becomes thinner and wider upon ion irradiation. This plastic deformation process has been described by a viscoelastic model [32,33] and a hammering model [34,35]. In the first model, the phenomenon is attributed to energy loss and it occurs efficiently at high electronic stopping powers. For intense electronic excitations a cylindrical region around the ion trajectory is heated and the shear stresses induced by the thermal dilatation are relaxed. The residual strains freeze-in upon cooling down. In the second one, a computer simulation of relaxation of mechanically polarized material is used to estimate the plastic flow. The viscoelastic model and ion hammering explain the deformation of amorphous colloids but not the resistance to deformation of crystalline ones. Other models were also proposed to explain material plastic deformation like: Ostwald ripening and creep deformation [36], and generation–relaxation of stress [6].

The viscoelastic model does not explain the deformation of core–shell colloids or nanoparticles embedded in an amorphous planar matrix. However, from the earliest observation of nanoparticle deformation it has been surmised that the visco-elastic response of the matrix plays an important role [1,9,14,15] and thermal spike models involving melting of the nanoparticle have been invoked as well [15–18]. In the current paper, we present experimental results that shed more light on possible physical deformation mechanisms of gold nanoparticles embedded in a silica matrix. We will show by modeling the SPR spectral position that the anisotropic deformation induced by ion irradiation can be controlled by the fluence, the energy and the nature of the ion beam. We will focus our attention on the role of the electronic stopping power in the modification of the optical and structural properties of gold/dielectric nanocomposite films.

2. Experimental methodology

Gold/silica nanocomposite films were deposited on fused silica substrates by simultaneous sputtering of a pure gold target and plasma-enhanced chemical vapor deposition of SiO_2 using a SiH_4–O_2 gas chemistry. High temperature (900 °C) annealing in ambient atmosphere for 9 h was used in order to increase the size of gold particles. These two preparation steps were studied and described in detail earlier [10].

A series of identical samples (~200 nm thick and 1.8 at.% gold concentration) were irradiated with 2 to 40 MeV Si and Cu ions accelerated using Tandem or Tandetron accelerators. During the ion implantation, the samples were mounted on a liquid nitrogen-cooled copper block but on a few occasions the samples were irradiated at room temperature. Irradiating at liquid nitrogen temperature may lead to slightly faster quenching rates, and to more efficient freezing-in of metastable features. All samples were implanted at 45° off the surface normal. The ion beam was electrostatically scanned to uniformly irradiate several areas (0.5×1.5 cm^2) of the same sample. The base pressure during ion irradiation was 1×10^{-6} Torr (1.33×10^{-4} Pa). The ion beam fluence ranged from 1×10^{13} to 4×10^{15} ions/cm^2. The beam flux was maintained between 6×10^{10} and 8×10^{11} ions/(cm^2.s). The initial charge state of ions varied from Si^+ to Si^{7+} and from Cu^{2+} to Cu^{7+}. The SRIM code [37] was used to calculate the projected ranges R, the electronic and nuclear energy losses in silica for different irradiating ions (Si and Cu), and energies (2 to 40 MeV). We assumed a SiO_2 density equal to 2.32 g/cm^3. The results confirm that the projected ranges are much larger than the Au/SiO_2 film thicknesses for all used energies. This means that most of the ions will end their trajectory in the substrate region, after irradiating the nanocomposite throughout its thickness. For each energy value, the electronic energy loss is considerably greater than the nuclear energy loss. Therefore, most of the engendered morphological and structural modifications in irradiated nanocomposite samples will result from electronic interactions.

The optical response and microstructural properties of gold nanoparticles before and after irradiation were investigated. Polarized transmission measurements were performed on a variable angle spectroscopic ellipsometer (J.A. Woollam). Transmission electron microscopy (TEM) observations were carried out using a JEOL JEM 2100F transmission electron microscope operating at 200 kV and equipped with a Gatan imaging filter and scanning (STEM) mode. The examined specimens were prepared in cross-sectional orientation using a conventional technique for mechanical polishing and ion thinning. The ion thinning was performed using a Precision Ion Polishing System.

3. Results and discussion

3.1. Size/shape versus fluence correlation

Fig. 1 shows cross-section TEM pictures of Au/SiO_2 nanocomposite films after irradiation with 8 MeV Cu^{+3} ions at two fluences: 2.5×10^{14} and 1.5×10^{15} ions/cm^2. One can see that spherical and ellipsoidal gold particles are present in both irradiated samples. The deformation is more marked in the high fluence case (Fig. 1b). The long axes of the ellipsoidal nanoparticles are aligned with the direction of the ion beam, indicated by an arrow in each of the two panels. We have measured the long (c) and short (a) axes of each ellipsoidal gold nanoparticle and calculated an effective particle diameter ($2r_{eff}$) corresponding to the diameter of a sphere of same volume ($^3/_4\pi a^2 c = {}^3/_4\pi r_{eff}^3$). The aspect ratio ($c/a$) was evaluated and plotted versus $2r_{eff}$ before and after irradiation with 8 MeV Cu ions in Fig. 2. In non-irradiated samples, all gold particles are spherical and their size does not exceed 14 nm. After irradiation the shape of the majority of the metallic particles changes from spherical to ellipsoidal ($c/a \neq 1$) with different aspect ratios. The maximum aspect ratio and effective particle size observed at a fluence of 2.5×10^{14} ions/cm^2 are smaller than those obtained for 1.51×10^{15} ions/cm^2. Fig. 2 also shows that the most elongated particles are those which have the largest effective size and that most of those which remain spherical are small, and that no particles smaller than 4 nm deform. Other reports found that particles smaller than 5 and larger than 50 nm don't deform [16] or that a deformation threshold of 7 nm exists [18], but in both of those studies, samples were presumably irradiated at room temperature. The volume of the majority of particles increases with ion fluence, which was of course not observed in our earlier experiments involving core–shell colloidal particles [9] but has been observed by other distributed-size systems [38]. Thus, the elongation of gold particles is not exclusively caused by a direct transformation as in the case of colloids. Since only two ion fluences were studied by TEM, the behavior at higher fluences will be investigated below, using optical characterization. At least one of three other phenomena seems to occur during ion irradiation: coalescence, Ostwald ripening, or growth from Au atoms still in solution. Indeed, when STEM pictures taken before and after irradiation at high magnification were analyzed (not shown here), very small gold clusters with size lower than 1 nm were observed in irradiated samples but were not present in non-irradiated ones. These could be pre-existing particles that have almost dissolved (Ostwald ripening) or newly formed particles from Au atoms still in the solution.

We have also observed coalescence processes, that is, when gold particles are in contact they merge together forming one larger and longer particle. Coalescence process reduces the surface in order to minimize the energy. Fig. 3 illustrates two examples of gold particle elongation by coalescence with a preferential direction due to the ion beam, both at liquid nitrogen (Fig. 3a) and room temperature (Fig. 3b). Fig. 3b presents a high resolution TEM picture of a sample irradiated at room temperature with 30 MeV Cu^{+5} at a fluence of 1×10^{15} ions/cm^2. One can observe the presence of gold atomic