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Swift heavy ion irradiation acts as a size filter to Ag nanoparticles embedded in silica glass

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ABSTRACT

The swift heavy ion (SHI) irradiation using as a tool for the ion-beam-shaping technique has attracted much attention in recently years, which can transform spherical metal nanoparticles (Nps) to prolate spheroids, nanorods or nanowires, with the elongation along the beam direction. In the present paper, we show that SHI irradiation can also act as a size filter to Ag Nps embedded in silica glass. In experiment, Ag Nps were introduced into silica glass by Ag ion implantation. Subsequently, 73 MeV Ca ions were used to irradiate the samples contained Ag Nps to different fluences. The direction of incident ions is perpendicular to sample surface. The surface plasmon resonance (SPR) absorbance peak of Ag Nps shifts to short wavelength with increase of irradiation fluence, meanwhile, the full width at half maximum (FWHM) of SPR peak decreases with increase of irradiation fluence. The decrease of FWHM indicates the reduction of Ag Nps size dispersion. TEM results show that Ag Nps smaller than 2.0 nm dissolve during irradiation, only Ag Nps larger than 2.0 nm survive and distribute in a narrow region. High energy Ca ion irradiation seems to act as a size filter. From TEM micrographs the size dispersion of Ag Nps is reduced comparing with that before irradiation, which is consistent with optical results.

1. Introduction

Metal nanoparticles (Nps) embedded in glass have stimulated the interest of scientists because of their linear and nonlinear optical properties [1]. The properties of the composites greatly depend on Nps size, shape, interparticle distance and dispersity of these parameters [2]. Thus new synthesis methods have been developed to optimize these parameters. Ion implantation is one of these methods, which has the advantage over other techniques for the versatility of control on Nps size, distribution and concentration. A large number of studies have been performed using ion plantation to synthesize metal [3], even semiconductor Nps [4] in different matrix over the past decades. However, the shape factor has not been addressed until the fabrication of anisotropic Nps becomes possible recently by using ion-beam shaping technique. The ion-beam shaping phenomenon was first reported in 2003 by Orleans [5]. This technique mainly uses swift heavy ion (SHI) irradiation to transform the spherical metal Nps to prolate spheroids, nanorods or nanowires, with the elongation along the beam direction. Anisotropic Nps have interesting properties due to the fact that the surface plasmon resonance bands split up for orientations along major and minor axes [6], and can be used as building blocks in a variety of optical devices [2].

The energy loss for SHI irradiation is dominated by electronic stopping (S_e) or inelastic interaction between the incident ion and target electrons. This interaction primarily generates a hot electron gas around the straight ion trajectory. If there exists an efficient coupling between the electron gas and the atoms of the solid, the later can locally attain very high temperatures so that it melts within a few picoseconds, rapid resolidification can lead to a trail of defective or even amorphous material, ion track [7]. Studies have revealed that the width of nanorod formed by SHI irradiation saturates at fluence higher than a certain value. The saturated width of nanorod never excesses the width of ion track in the matrix [8]. Thus it is considered that metal Nps deformation is related to ion track formation, and thermal spike model is always used to explain the phenomena of metal Nps deformation [9]. A lot of studies have been performed to investigate the details of metal Nps deformation. The role of the Nps size and density has been investigated by Dawi et al. [10]. The thermodynamic properties of ion-shaped Nps have been studied by Ridgway's group [8,11]. Even the deformation of a core–shell configuration (Au-core/silica-shell) has also been investigated by Polman's group [2,12]. The metal Nps always refer to Au [2,10,12], Ag [6], Co [5,13,14] and Pt [15].

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In this paper, we present another application of SHI irradiation acting as a size filter to Ag Nps in silica glass, which can be used to fabricate a narrow Nps buried layer with small size dispersion in matrix.

2. Experimental

Ag Nps were introduced in silica glass by 200 keV Ag ion implantation to the fluence of 2.0×10^{16} ions/cm^2 at room temperature. Ag atom concentration reached a maximum at the depth around 100 nm according to the SRIM 2006 simulation [16]. The samples contained Ag Nps were subsequently irradiated with 73 MeV Ca ions to fluences of 0.4, 1.0 and 3.8×10^{14} ions/cm^2, respectively, at an irradiation terminal of the separate-fan cyclotron in the national laboratory of heavy-ion accelerators in Lanzhou, China. The direction of incident ions is perpendicular to sample surface. The electronic energy loss (S_e) of 73 MeV Ca ions in silica glass and silver are 5.0 and 13.0 keV/nm [16], respectively. After irradiation samples were characterized by optical absorption spectrometry (UV–VIS, PerkinElmer lambda900) and transmission electron microscope (TEM, JEOL JEM-2010). For the TEM observation, the size of detectable Ag Nps should be larger than ~1.0 nm. Optical technique is nondestructive and can provide statistical properties of the whole sample. TEM gives local information about the microstructure. Therefore, the two kinds of techniques can provide relatively comprehensive information for fully understanding the experiment phenomena.

3. Results and discussion

After Ag ion implantation, an absorption peak around 400 nm is observed, which is from the surface plasmon resonance (SPR) absorption of Ag Nps. The SPR peak position is consistent with the predicted value from Mie theory calculation [17]. The appearance of this peak indicates the formation of Ag Nps in matrix. After irradiation with 73 MeV Ca ions, the SPR peak shifts continually to short wavelength with increase of irradiation fluence, as shown in Fig. 1.

The average Nps diameter can be estimated from the SPR peak position and the full width at half maximum (FWHM) of the peak using the formula $D = \frac{V_f}{\pi c} \times \frac{\lambda^2_{max}}{\Delta\lambda_{1/2}}$, where D is the Ag Nps average diameter, V_f is the electron velocity corresponding to the Fermi energy of Ag, c is the velocity of light, $\Delta\lambda_{1/2}$ is Full Width at Half Maximum wavelength (FWHM) and λ_{max} is peak wavelength [18]. In addition, a wide size dispersion of Nps can cause broadening of SPR peak, thus the FWHM of the peak can be used as a parameter to characterize Nps size dispersion. The evolution of SPR peak position, Nps average diameter and FWHM of SPR peak with irradiation fluence is shown in Fig. 2. It can be seen that Ag Nps average diameter increases and becomes saturated with increase of irradiation fluence, meanwhile the Nps size dispersion (FWHM) gradually decreases with increase of irradiation fluence. From TEM micrographs shown in Fig. 3, it is seen that the size of Ag Nps indeed increases after irradiation. The blue shift of Ag SPR peak could be related with the change of Ag Nps size [19,20] or the change of refractive index of matrix [21]. Based on the Mie theory calculation, the blue shift is ~6 nm in wavelength for Ag Nps with size increasing from 2 to 20 nm in diameter. However, it can be found that the blue shift can reach ~17 nm in wavelength after irradiation with fluence of 3.8×10^{14} ions/cm^2. Therefore, the change of refractive index of matrix could have more contribution to the blue shift of SPR peak. In addition, the change of refractive index of matrix due to the existence of defects produced by SHI irradiation can be verified by the appearance of absorption peak around 245 nm from point defects in silica (such as NBOHC, POR, ODC(II) or O3) [22].

TEM micrograph for Ag ion implanted sample (Fig. 3a) reveals that Ag Nps with wide size dispersion distribute in the depth ranging from 40 to 220 nm, and the largest Nps distribute around the depth of 80 nm. However, Ag Nps smaller than ~2.0 nm in shallower or deeper region disappear after Ca ion irradiation (Fig. 3b). As a result, only Ag Nps larger than ~2.0 nm survive and distribute in a narrow region, moreover, the size dispersion of Ag Nps is also reduced. The statistical results of Ag Nps distribution before and after Ca ion irradiation are shown in Fig. 3c. It is seen that the fraction of Ag Nps with diameter smaller than 2.0 nm obviously decreases after irradiation. High energy Ca ion irradiation seems to act as a size filter, Nps smaller than ~2.0 nm are filtered. From the statistical results of Nps size distribution with depth (Fig. 4), Ag Nps mainly locate in depth ranging from 40 to 140 nm after irradiation to fluence of 1.0×10^{14} ions/cm^2. The position dispersed with the largest Nps does not change, but the size of the largest Nps slightly increases comparing with that before irradiation. With increasing of irradiation fluence (3.8×10^{14} ions/cm^2), the area dispersed with Ag Nps shifts to dee-

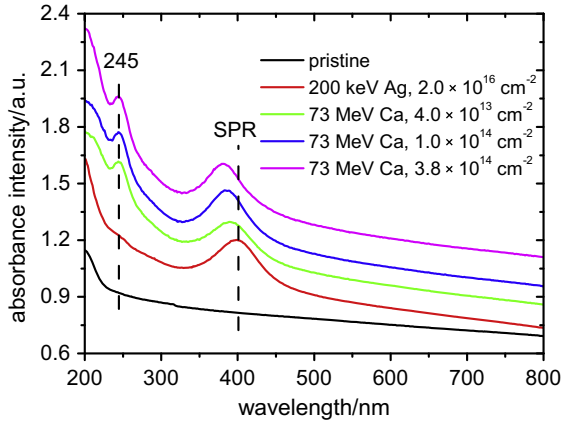

Fig. 1. UV–VIS spectra for pristine sample, sample embedded with Ag Nps and samples contained Ag Nps and irradiated with 73 MeV Ca to different fluences.

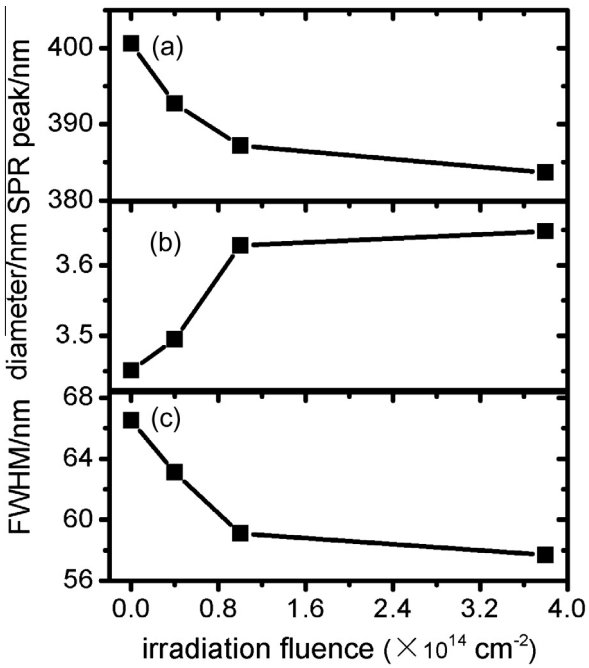

Fig. 2. SPR peak position (a), Ag Nps average diameter (b) and FWHM of the SPR peak (c) evolution with irradiation fluence.