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Aligned Elongation of Ag Nanoparticles Embedded in Silica Irradiated with High Energy Ni Ions *

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Metallic nanoparticle (NP) shapes have a significant influence on the property of composite embedded with metallic NPs. Swift heavy ion irradiation is an effective way to modify shapes of metallic NPs embedded in an amorphous matrix. We investigate the shape deformation of Ag NPs with irradiation fluence, and 357 MeV Ni ions are used to irradiate the silica containing Ag NPs, which are prepared by ion implantation and vacuum annealing. The UV-vis results show that the surface plasmon resonance (SPR) peak from Ag NPs shifts from 400 to 377 nm. The SPR peak has a significant shift at fluence lower than 1×10^{14} ions/cm^2 and shows less shift at fluence higher than 1×10^{14} ions/cm^2. The TEM results reveal that the shapes of Ag NPs also show significant deformation at fluence lower than 1×10^{14} ions/cm^2 and show less deformation at fluence higher than 1×10^{14} ions/cm^2. The blue shift of the SPR peak is considered to be the consequence of defect production and Ag NP shape deformation. Based on the thermal spike model calculation, the temperature of the silica surrounding Ag particles first increases rapidly, then the region of Ag NPs close to the interface of Ag/silica is gradually heated. Therefore, the driven force of Ag NPs deformation is considered as the volume expansion of the first heated silica layer surrounding Ag NPs.

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Composites embedded with metallic nanoparticles (NPs) show large nonlinear optical susceptibility and strong surface plasmon resonance absorption,[1−3] which enable promising applications in opto-electronics. Properties of composites greatly depend on NP size, shape, interparticle distance, and dispersity of these parameters.[4] The shape factor has not been addressed until fabrication of anisotropic NPs beaomes possible recently using the ion-beam shaping technique.[5] This technique mainly uses swift heavy ion (SHI) irradiation to transform the spherical metallic 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 the major and minor axes,[6] and can be used as building blocks in a variety of optical devices.[4] Many studies have been performed to investigate the shape deformation of metallic NPs, which always refer to Au,[4,7,8] Ag,[6] Cu,[9] Co,[5,10,11] Pt,[12] Ni,[13] and Zn.[14] Roles of NP size and density have been investigated by Dawi *et al.*[7] The thermodynamic properties of ion-shaped NPs have also been studied.[15,16] Even the deformation of special configurations (e.g., Au-core/silica-shell,[4,8] Au-hollow-nanoshell[17]) has also been investigated.

Researchers 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 exceeds the width of ion track in the matrix.[15] Thus it is considered that deformation of metal NPs is related to ion track formation, and the thermal spike model is always used to simulate the thermal dynamic process of metallic NP shape deformation, which shows good validation in explanation to the observed phenomena.[18] However, where the driven force for the shape deformation comes from under irradiation is still an open problem.[19] In this Letter, we investigate the deformation of Ag NPs embedded in silica under irradiation of 357 MeV Ni ions. A simulation based on the thermal spike model is conducted to understand the deformation mechanism.

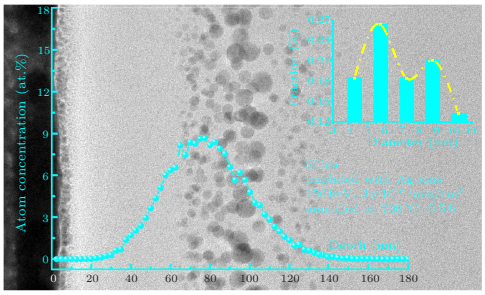

Fig. 1. TEM results of the silica implanted with Ag and annealed at 700℃ for 0.5 h, and Ag NP size distribution is shown on the top right. Ag atom distribution with depth obtained from SRIM 2013 is also shown.

Silica samples were implanted with 150 keV Ag ions to the fluence of 3×10^{16} ions/cm^2 at room temperature. SRIM 2013 calculation indicated that Ag atoms mainly distributed at the depth around 75 nm,[20] as shown in Fig. 1. To obtain large-size Ag NPs, the im-

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planted samples were annealed at 700℃ for 0.5 h under a vacuum condition (1×10^{-4} Pa). After annealing, the samples were irradiated with 357 MeV Ni ions to fluences of 5×10^{13}, 1×10^{14}, and 2×10^{14} ions/cm^2 at room temperature at an irradiation terminal of the sector-focused cyclotron (SFC) at the Heavy Ion Research Facility in Lanzhou (HIRFL, China). To reduce the effect of beam heating, the beam intensity was sustained around 15–20 nA, meanwhile a thermal couple was fixed on the back side of the sample stage to monitor the temperature fluctuation, showing 27–29℃ during irradiation. From SRIM 2013 calculation the electronic energy loss (S_e) of 357 MeV Ni ions in silica and Ag were 6.0 and 16.3 keV/nm,[20] respectively. After irradiation, samples were characterized by optical absorption spectrometry (UV-vis, PerkinElmer lambda 900) and a transmission electron microscope (TEM, JEOL JEM-2010). The sample for the TEM observation was prepared by the focused ion beam (FIB) technique.

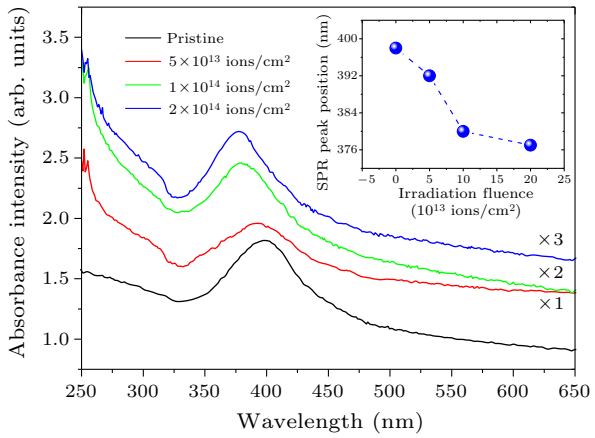

Fig. 2. UV-vis spectra of silica embedded with Ag NPs before and after 357 MeV Ni ion irradiation. The evolution of the SPR peak position with irradiation fluence is shown on the top right.

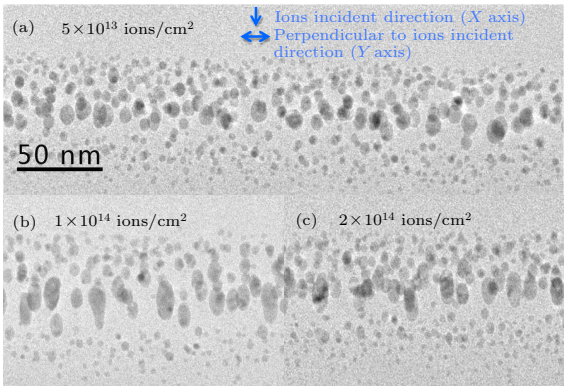

Fig. 3. TEM results of Ag NPs after irradiation at different fluences: (a) 5×10^{13}, (b) 1×10^{14}, and (c) 2×10^{14} ions/cm^2.

A strong absorbance peak around 400 nm is observed for the Ag ions implanted and annealed silica samples, which is from the surface plasmon resonance (SPR) of Ag NPs,[21] as shown in Fig. 2. The appearance of the SPR absorbance peak indicates the formation of Ag NPs in silica. The TEM results reveal that Ag NP has a broad size distribution, and distributes in the depth region from 60 to 140 nm, as shown in Fig. 1. The average diameter of Ag NPs is 7.0±2.1 nm, larger Ag NPs disperse in the depth region from 90 to 105 nm, and smaller Ag NPs disperse in a shallower or deeper region, which is a typical distribution of metallic nanoparticles fabricated by ion implantation.[1] Compared with SRIM simulation results, the region dispersed with Ag NPs shifts slightly to a deeper region, which probably results from rapid diffusion of Ag atoms during annealing.

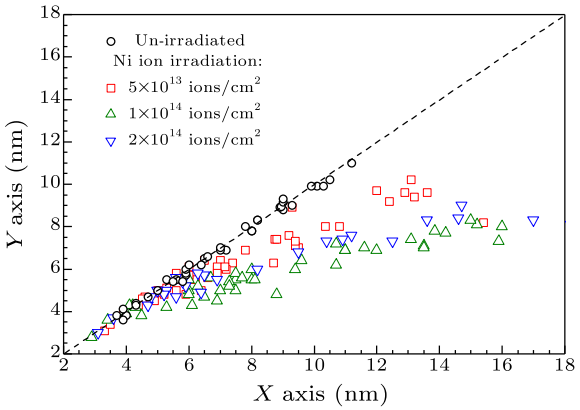

Fig. 4. The size of Ag NPs in X and Y directions before and after Ni ion irradiation.

As shown in Fig. 2, Ni ion irradiation results in a blue shift of the SPR peak from 400 to 377 nm when the irradiation fluence increases from 5×10^{13} to 2×10^{14} ions/cm^2. The SPR peak has a rapid shift to a short wavelength at the fluence lower than 1×10^{14} ions/cm^2. However, it does not shift much at the fluence higher than 1×10^{14} ions/cm^2. The TEM results reveal that spherical Ag NPs have deformed into prolate spheroids after Ni ion irradiation, as shown in Fig. 3. From the size statistical results, it is seen that the size of Ag NPs decreases in the direction perpendicular to Ni ions' incident direction (Y axis) and increases in the direction parallel to Ni ions' incident direction (X axis), as shown in Fig. 4. After irradiation at the fluence of 5×10^{13} ions/cm^2, Ag NPs are deformed into prolate spheroids with small aspect ratio. Significant deformation can be observed after irradiation at fluence of 1×10^{14} ions/cm^2, but it seems that Ag NPs show less deformation with further increasing the fluence (e.g., the size along the X or Y axis seems to show less change after irradiation at 2×10^{14} ions/cm^2). In addition, from Fig. 4, it is found that Ag NPs smaller than 5.0 nm do not show deformation under irradiation. Therefore, the size threshold of Ag NP deformation induced by SHI irradiation is around 5.0 nm.

From the TEM and UV-vis results, it can be found that the elongation behavior of Ag NPs is similar with the blue shift behavior of the SPR peak under Ni ion irradiation. At irradiation fluence lower than 1×10^{14} ions/cm^2, the SPR peak has a rapid blue shift

and the Ag NP has significant deformation under irradiation. At fluence higher than 1×10^{14} ions/cm^2, the SPR peak exhibits small blue shift and the Ag NP also shows slight deformation with the increase of irradiation fluence. This phenomenon makes it easy to conclude that the blue shift of the SPR peak results from the deformation of Ag NPs. However, the blue shift of the SPR peak from Ag NPs without deformation is also observed after SHI irradiation.[22] The SPR peak of Ag NPs shifts from 400 nm to 384 nm under irradiation of 73 MeV Ca ions with fluence from 4×10^{13} to 3.8×10^{14} ions/cm^2, and the SPR peak also shows a small shift when the fluence is higher than 1.0×10^{14} ions/cm^2. However, the TEM results reveal that Ag NPs only have a change in size and distribution, shape deformation does not occur after irradiation. The reason for the blue shift of Ag NPs without deformation is considered as the change of refractive index of matrix due to the existence of defects produced by swift heavy ion irradiation. However, in this study the SPR peak has already shifted to 377 nm after irradiation at the fluence of 2×10^{14} ions/cm^2. Therefore, other factors should be considered for the significant blue shift in this study. According to the Mie theory,[21] the position of the SPR peak is related to two factors, one is the refractive index of the matrix and the other is the NP size. In this study, Ni ion irradiation causes the deformation of spherical Ag NPs into a prolate spheroid along the ion incident direction. As shown in Fig. 4, the deformation causes a decrease in size of Ag NPs in the direction perpendicular to ions' incident direction, which makes the effective size in response to surface plasmon resonance decrease when the light impinges onto Ag NPs along the ion incident direction. Therefore, the change in both size and matrix refractive index is considered to be the reason for the significant blue shift of the SPR peak of Ag NPs after Ni ion irradiation.

Because the width of the deformed particles saturates at a value less than or equal to the width of the ion track,[15] the shape deformation of metallic NPs is considered to be the flow of the metallic species within the liquid ion track, and an indirect heating mechanism based on the thermal spike model has been proposed for the thermal dynamic process of shape deformation of metallic NPs under swift heavy ion irradiation.[23] The majority of the energy of incident ions is transferred to electrons around the straight ion trajectory. Due to high electron thermal conductivity and weak electron-phonon coupling for metal and a reverse situation for silica, the energy transferred to the electronic subsystem of the metallic NP diffuses rapidly outwards to the interface of NP/silica. When the diffused energy reaches the interface, it is transferred to electrons of the neighboring silica matrix. The high electron-phonon coupling of silica results in the formation of a hot silica layer surrounding the metallic NP. This layer acts as a barrier for the diffusion of energy in the electronic subsystem of metallic NP, enabling the transformation into heat within the metallic NP atomic subsystem. Based on the indirect heating model, metallic NP with smaller size is easily heated to a very high temperature and is molten or vaporized in a short time. It needs a longer time to heat/melt metallic NP with large size. A three-dimensional implementation of the thermal spike model has been developed to simulate the thermal dynamic process of metallic NP embedded in a silica matrix, which demonstrates good validation in the description of phenomena observed in the metallic particle deformation process.[24]

However, this model does not give an explanation for where the driving force comes from for the metallic NP deformation under irradiation. For the convenience of calculation, the structure of Ag cylinder (e.g., 2 nm in diameter) is considered to be surrounded by silica with a central impact (swift heavy ion passes though the center of the metallic cylinder), as schematically shown in the inset of Fig. 5. The dependence of temperature on displacement at difference time for the structure of Ag cylinder surrounded by silica, obtained from the calculation based on the thermal spike model,[25] is shown in Fig. 5. The parameters used for the calculation are adopted from those in Ref. [26]. It can be seen that the temperature of the silica surrounding the cylinder first increases rapidly, then the region of the cylinder close to the interface is gradually heated, as shown in the marked region of Fig. 5.

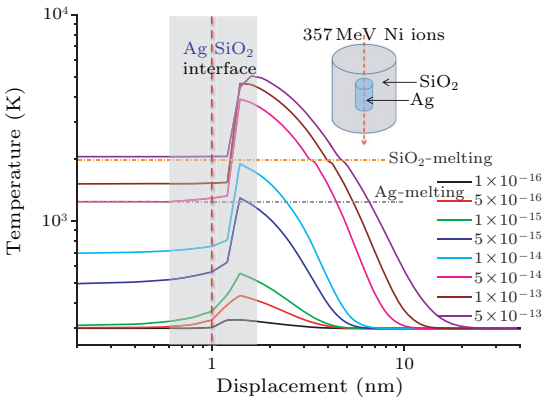

Fig. 5. Time/displacement dependent lattice temperature of Ag cylinder surrounded by silica with impact of 357 MeV Ni ions obtained from thermal spike calculation.

Experimental results have shown that the shape deformation only occurs for the metallic NPs embedded in amorphous matrix, and the deformation is not observed for metallic NPs adhered to a substrate surface.[4] Therefore, the matrix plays an active role in the shape deformation process. The calculation results indicate that the silica layer close to the interface of Ag/silica is firstly heated prior to the Ag particle. The temperature increase results in the occurrence of volume expansion. Therefore, the volume of the thin silica layer surrounding the Ag particle expands

sharply when this thin layer is heated to high temperature in a short time. This volume expansion leads to the generation of in-plan mechanical stress. Because the surrounding silica layer is heated prior to the Ag particle, a radical pressure is applied on the Ag particle. When the region of the Ag particle close to the interface of Ag NP/silica is molten, the radical pressure makes the molten Ag flow along the ion incident direction to release the pressure from volume expansion of the hot silica surrounding layer. Subsequently, the fast cooling of the heated region freezes the particle shape deformation. This shape deformation process induced by SHI irradiation is schematically shown in Fig. 6. In the experiment, the perceptible changes in Zn and Co NPs' shapes are measured after a single ion impact.[14] Therefore, the deformation of metallic nanoparticles embedded in silica starts from the region close to the metallic NPs/silica interface rather than the central region, which results in the NPs with larger size transforming to faced NPs after SHI irradiation (e.g., Ag NPs with diameter 43 nm transforms into faced Ag NPs after 74 MeV Kr ion irradiation to fluence of 5×10^{15} ions/cm^2).[23]

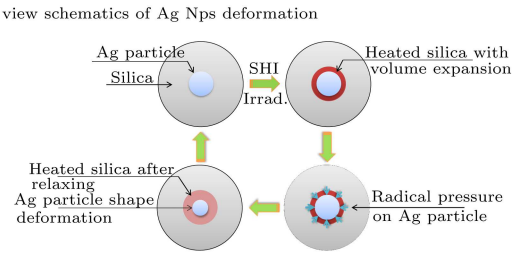

Fig. 6. The schematics of shape deformation of Ag NPs embedded in silica under irradiation with SHIs.

In summary, blue shift of the SPR peak from Ag NPs has been observed after Ni ion irradiation. The TEM results reveal that Ag NPs elongate along the ion incident direction after irradiation. The blue shift of the SPR peak is considered to be the consequence of defect production and Ag particle shape deformation. Based on the thermal spike model simulation, it is found that the silica layer surrounding a Ag NP is first heated rapidly, and then the region of the Ag particle close to the Ag/silica interface is gradually heated. Rapid increase of temperature is accompanied by sharp expansion of volume of the thin heated silica layer, which results in the generation of in-plan stress on the Ag particle. Therefore, the driven force for Ag particle shape deformation is considered to be the sharp volume expansion induced by swift heavy ion irradiation.

References

[1] Meldrum A, Haglund Jr R F, Boatner L A and White C W 2001 *Adv. Mater.* **13** 1431
[2] Kreibig U and Genzel L 1985 *Surf. Sci.* **156** 678
[3] Mulvaney P 2011 *MRS Bull.* **26** 1009
[4] Roorda S, Dillen T, Polman A, Graf C and Blaaderen A 2004 *Adv. Mater.* **16** 235
[5] Orleans C D, Stoquert J P, Estournes C, Cerruti C, Grob J J, Guille J L, Hass F, Muller D and Richard-Plouet M 2003 *Phys. Rev.* B **67** 220101
[6] Oliver A, Reys-Esqueda J A, Cheang-Wong J C, Roman-Velazquez C E, Crespo-Sosa A, Rodriguez-Fernandez L, Seman J A and Noguez C 2006 *Phys. Rev.* B **74** 245425
[7] Dawi E A, Rizza G, Mink M P, Vredenberg A M and Habraken F H P M 2009 *J. Appl. Phys.* **105** 074305
[8] Penninkhof J J, van Dillen T, Roorda S, Graf C, van Blaadern A, Vredenberg A M and Polman A 2006 *Nucl. Instrum. Methods Phys. Res. Sect.* B **242** 523
[9] Ridgway M C, Giulian R, Sprouster D J, Kluth P, Araujo L L, Llewellyn D J, Byrne A P, Kremer F, Fichtner P F P, Rizza G, Amekura H and Toulemonde M 2011 *Phys. Rev. Lett.* **106** 095505
[10] Orleans C D, Stoquert J P, Estournes C, Grob J J, Muller D, Guille J L, Richard-Plouet M, Cerruti C and Hass F 2004 *Nucl. Instrum. Methods Phys. Res. Sect.* B **216** 372
[11] Orleans C D, Stoquert J P, Estournes C, Grob J J, Muller D, Cerruti C and Hass F 2004 *Nucl. Instrum. Methods Phys. Res. Sect.* B **225** 154
[12] Giulian R, Kluth P, Sprouster D J, Araujo L L, Byrne A and Ridgway M C 2008 *Nucl. Instrum. Methods Phys. Res. Sect.* B **266** 3158
[13] Kumar H, Ghosh S, Avasthi D K, Kabiraj D, Mücklich A, Zhou S Q, Schmidt H and Stoquert J P 2011 *Nanoscale Res. Lett.* **6** 155
[14] Amekura H, Ishikawa N, Okubo N, Ridgway M C, Giulian R, Mitsuishi K, Nakayama Y, Buchal Ch, Mantl S and Kishimoto N 2011 *Phys. Rev.* B **83** 205401
[15] Giulian R, Kluth P, Araujo L L, Sprouster D J, Byrne A P, Cookson D J and Ridgway M C 2008 *Phys. Rev.* B **78** 125413
[16] Ridgway M C, Kluth P, Giulian R, Sprouster D J, Araujo L L, Schnohr C S, Llewellyn D J, Byrne A P, Foran G J and Cookson D J 2009 *Nucl. Instrum. Methods Phys. Res. Sect.* B **267** 931
[17] Coulon P, Amici J, Clochard M, Khomenkov V, Durour C, Monnet I, Grygiel C, Perruchas S, Ulysse C, Largeau L and Rizza G 2016 *Sci. Rep.* **6** 21116
[18] Awazu K, Wang X, Fujimaki M, Tominaga J, Aiba H, Ohki Y and Komatsubara T 2008 *Phys. Rev.* B **78** 054102
[19] Ridgway M C, Djurabekova F and Nordlund K 2015 *Curr. Opin. Solid State Mater. Sci.* **19** 29
[20] Ziegler J F, Biersack J P and Littmark U 1985 *The Stopping and Range of Ions in Solids* (New York: Pergamon)
[21] Mie G 1908 *Ann. Phys.* **330** 377
[22] Yang Y, Zhang C, Song Y, Gou J, Zhang L Q, Meng Y C, Zhang H Q and Ma Y Z 2013 *Nucl. Instrum. Methods Phys. Res. Sect.* B **308** 24
[23] Rizza G, Coulon P E, Khomenkov V, Dufour C, Monnet I, Toulemonde M, Perruchas S, Gacoin T, Mailly D, Lafosse X, Ulysse C and Dawi E A 2012 *Phys. Rev.* B **86** 035450
[24] Dufour C, Khomenkov V, Rizza G and Toulemonde M 2012 *J. Phys.* D **45** 065302
[25] Toulemonde M, Dufour C and Paumier E 1992 *Phys. Rev.* B **46** 14362
[26] Singh F, Mohapatra S, Stoquert J, Avasthi D K and Pivin J C 2009 *Nucl. Instrum. Methods Phys. Res. Sect.* B **267** 936