Synthesis of elongated Au nanoparticles in silica matrix by ion irradiation

Y. K. Mishra,[a),b)] F. Singh, and D. K. Avasthi[a),c)]
Inter University Accelerator Centre, Post Box 10502, New Delhi 110067, India

J. C. Pivin
CSNSM, IN2P3-CNRS, Bâtiment 108, F-91405 Orsay Campus, France

D. Malinovska
CLSENES, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria

E. Pippel
Max-Planck-Institut fur Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

(Received 25 May 2007; accepted 3 July 2007; published online 6 August 2007)

The present work reports the synthesis of elongated Au nanoparticles (NPs) parallel to each other, embedded in silica matrix. Au NPs in silica, prepared using rf magnetron sputtering, were irradiated by 120 MeV Au ions at different fluences to induce elongation. Optical absorption study of irradiated film showed a clear splitting of surface plasmon bands corresponding to transverse and longitudinal modes. Transmission electron microscopy investigations of pristine and irradiated samples revealed an elongation (aspect ratio of ~3.5) in Au NPs occurred as a result of irradiation. The results are discussed in the framework of thermal spike model. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2764556]

Noble metal particles embedded in transparent matrices have stimulated enormous interest for their exceptional linear and nonlinear optical properties[1] and quantum size effects in nanodimensional region.[2] The crucial parameters responsible for controlling their optical properties are the particles size, their shape, interparticle separation, and the matrix dielectric constant. Size and interparticle separation are often well controlled by deposition parameters but the shape is rather difficult to control. The anisotropically shaped metal particles show a splitted surface plasmon resonance (SPR) band due to transverse and longitudinal modes of charge density oscillations in the presence of electromagnetic radiation.[3–6] As the aspect ratio increases, the splitting becomes more prominent and is also technologically important.[3] It is difficult to synthesize nanoparticles (embedded in thin film) with the desired aspect ratio using physical and chemical routes because of the minimization of surface energy criterion for stability, which is minimum for spherical nanoparticles. Ion beam techniques provide a unique possibility for shaping the nanoparticles with the desired aspect ratio. Anisotropy is created in the metal particles covered with silica shell by MeV ion beam irradiation.[3] Silica surrounding the nanoparticles expands perpendicular to the ion beam direction due to hammering effect[7] which creates a high pressure on metal particle, and metal particles expand along ion track and thus forms nanorods. It was shown[3] that gold nanoparticles (14 nm diameter) coated with silica shell (72 nm thick) could be elongated by 30 MeV Se ions irradiation. Thus silica shell containing Au nanorod such as Au particles was synthesized.[3] However, for most practical applications, it is necessary that the elongated particles must be embedded in a thin film. The present work reports the synthesis of the elongated Au nanoparticles embedded in a thin film deposited on quartz substrate using the unique feature of high energy ions. The aspect ratio of the Au nanorod (elongated Au nanoparticles) can be controlled by ion beam parameters. The direction of elongation is decided by the ion beam direction.

Thin films of silica containing Au were deposited on silica substrates by rf-magnetron sputtering in an Ar atmosphere (5 Pa) of a silica target on which Au sheets were placed in the maximum erosion zone. The films were annealed in Ar:5% H_2 atmosphere for 1 h at different temperatures for promoting the growth of Au particles. The composition of nanocomposite films was determined by Rutherford backscattering spectroscopy (RBS) using 2.4 MeV He^+ ions provided by ARAMIS accelerator of CSNSM, Orsay. The measured thickness of films found by fitting the RBS spectra with Rutherford universal manipulation program (RUMP) code[8] was of 200 nm and the mean Au fraction of 15 ± 1 at. % with depth. No loss of Au by evaporation or diffusion inside the substrate was observed after annealing at 950 °C for 1 h. Annealed films were irradiated with 120 MeV Au ions delivered by 15 unit double pelletron at IUAC, New Delhi. The samples were irradiated with an ion beam 45° off normal at fluence of 3×10^{13} ions cm^{-2}. The electronic (S_e) and nuclear (S_n) stopping powers of these ions were calculated with SRIM (Ref. 9) program and were found to be ~14.1 keV and ~0.2 keV/nm, respectively, with ion range of ~16 μm. Optical absorption spectra were recorded with linearly polarized light along two perpendicular directions: one being the projection of the ion beam in the surface plane (noted $\parallel$) and the other being in transverse direction (noted $\perp$). Cross sections of the pristine and irradiated samples were observed by transmission electron microscopy (TEM) using the high resolution Philips CM 20 FEG field emission electron microscope of Max Planck Institute, Halle.

Cross-sectional TEM image of pristine sample shown in Fig. 1(a) clearly reveals the existence of spherically shaped nanoparticles with average size (diameter) of ~14 nm. Figure 1(b) shows the particles size distribution of pristine sample. Figure 2(a) shows the cross-sectional TEM image of the sample irradiated with 120 MeV Au ions at a fluence (ϕ)

[a)]Author to whom correspondence should be addressed.
[b)]Electronic mail: ykmnsc@gmail.com
[c)]Electronic mail: dka@iuac.ernet.in

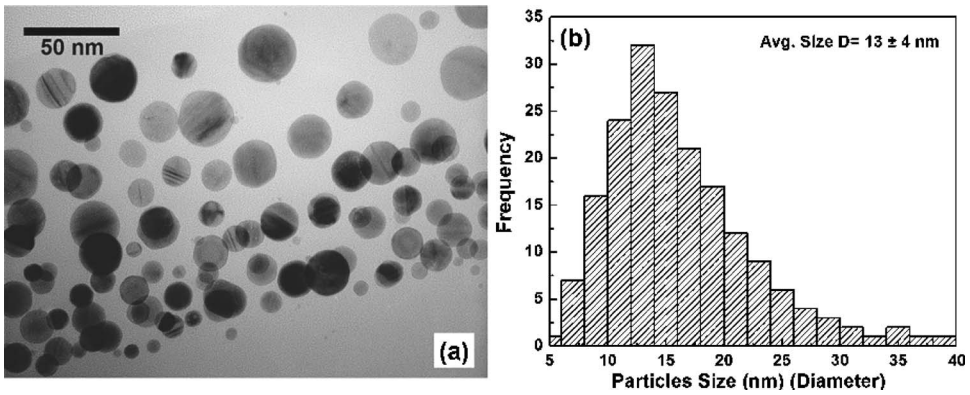

FIG. 1. (a) Cross-sectional transmission electron microscopy image of pristine film and (b) corresponding particle size distribution.

3×10^{13} ions cm^{-2} with the ion beam 45° off normal. Clearly after irradiation, elongation of Au nanoparticles occurs along the ion beam direction forming prolate shaped particles. The major axis length is ~25 nm while the minor is ~10 nm as evident from Figs. 2(a) and 2(b). The average aspect ratio of the elongated nanoparticles is 2.5. Correcting for the 45° projection of the TEM image with respect to the ion beam direction, the actual aspect ratio is ~3.5. However, it can also be clearly observed from TEM image of irradiated samples that a few nanoparticles smaller than track size remain spherical after irradiation. Figure 3 shows the average size of Au nanoparticles (average of major and minor axis lengths) after irradiation. It is clear from Fig. 3 that ion irradiation leads to a relatively narrower size distribution. There is not much growth along the oblate axis (perpendicular direction). Due to the modification induced by ion beam, the nanoparticles expand along ion beam direction and thus transform spherical particles to prolate shaped particles. It is noticed that when the longitudinal separation between the spherical nanoparticles was small, the end of prolate spheroid join together and thus formation of a large prolate spheroid such as a nanorod with large aspect ratio occurs. A close perusal of the TEM image of the irradiated sample suggests that the ion beam induced elongation occurs beyond a thresh-

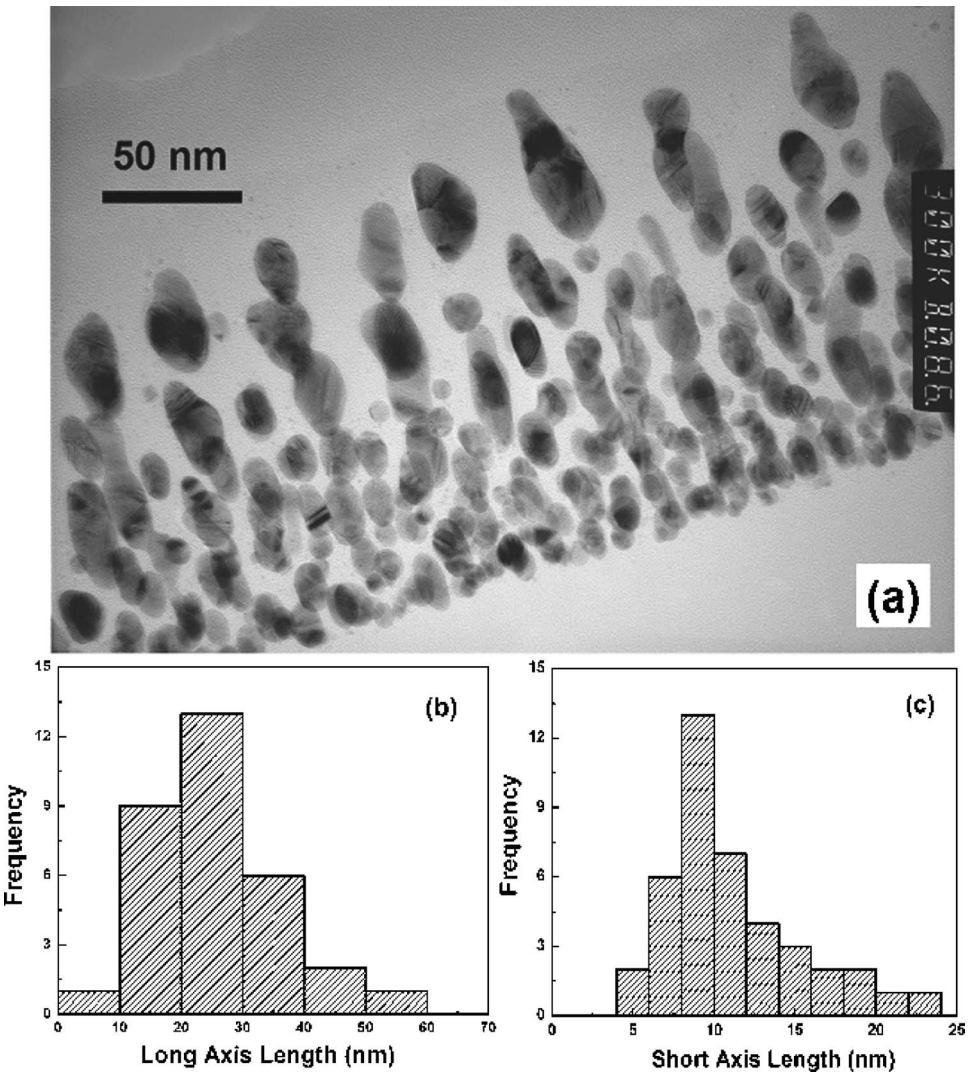

FIG. 2. (a) Cross-sectional transmission electron microscopy image of an irradiated film at 45° beam incident normal and [(b) and (c)] size distribution of major and minor axis lengths of elongated nanoparticles, respectively.

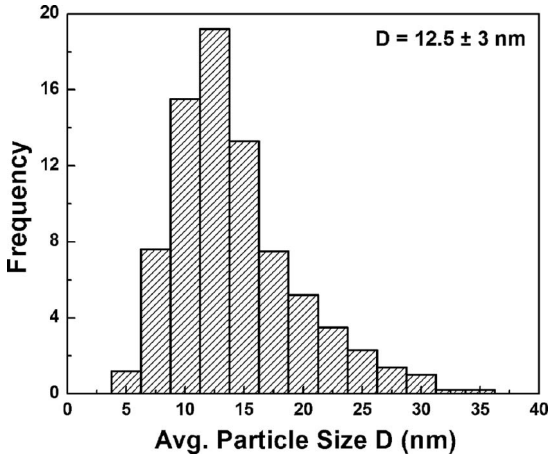

FIG. 3. Particle size distribution (average of major and minor axis lengths) of irradiated samples.

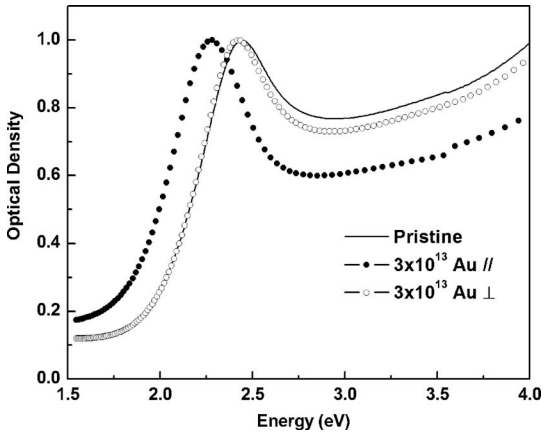

FIG. 4. Optical absorption spectra of pristine and irradiated samples with polarized light (//-s and ⊥-p polarized).

old size of nanoparticles and below that nanoparticles grow. A nominal growth in smaller particles with ion irradiation is observed due to Ostwald ripening induced by large electronic energy deposition. The growth of Au nanoparticles from 4 to 9 nm by electronic excitation (induced by ion irradiation) has been recently reported by us in an *in situ* x-ray diffraction experiment.[10]

The passage of 120 MeV Au ions through thin silica film containing the Au nanoparticles deposits the electronic energy (S_e) of 14.1 keV/nm.[9] It is known from the work done by Meftah *et al.*[11] and Toulemonde *et al.*[12] that an electronic energy loss of ~14 keV/nm in silica creates the track diameter of ~9 nm in silica. Hence, 120 MeV Au ions in present case create the track of diameter about 9 nm. Each individual Au ion impact in silica leads to the formation of thermal spike (duration of $\sim 10^{-12}$ s) which results in plastic flow of silica.[13] This plastic flow induces an in-plane stress perpendicular to the ion beam direction.[14] The combined effect of stress[14] and thermal spike[15] of all ion impacts on planar Au-silica nanocomposite film lead to the elongation of Au NPs. If the elongation is only due to the pressure effect, then the smaller nanoparticles should also elongate, which has not been observed in present case. Therefore it is more likely that the NPs grow when their size is smaller than the track size and elongate when their size is larger than track size due to dissolution-reprecipitation mechanism.[16] The process of elongation depends on the product of $S_e\tilde{\phi}$. The aspect ratio achieved in the irradiation (S_e=6.2 keV/nm and ϕ=2 $\times 10^{14}$ ions cm^{-2}) of Au-silica core shell was ~8.4, whereas the aspect ratio in the present experiment is ~3.5 for irradiation parameters of S_e=14.1 keV/nm and ϕ=3 $\times 10^{13}$ ions cm^{-2}. It is clear from the above data on aspect ratio and ion parameters that when the product of $S_e\phi$ changes by approximately three times, the aspect ratio changes by a similar factor. Thus one can engineer the shape by ion beam parameters.

Optical absorption spectra of pristine and irradiated samples are shown in Fig. 4. The pristine sample shows a clear SPR absorption band at ~2.44 eV confirming the presence of Au nanoparticles in pristine sample. Optical absorption spectra for irradiated sample were recorded with polarized light parallel (∥) and perpendicular (⊥) to the ion incident direction. The significant redshift (~0.17 eV) in SPR peak position of Au nanoparticles along parallel direction reveals the elongation of Au nanoparticles. However, insignificant shift in SPR band along perpendicular direction indicates a small compaction in the direction perpendicular to ion beam.

In conclusion, we report the synthesis of perfectly aligned Au nanorods embedded in silica matrix using the unique feature of ion irradiation. The angle of alignment with respect to the substrate is controllable by incident ion direction. A desired aspect ratio can be achieved by suitable ion beam parameters. In the present case, 120 MeV Au ion induced elongation in spherical nanoparticles (~13 nm) has been observed with an aspect ratio of 3.5.

Two of the authors (D.K.A. and J.C.P.) are thankful to the Indo French Centre for the Promotion of Advance Research (IFCPAR) for financial support of the project "Generation of nanopahse by energetic ion beams."

[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).
[2] M. C. Daniel and D. Astruc, Chem. Rev. (Washington, D.C.) **104**, 293 (2004).
[3] S. Roorda, T. van Dillen, A. Polman, C. Graf, A. van Blaaderen, and B. J. Kooi, Adv. Mater. (Weinheim, Ger.) **16**, 235 (2004).
[4] J. J. Penninkhof, C. Graf, T. V. Dillen, A. M. Vredenberg, A. van Blaaderen, and A. Polman, Adv. Mater. (Weinheim, Ger.) **17**, 1484 (2005).
[5] K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, J. Phys. Chem. B **107**, 668 (2003).
[6] S. Link, M. B. Mohamed, and M. A. El-Sayed, J. Phys. Chem. B **103**, 3073 (1999).
[7] S. Klaumunzer, M. D. Hou, and G. Schumacher, Phys. Rev. Lett. **57**, 850 (1986).
[8] R. Doolittle, Nucl. Instrum. Methods Phys. Res. B **9**, 291 (1985).
[9] J. F. Ziegler, Z. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York 1985), www.srim.org
[10] Y. K. Mishra, D. K. Avasthi, P. K. Kulriya, F. Singh, D. Kabiraj, A. Tripathi, J. C. Pivin, I. S. Bayer, and A. Biswas, Appl. Phys. Lett. **90**, 073110 (2007).
[11] A. Meftah, F. Brisard, M. Costantini, E. Dooryhee, M. Hage-Ali, M. Hervieu, J. P. Stoquert, F. Studer, and M. Toulemonde, Phys. Rev. B **49**, 12457 (1994).
[12] M. Toulemonde, J. M. Costantini, Ch. Dufour, A. Meftah, E. Paumier, and F. Studer, Nucl. Instrum. Methods Phys. Res. B **116**, 37 (1996).
[13] M. L. Brongersma, E. Snoeks, and A. Polman, Appl. Phys. Lett. **71**, 1628 (1997).
[14] H. Trinkaus and A. I. Ryazanov, Phys. Rev. Lett. **74**, 5072 (1995).
[15] C. D'Orleans, J. P. Stoquert, C. Estourne's, C. Cerruti, J. J. Grob, J. L. Guille, F. Haas, D. Muller, and M. Richard-Plouet, Phys. Rev. B **67**, 220101(R) (2003).
[16] J. C. Pivin, G. Roger, M. A. Garcia, F. Singh, and D. K. Avasthi, Nucl. Instr. and Methods B **215**, 373 (2004).