Energy-dependent anisotropic deformation of colloidal silica particles under MeV Au irradiation

T. van Dillen and A. Polman
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, NL-1098 SJ Amsterdam, The Netherlands

W. Fukarek
Research Center Rossendorf, Institute of Ion Beam Physics and Materials Research, P.O. Box 510119, D-01314 Dresden, Germany

A. van Blaaderen
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, NL-1098 SJ Amsterdam and Debye Institute, Condensed Matter, Utrecht University, Princetonplein 5, NL-3584 CC Utrecht, The Netherlands

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Spherical silica colloids with a diameter of 1.0 μm, made by wet chemical synthesis, were irradiated with 2–16 MeV Au ions at fluences in the range (2–11)×10^{14} cm^{-2}. The irradiation induces an anisotropic plastic deformation turning the spherical colloids into ellipsoidal oblates. After 16 MeV Au irradiation to a fluence of 11×10^{14} cm^{-2}, a size aspect ratio of 5.0 was achieved. The size polydispersity (∼3%) remains unaffected by the irradiation. The transverse diameter increases exponentially with ion fluence. By performing measurements as a function of ion energy at a fixed fluence, it is concluded that the transverse diameter increases linearly with the average electronic energy loss above a threshold value of ∼0.6 keV/nm. Nonellipsoidal colloids are observed in the case where the projected ion range is smaller than the colloid diameter. The data provide strong support for the thermal spike model of anisotropic deformation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1345827]

MeV ion irradiation of amorphous materials such as metallic or silica glasses is known to cause anisotropic plastic deformation.\textsuperscript{1–5} The result is an increase of the sample dimension perpendicular to the ion beam and a decrease in the direction parallel to the ion beam. This deformation process has been described mesoscopically by a viscoelastic model in which it is assumed that, due to the high electronic stopping power, a cylindrically shaped region around the ion track is subject to transient heating (thermal spike).\textsuperscript{6–8} During the thermal spike, shear stresses in the heated region relax, resulting in an associated shear strain that would freeze upon cooling of the thermal spike.

Experimentally, the anisotropic deformation has been studied by observing macroscopic dimensional changes of (metallic) glass foils\textsuperscript{1–2} or by studying the wafer curvature induced by irradiated thin films constrained on a substrate.\textsuperscript{4,5,9} Recently, we discovered that the deformation process also occurs in free-standing colloidal particles.\textsuperscript{10} Spherical colloidal SiO\textsubscript{2} and ZnS particles can be changed into ellipsoidal-shaped particles (oblates) due to a biaxial expansion perpendicular to the ion beam and a concomitant contraction along the ion beam. Colloidal particles with variable shape can find many applications in studies of self-assembly and phase behavior\textsuperscript{11} and, except ion irradiation, no other methods exist that can produce nonspherical colloids that are monodisperse in size and shape. It is therefore important to study the dependence of the deformation effect on irradiation parameters such as ion energy and fluence.

In this letter, we study the dependence of the deformation of spherical silica particles on Au ion fluence and energy in the range 2–16 MeV. We find that the anisotropic deformation shows a gradual linear increase with electronic stopping power in the colloid, above a threshold of ∼0.6 keV/nm. We also study the special case in which the ion beam only partly penetrates the colloids, and find that nonellipsoidal particles are formed. This, together with the observed threshold, provides strong evidence for the thermal spike model for anisotropic deformation.

Colloidal silica spheres were made in a solution containing tetra-ethoxysilane, ammonia, and ethanol.\textsuperscript{12} A drop of the colloidal dispersion was dried on a Si(100) substrate which had previously been cleaned for 10 min in a 1.0 M KOH–ethanol solution. Next, the particles were irradiated with Au ions using the 3 MV tandetron accelerator at the ion beam facility in Rossendorf.\textsuperscript{13} The ion beam was electrostatically scanned across a 5.1×5.1 cm\textsuperscript{2} area. The ion energy was varied between 2 and 16 MeV and fluences ranged from 2 to 11×10^{14} cm^{-2}. The ion beam energy flux was kept constant at a value of 0.16 W/cm\textsuperscript{2} during all irradiations. The substrate holder was cooled with liquid nitrogen, and all irradiations were performed at an angle of 45° with respect to the Si surface. Vacuum grease at the backside of the sample was used to improve the heat contact between the sample and the cooled substrate holder. Note that the actual colloid temperature during irradiation might be higher than that of the holder. Ion ranges and electronic energy losses were calculated using TRIM98,\textsuperscript{14} a Monte Carlo calculation, using a silica structure with a density of 2.0 g/cm\textsuperscript{3}.\textsuperscript{15} Scanning electron microscopy (SEM) was performed at an energy of 10
keV under different angles to image the particle shape before and after irradiation. Image processing and analysis software were used to characterize the particles before and after irradiation.

Figure 1(a) shows a SEM image of unirradiated silica particles on a silicon substrate viewed under normal incidence (see schematic in Fig. 1). The size distribution of 65 analyzed colloids is displayed in Fig. 2 (black histogram). The average colloid diameter is $1004 \pm 20$ nm, with a standard deviation characterizing the size polydispersity $\sigma = 31 \pm 3$ nm. This is typical for the colloid fabrication method used.\textsuperscript{12}

Next, the colloids were irradiated with a 14 MeV Au\textsuperscript{4+} ion beam to a fluence of $4 \times 10^{14}$ cm\textsuperscript{-2} under an angle of $45^\circ$ (see schematic in Fig. 1). The projected ion range was calculated to be about 3.5 $\mu$m, well beyond the particle diameter. Figure 1(b) shows a SEM micrograph after irradiation taken in the direction perpendicular to the ion beam. Clearly, the originally spherical particle has turned into an ellipsoidal oblate with a dimensional expansion perpendicular to the ion beam and a contraction parallel to the ion beam.

Figure 2 also shows the size distribution of the transverse diameter of 33 oblates after irradiation (gray histogram). This axis has increased to a mean value of $1181 \pm 20$ nm, with $\sigma = 27 \pm 3$ nm. This indicates that the ion irradiation process does not significantly increase the particle size polydispersity. Note that at a fluence of $4 \times 10^{14}$ cm\textsuperscript{-2} each colloid has been impacted by some $10^7$ ions. Any statistical variations are expected to be averaged out at this large number of ions. Assuming the colloidal volume remains constant after irradiation,\textsuperscript{10} the aspect ratio of the deformed colloids in Fig. 1(b) is calculated to be 1.63.

Figure 1(c) shows a SEM micrograph of a colloid after irradiation with 2 MeV Au\textsuperscript{2+} ions to a fluence of $4 \times 10^{14}$ cm\textsuperscript{-2}, viewed in the direction perpendicular to the ion beam. The projected range of 2 MeV Au ions in SiO\textsubscript{2} is about 0.55 $\mu$m, roughly equal to half the colloid diameter. This implies that the lower half of the colloid is not fully irradiated, except at the lateral side edges. Figure 1(c) clearly shows a nonellipsoidal shape of the colloid: the upper part of the colloid is deformed, whereas the lower part remains undeformed (see white dashed line). This clearly indicates that the deformation only takes place in the irradiated region of the colloid. From this we can conclude that the plastic deformation does not result from a uniaxial hydrostatic pressure generated by the ion beam, but results from single-ion impacts only. This is in agreement with the thermal spike model.

Figure 3 shows the transverse particle diameter as function of ion fluence. Results are shown for irradiations with 8 MeV Au\textsuperscript{3+} and 16 MeV Au\textsuperscript{5+}. Exponential fits to the data are included.
Au irradiation to a fluence of $10^{16}$ cm$^{-2}$. The drawn line is a linear fit to the data. A data point for 500 keV Xe irradiation ($1 \times 10^{16}$ cm$^{-2}$) of 290 nm colloids for which no deformation was found is also indicated (solid square).

In conclusion, spherical colloidal silica particles undergo anisotropic plastic deformation under 2–16 MeV Au irradiation. The size polydispersity is not affected by irradiation. The transverse diameter increases exponentially with ion fluence at a rate that increases linearly with the average electronic energy loss in the colloid, above a threshold value of ~0.6 keV/nm. Nonellipsoidal shapes are formed when the ion range is smaller than the colloid diameter. These data provide strong support for the thermal spike model for anisotropic deformation.

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