Ion beam-induced anisotropic plastic deformation at 300 keV

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

C. M. van Kats and A. van Blaaderen
Soft Condensed Matter, Debye Institute, Utrecht University, P.O. Box 80.000, NL-3508 TA Utrecht, The Netherlands

(Received 7 July 2003; accepted 1 October 2003)

Contrary to earlier predictions, ion irradiation at energies as low as 300 keV causes dramatic anisotropic plastic deformation of silica glass. Spherical colloidal silica particles with diameters of 125, 305, and 1030 nm were irradiated with Xe ions at energies in the range 0.3–4.0 MeV at temperatures between 85 and 380 K. Irradiation-induced anisotropic plastic deformation changes the colloid shape from spherical into oblate ellipsoidal at a rate that strongly increases with ion energy. At a fixed fluence, the transverse diameter increases with electronic energy loss. Even at an energy as low as 300 keV large particle anisotropy was found (size aspect ratio of 1.43 at 1×10^{15} cm^{-2}). The transverse plastic strain gradually decreases with increasing irradiation temperature: it decreases by a factor 4.5 between 85 and 380 K. The data are in agreement with a viscoelastic thermal spike model for anisotropic deformation. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1629793]

Amorphous materials subject to high-energy ion irradiation can undergo anisotropic plastic deformation at constant volume.[1–3] One of the most striking examples of this effect is the deformation of single colloidal particles under mega-electron-volt ion irradiation.[4,5] Spherical silica colloids expand perpendicular to the ion beam and contract parallel to the ion beam changing their shape to oblate ellipsoidal. This ion beam deformation technique provides a unique method to tailor the shape of colloidal particles and aggregates. For example, prolate ellipsoids can be made by using subsequent ion irradiations from different directions.[4] Also, the optical properties of three-dimensional colloidal photonic crystals can be tailored by ion beam deformation.[6] And recently we demonstrated how a colloidal mask for nanolithography can be modified by ion irradiation.[7] With these different applications evolving, and in order to obtain fundamental understanding of the deformation process it becomes important to determine the critical parameters that determine the deformation rate.

Previously, we have shown that for 16 MeV Au irradiation the deformation rate (relative expansion per unit fluence) remains constant for increasing fluence, thus leading to an exponential growth of the transverse diameter with ion fluence.[8] It was also shown that the deformation rate increases with ion energy for energies >4 MeV. In fact, many studies on anisotropic deformation are performed at very high energies (several 100 MeV).[3]

A natural question that has remained open is what the lowest ion energy is at which anisotropic deformation occurs. Extrapolation of high-energy deformation data has suggested it will not occur below 1 MeV.[3,8] In this letter we study anisotropic deformation at Xe ion energies in the range 0.3–4 MeV. We find that significant deformation still occurs at energies as low as 300 keV, in contradiction with the earlier extrapolations. The transverse plastic strain increases with electronic energy loss of the Xe ions, with no or only a small threshold stopping. The deformation gradually decreases with increasing substrate temperature in the range 85–380 K. The results are in qualitative agreement with a mesoscopic viscoelastic model for anisotropic deformation.

Several dispersions of spherical colloidal silica particles were synthesized in solution using methods described in Ref. 9. A drop of the colloidal dispersion was dried on a Si(100) substrate leading to a coverage well below 1 monolayer. The sample was mounted on a copper block of which the temperature was kept constant in the range 85–380 K by cooling with liquid nitrogen or by resistive heating. Vacuum grease was used to improve the heat contact between sample and copper block. The colloidal particles were irradiated with Xe ions accelerated to energies in the range 0.3–4 MeV using a 1 MV Van de Graaff accelerator and a Xe charge state up to 4+. The samples were homogeneously irradiated to ion fluences as high as 1×10^{15} Xe/cm^2 by electrostatically scanning the ion beam through an aperture of 2.7×2.7 cm^2. The ion energy flux was kept constant at 0.04 W/cm^2 for all ion energies. All irradiations were performed at 45° with respect to the surface normal to enable investigation of the particles parallel and perpendicular to the ion beam. Scanning electron microscopy (SEM) using a 5 keV electron beam was used to determine the size and shape of the colloids before and after irradiation. The diameter of the unirradiated silica spheres was determined to be 125, 305, and 1030 nm, respectively, with a relative polydispersity $\leqslant3\%$.

Figure 1(a) shows a SEM image taken after 4 MeV Xe irradiation of 305 nm diameter silica colloids to a fluence of 1×10^{15} cm^{-2} at a temperature of 85 K. The image is taken perpendicular to the ion beam. The dashed sphere indicates the original perimeter of the colloid before irradiation. It can clearly be seen that the colloid has expanded perpendicular to the ion beam and contracted parallel to the ion beam. The

[a]Electronic mail: t.v.dillen@amolf.nl

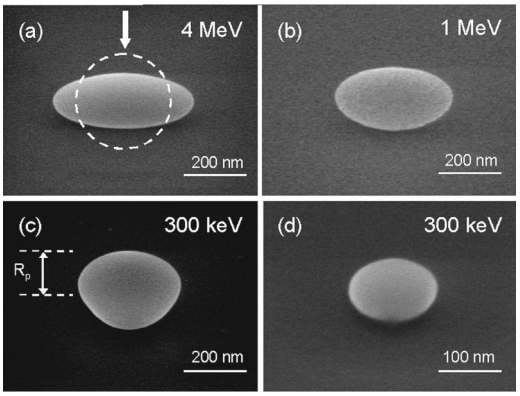

FIG. 1. Scanning electron microscopy images of silica colloids after Xe ion irradiation to a fluence of 1×10^{15} cm^{-2} at an energy of 4 (a), 1 MeV (b), and 300 keV (c,d). Irradiations were performed at a temperature of 85 K and at an angle of 45°. All images are taken perpendicular to the ion beam. The arrow in (a) indicates the ion beam direction. The dashed circle in (a) with a diameter of 305 nm represents the original spherical size before irradiation for (a), (b), and (c). The diameter of the colloids used in (d) is 125 nm. The mean projected ion range R_p for 300 keV Xe is indicated in (c).

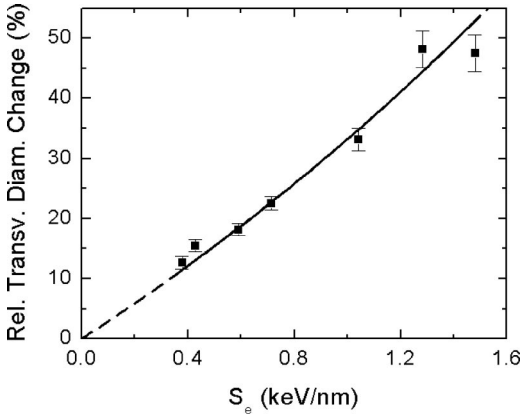

FIG. 2. Relative transverse diameter change of the silica colloids as a function of average electronic energy loss S_e at a fixed fluence of 1×10^{15} cm^{-2} at 85 K. The data are determined from the colloid deformation after Xe irradiation with energies in the range between 300 keV and 4.0 MeV. The original diameter of the colloids was 305 nm for all irradiations, except for the 300 keV irradiation, where the original diameter was 125 nm [Fig. 1(d)]. The solid line is a fit to the data using $\varepsilon_T=\exp(A\phi)-1$ and Eq. (1) taken from a viscoelastic model. The dashed line represents the extrapolation of this model to small S_e.

apparent colloid size aspect ratio (major over minor axis) is 2.52. Previous SEM studies have shown that during ion irradiation at 45°, the colloids perform a gradual angular ''roll-off'' with respect to the perpendicular ion beam direction.[5] For the sample in Fig. 1(a) the angle between the colloid's minor axis and the ion beam is 15°±1°, upon completion of the irradiation. Taking this effect into account in the SEM projection, the actual size aspect ratio is calculated to be 3.21±0.20. No significant volume change is observed upon irradiation.

Figure 1(b) shows a SEM image taken after irradiation at a lower Xe ion energy of 1 MeV (1×10^{15} cm^{-2}). The size aspect ratio determined from the SEM analysis (after correcting for the roll-off angle of 6°) is 1.84±0.05. This shows the anisotropic deformation process is strongly dependent on the ion energy used, in agreement with experiments performed at much higher energies.[3]

Figures 1(c) and 1(d) show silica colloids after irradiation at an even lower energy of 300 keV. It can clearly be seen that the shape of the colloids in Fig. 1(c) is nonellipsoidal. This is due to the fact that the projected Xe ion range (136 nm as calculated using a Monte Carlo simulation program)[10] is much smaller than the original colloid diameter of 305 nm. Only the ion-modified top part of the colloid has deformed. Additional experiments were then performed with colloids having a diameter of 125 nm, smaller than the ion range. These do have an ellipsoidal shape as can be seen in Fig. 1(d). The size aspect ratio of these colloids is 1.43 ±0.04, again without observable volume change.

The fact that considerable deformation is observed at Xe ion energies as low as 300 keV is striking. The typical deformation rate, defined as the differential length change perpendicular to the ion beam per unit fluence, is 1×10^{-16} cm^2/ion: at this rate a 300 keV Xe fluence of 10^{14} cm^{-2} will result in a transverse expansion of 1%.

For 300 keV and 4 MeV Xe ions the average total energy lost in atomic and electronic stopping processes[10] in silica is roughly identical (~2.3 keV/nm). In this energy range, the electronic stopping S_e increases monotonically with ion energy, the nuclear stopping decreases correspondingly. Since the deformation increases with ion energy it must therefore be mainly dependent on the electronic stopping. This is consistent with earlier work at very high energy.[3] Figure 2 shows the relative increase of the transverse diameter as a function of the average electronic stopping of the Xe ions in the silica colloids at a fixed fluence of 1×10^{15} Xe/cm^2 and at a constant temperature of 85 K. For this experiment we used 0.3, 0.5, 0.75, 1.0, 2.0, 3.0, and 4.0 MeV Xe ions. The data in Fig. 2 were determined from deformation experiments on 305 nm diameter colloids [e.g., Figs. 1(a) and 1(b)] except for the 300 keV Xe irradiation, where the deformation was determined on 125 nm diameter colloids [Fig. 1(d)]. As can be seen in Fig. 2 the transverse plastic strain gradually increases with S_e (solid squares).

Trinkaus *et al.* have proposed a model to explain the ion irradiation-induced deformation phenomena in terms of a viscoelastic thermal spike model.[11,12] In this model the deformation is attributed to the high degree of anisotropy of the ion-induced thermal spike. For high values of S_e a cylindrical region around the ion track is heated. Shear stresses brought about by the thermal expansion of the highly anisotropic heated region would then relax, resulting in a local in-plane expansion perpendicular to the ion track. The latter then freezes in upon cooling down of the thermal spike. The macroscopic anisotropic deformation then is the result of a large number of individual ion impacts (10^5–10^7 for the colloids in this study). Within this viscoelastic model two factors determine the energy dependence of the deformation. First of all, at low energy the ion trajectory angle is distributed due to Rutherford scattering that is quite prominent (high nuclear stopping), leading to less anisotropic deformation. At 300 keV the average angular variation over the colloid thickness is below 15° and thus the angular anisotropy is relatively small. Second, a higher energy will cause a higher temperature in the spike and thus a higher in-plane expansion.

Within the viscoelastic thermal spike model, the transverse plastic strain rate A (per unit fluence) is given by[11]

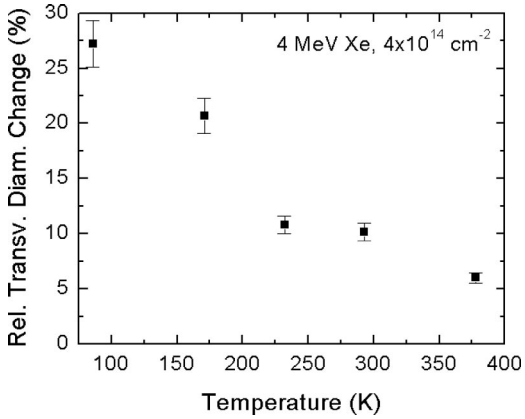

FIG. 3. Relative transverse diameter change of 1030 nm diameter silica colloids as a function of sample temperature measured after irradiation with 4 MeV Xe to a fluence of 4×10^{14} cm^{-2}.

$$A=\frac{1.16}{e}\,\frac{1+\nu}{5-4\nu}\,\frac{\alpha}{\rho c}S_e\,, \tag{1}$$

with $e=2.72$, ν is Poisson's ratio (typically 0.2 for silica), α is the linear thermal expansion coefficient, ρ is the density, and c is the specific heat of the target material. Equation (1) holds for low enough substrate temperatures to ensure freezing-in of the viscous strain and high enough values of S_e to ensure cylindrical symmetry of the thermal spike. For a constant strain rate A during irradiation, the transverse diameter should increase exponentially with ion fluence ϕ. In that case the transverse plastic strain is given by: $\varepsilon_T=\exp(A\phi)-1$. The solid line in Fig. 2 is a fit of the transverse strain data using this relation and Eq. (1) and $\phi=1\times10^{15}$ cm^{-2}. The model provides a very good description of the data for $\alpha/\rho c=1.5\times10^{-12}$ m^3/J. For typical values of $\rho=2.0$ g/cm^3 and $c=10^3$ J kg^{-1} K^{-1}, this results in a value of $\alpha=3.0\times10^{-6}$ K^{-1} for the colloidal silica.

These data imply that anisotropic deformation is a general phenomenon that must be taken into account even in the tens to hundreds of kilo-electron-volt energy range that is commonly used in many experiments and technological applications. Previous high-energy irradiation experiments indicated an apparent threshold value for the electronic stopping in the order of 1 keV/nm below which no deformation would be expected.[3,8] Our data show that deformation occurs well below this value and in fact the model that fits the data well does not predict such a threshold (dashed line, Fig. 2). Ion beam-induced deformation is thus expected at energies well below 300 keV, although it should be noted that for low energy Eq. (1) must be corrected for the large angular straggle. More measurements are needed to study this in detail.

We have also studied the dependence of the deformation process on irradiation substrate temperature. Spherical silica colloids of 1030 nm in diameter were irradiated with 4 MeV Xe ions to a fluence of 4×10^{14} cm^{-2} at temperatures in the range of 85–380 K. Figure 3 shows the relative transverse diameter change as a function of temperature.

As can be seen, the transverse plastic strain gradually decreases with increasing temperature. It is about 4.5 times less at 380 than at 85 K. A similar temperature dependence has been observed for the deformation of thin foils of vitreous silica and metallic glasses at very high energies.[1,3] Within the viscoelastic model the decrease in deformation with increasing substrate temperature is attributed to the relaxation of the strained ion tracks that are under compression due to the interaction with the surrounding silica matrix.[12] The local compressive stress would be partly relaxed at a rate determined by the reduced viscosity of the silica at elevated substrate temperature. This relaxation is more efficient at higher irradiation temperatures, therefore reducing the net amount of anisotropic deformation as observed in Fig. 3. It should be noted that under high-flux irradiation (beam fluxes much higher than used in this study), sample heating may also lead to reduced anisotropic deformation.[13]

In conclusion, ion irradiation-induced anisotropic plastic deformation of colloidal silica particles occurs at energies as low as 300 keV. The deformation strain at 300 keV is 1% for each Xe fluence of 10^{14} ions/cm^2. In the energy range 300 keV–4 MeV, the transverse strain increases with electronic stopping, without indication of a threshold. The transverse expansion gradually decreases with increasing substrate temperature. The data can be explained by a viscoelastic model for local shear stress relaxation in the high-temperature ion-induced thermal spike. With this observation the deformation of a wide variety of colloidal materials becomes possible using readily available accelerator energies.

This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM) and was financially supported by the Dutch Organization for Scientific Research (NWO).

[1] S. Klaumünzer and G. Schumacher, Phys. Rev. Lett. **51**, 1987 (1983).
[2] M.-D. Hou, S. Klaumünzer, and G. Schumacher, Phys. Rev. B **41**, 1144 (1990).
[3] A. Benyagoub, S. Löffler, M. Rammensee, S. Klaumünzer, and G. Saemann-Ischenko, Nucl. Instrum. Methods Phys. Res. B **65**, 228 (1992).
[4] E. Snoeks, A. van Blaaderen, T. van Dillen, C. M. van Kats, M. L. Brongersma, and A. Polman, Adv. Mater. (Weinheim, Ger.) **12**, 1511 (2000).
[5] T. van Dillen, E. Snoeks, W. Fukarek, C. M. van Kats, K. P. Velikov, A. van Blaaderen, and A. Polman, Nucl. Instrum. Methods Phys. Res. B **175–177**, 350 (2001).
[6] K. P. Velikov, T. van Dillen, A. Polman, and A. van Blaaderen, Appl. Phys. Lett. **81**, 838 (2002).
[7] E. Snoeks, A. van Blaaderen, T. van Dillen, C. M. van Kats, K. Velikov, M. L. Brongersma, and A. Polman, Nucl. Instrum. Methods Phys. Res. B **178**, 62 (2001).
[8] T. van Dillen, A. Polman, W. Fukarek, and A. van Blaaderen, Appl. Phys. Lett. **78**, 910 (2001).
[9] A. van Blaaderen and A. Vrij, Langmuir **8**, 2921 (1992).
[10] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York, 1985).
[11] H. Trinkaus and A. I. Ryazanov, Phys. Rev. Lett. **74**, 5072 (1995).
[12] H. Trinkaus, Nucl. Instrum. Methods Phys. Res. B **146**, 204 (1998).
[13] Such a beam heating effect caused by high beam current and possibly poor heat contact between sample and substrate holder is most likely the origin of an earlier claim that deformation would not occur at 500 keV Xe irradiation [E. Snoeks, A. van Blaaderen, T. van Dillen, C. M. van Kats, M. L. Brongersma, and A. Polman, Adv. Mater. (Weinheim, Ger.) **12**, 1511 (2000)].