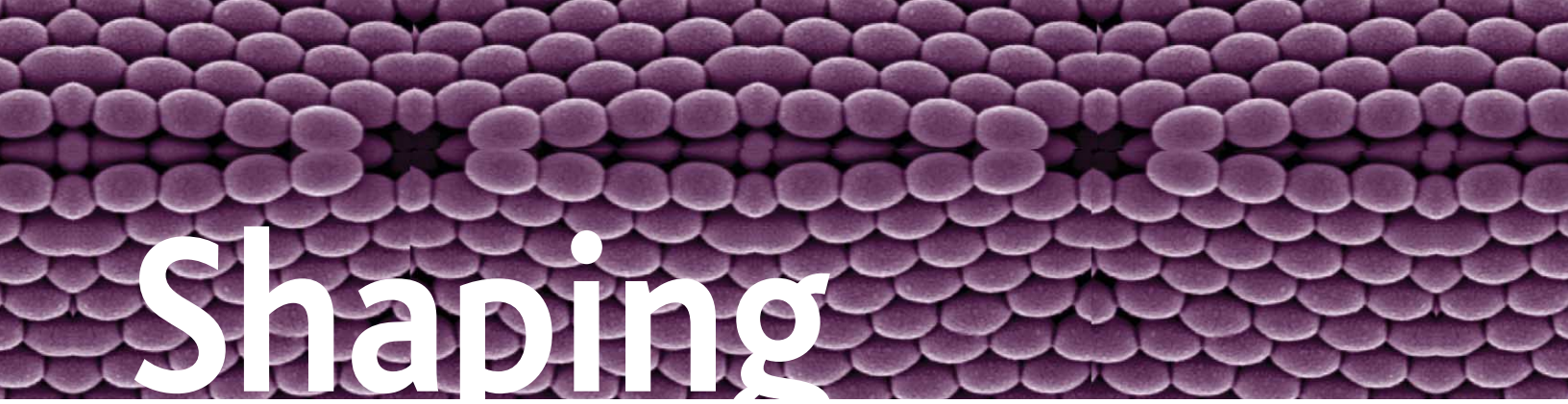

Shaping colloidal assemblies

by Teun van Dillen[†], Alfons van Blaaderen[‡], and Albert Polman[†*]

An MeV ion beam penetrating an amorphous material causes rapid heating of a cylindrically shaped region around the ion track, which leads to anisotropic deformation: the irradiated material shrinks in the direction of the ion beam and expands perpendicular to it. This provides a unique way to tailor the shape of colloidal materials. Spherical silica particles are transformed into oblate ellipsoids, with anisotropy tuned by ion fluence. Ellipsoid suspensions can be used to test theories of colloidal phase transformations. Photonic crystals of ellipsoidal colloids can have enlarged optical band gaps. Deforming metal-silica or silica-metal core-shell particles leads to control over their surface plasmon resonance frequency. Two-dimensional colloidal crystals show complex deformation behavior, providing unique masks for nanolithography.

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Colloidal particles play an important role in studies of self-assembly and phase behavior, and can find many applications in practical materials with interesting optical properties. The synthesis of colloidal model suspensions is well explored and understood for a wide variety of inorganic materials[1]. However, most model systems with a narrow size distribution consist of spherical particles. It appears very difficult to synthesize nonspherical particles, such as oblate and prolate ellipsoids, with low polydispersity[2]. A system of optically transparent ellipsoidal colloids with adjustable aspect ratio would be ideal to investigate the effect of anisotropic particle shape on phase behavior[3,4] and optical properties.

For example, simulations predict that oblate ellipsoids with an aspect ratio larger than 2.75 can form a nematic colloidal liquid-crystalline phase[5]. This can only be tested using particles with small size and shape polydispersity. Photonic crystals are composed of regular arrangements of dielectric materials, such as colloids, and can be used to control spontaneous emission and propagation of light. Calculations predict that photonic crystals composed of ellipsoidal colloids will have larger optical band gaps than their spherical counterparts[6] and, thus, the control of light can be improved. As a third example, metallic colloids show strong optical absorption as a result of surface plasmon resonances. The characteristic resonance frequency is a sensitive function of shape and size. Ellipsoidal metal colloids show plasmon resonances shifted to the infrared, an important range for telecommunications.

ISSN:1369 7021 © Elsevier Ltd 2004

In this review, we describe our research on the fabrication of ellipsoidal colloids using an ion irradiation technique[7]. Monodisperse silica microspheres show a dramatic anisotropic plastic deformation[8,9] under Xe ion irradiation that can be tuned by varying the ion fluence (number of incident ions per unit area). The deformation characteristics are described and explained by a viscoelastic thermal spike model[10-13] for anisotropic plastic deformation. We describe the deformation of several different colloidal materials and demonstrate how the shape and geometry of colloidal assemblies, such as photonic crystals, colloidal masks, and core-shell composites, can be modified by ion irradiation, leading to the formation of unique nano- or microstructures with distinct optical properties.

Deformation of silica colloids

We synthesized silica microspheres via hydrolysis and condensation reactions from tetraethoxysilane[14,15]. Drops of a dilute dispersion were placed on the clean surface of a Si(100) substrate and the ethanol solvent left to evaporate. The colloidal particles were irradiated with Xe ions accelerated to energies between 0.3-4 MeV. The ion beam was scanned to irradiate the entire sample to ion fluences in the range of 3 x 10^{13}-1 x 10^{15} ions/cm^2. The beam flux was in the range 3 x 10^{10}-8 x 10^{10} ions/cm^{2}s. The Si substrate was clamped against a Cu sample stage and cooled to 85 K. Before and after irradiation, the shape and size of the colloidal particles was measured by scanning electron microscopy (SEM) using an electron beam at 5 keV or 10 keV.

Fig. 1a shows an SEM image of unirradiated silica spheres on the Si surface viewed at normal incidence to the substrate. The particle diameter is 1030 nm[16] with a relative size polydispersity of 3%. The particles were irradiated with 4 MeV Xe ions to a fluence of 3 x 10^{14} ions/cm^2 at 85 K with the ion beam tilted +45° away from the surface normal, as indicated in the inset in Fig. 1. Figs. 1b-d show SEM images taken after the irradiation at different tilt angles. In Fig. 1b, the ellipsoids are viewed along the direction of the ion beam, i.e. at +45° tilt angle. In this projection, the ellipsoids appear circular. The dashed circle represents the circumference of unirradiated spheres. The particle has expanded perpendicular to the direction of the ion beam with the transverse diameter of the particles increasing by 24%. Fig. 1c shows an SEM image taken perpendicular to the ion beam, at an angle of -45°. The original ion beam direction is in the plane of the image, as indicated by the white arrow. It is clear that the colloidal particles have contracted parallel to the ion beam. Fig. 1d shows a side view SEM image (15° tilt angle) taken perpendicular to the ion beam. From Figs. 1c and 1d it follows that the longitudinal diameter of the deformed particles (along the direction of the ion beam) has decreased by about 35%. From these measurements, it follows that the volume of the colloids remains constant during irradiation.

The deformation process can be described by the following viscoelastic thermal spike model[10]. The incident ion causes electronic excitation and ionization of target atoms along the ion trajectory. For example, a 4 MeV Xe ion in silica looses 1.5 keV/nm by such excitations. For MeV ion energies, the ion trajectory is roughly linear and a cylindrically shaped, narrow thermal spike evolves around the ion track with a temperature of a few thousand kelvin[17]. Thermal expansion of this heated region in its elastic surrounding medium leads to the build up of a nonisotropic stress distribution and, thus, a local shear stress. In the short (~10 ps) duration of the thermal spike, this shear stress relaxes by Newtonian viscous flow. This leads to a build up of viscous strains that freeze in

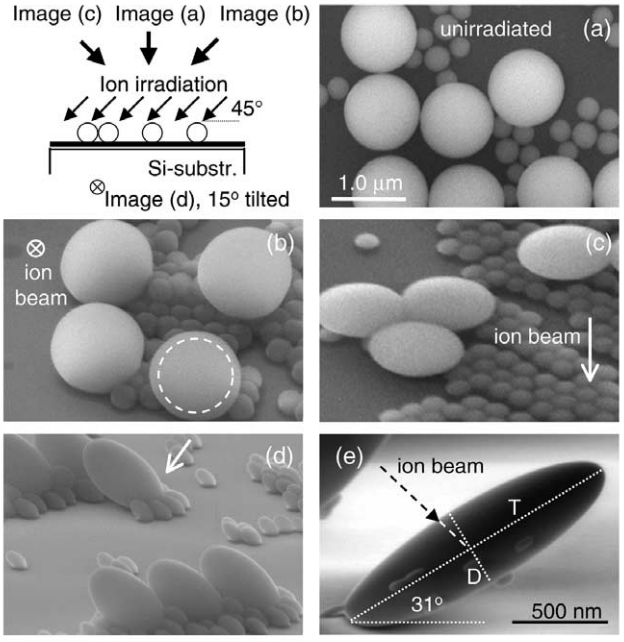

Fig. 1 SEM images of silica particles on an Si substrate. (a) Top view (0° tilt) of as-deposited silica spheres with two different diameters. (b-d) Silica ellipsoids formed after irradiation at an angle of 45° relative to the surface normal. The ion beam direction and viewing angles are indicated in the schematic inset. The ion beam direction is also indicated in the images. The dashed sphere in (b) indicates the size of the colloids before irradiation. Images (a-d) are taken at the same magnification. (e) A silica colloid irradiated with 1 x 10^{15} ions/cm^2 at an angle of 45°. The ion beam direction, the angle between the colloid and substrate, and the major axis T and minor axis D are indicated. (Adapted from[7] with permission. © 2000 Wiley-VCH Verlag.)

upon rapid cooling of the thermal spike region. The result is a local plastic expansion perpendicular to the cylindrical axis and a contraction along the axis.

The observed macroscopic deformation is the result of the integrated effect of a large number of single ion impacts, some 10^6-10^7 ions for a fluence of 3 x 10^{14} ions/cm^2. Over such large numbers, any statistical variations are expected to average out, so that the deformed particles are very monodisperse in both size and shape[18].

Experiments were performed as described above for various Xe ion fluences from 3 x 10^{13}-1 x 10^{15} ions/cm^2. Fig. 2a shows the ellipsoids' major diameter *T* (open circles) and minor diameter *D* (solid circles), obtained from SEM micrographs, as a function of ion fluence, measured by averaging over a large number of colloids[19]. The major diameter *T* increases monotonically with ion fluence, whereas the minor diameter *D* shows a monotonic decrease. The deformation strain rate, defined as the differential length change perpendicular to the ion beam per unit ion fluence, is equal to 6.0 x 10^{-16} cm^2/ion. This corresponds to a transverse expansion of 6% for each unit fluence of 1 x 10^{14} ions/cm^2.

Fig. 1e shows a side view SEM image (10° tilt with respect to the substrate surface) of colloidal silica particles irradiated with 4 MeV Xe ions to a fluence of 1 x 10^{15} ions/cm^2. The diameters *T* and *D* are indicated. At this large deformation (*T*/*D* = 4.8 ± 0.3), the angle α between the major particle axis (*T*) and the substrate is 31°, much smaller than the expected angle of 45° (perpendicular to the original ion beam). At this high ion fluence, the colloids have performed an angular 'roll-off' with respect to the ion beam direction. For the colloid in Fig. 1e, the roll-off angle is 14° and an average angle of 17±3° was found by analyzing ten colloids. Fig. 2b shows the angle α as a function of ion fluence (solid squares). An angle of 45° is observed for small fluences (1 x 10^{14} ions/cm^2), while a gradual decrease is observed for higher fluences. The fluence-dependent angular roll-off is in agreement with a macroscopic model developed by Klaumünzer[13], which describes the shape evolution of a colloidal particle in fixed contact with the substrate at a constant deformation strain rate. The particle angle as a function of fluence calculated using this model is shown by the solid curve in Fig. 2b and is in good agreement with the data.

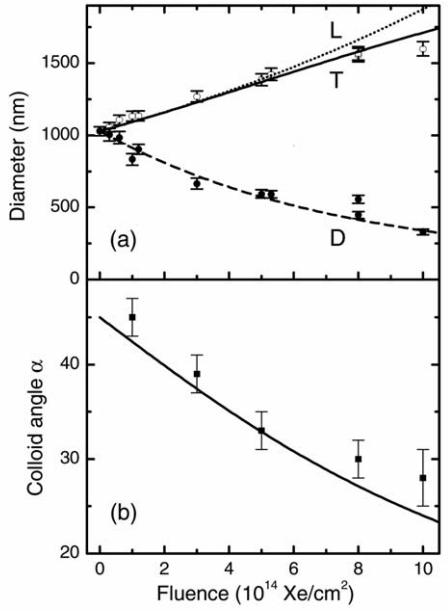

Fig. 2 (a) Major diameter T (open circles) and minor diameter D (solid circles) of silica ellipsoids as a function of 4 MeV Xe ion irradiation fluence (85 K). (b) Angle α between substrate and major axis T of deformed silica colloids as a function of ion fluence. The curves in (a) (T – solid, L – dotted, and D – dashed) and (b) (α – solid) are calculations by the phenomenological model[13] using a deformation strain rate of A = 6.0 x 10^{-16} cm^2/ion. (Part (a) adapted from[7] with permission. © 2000 Wiley-VCH Verlag. Part (b) adapted from[47]. © 2001 Elsevier Ltd.)

As a consequence of angular roll-off, ellipsoids form with three principle axes of different lengths[13]: the transverse diameter *L* (perpendicular to the image plane in Fig. 1e), which is perpendicular to the ion beam irrespective of angular roll-off, will continuously grow with increasing ion fluence, while the diameter *T* (see Fig. 1e) will grow with fluence, reach a maximum, and (for high fluence) decrease because of roll-off. The different behavior of *L* and *T* with increasing roll-off is reflected by the solid and dotted curves in Fig. 2a. Colloidal particles with three different principal axes could find use in studies of self-assembly and phase formation.

We have studied the dependence of the deformation on substrate temperature[20]. The deformation strain rate is about 4.5 times less at 380 K than at 85 K. This is in qualitative agreement with the viscoelastic thermal spike model in which local viscous strains are frozen in more efficiently at low temperatures, yielding a larger macroscopic deformation[11].

To study the ion energy dependence of the deformation process, spherical silica colloids were irradiated with 0.3, 0.5, 0.75, 1.0, 2.0, 3.0, and 4.0 MeV Xe ions to a fixed fluence of 1 x 10^{15} ions/cm^2 at a temperature of 85 K[20]. To ensure that the penetration depth of Xe ions was larger than the colloid diameter at all ion energies, 305 nm diameter colloids were used, except for the 300 keV Xe irradiation where 125 nm diameter colloids were used. Fig. 3 shows the relative increase of the transverse diameter as a function of the

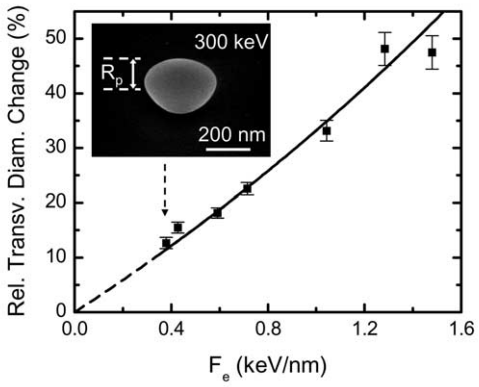

Fig. 3 Relative transverse diameter change of silica colloids as a function of average electronic energy loss F_e at a fixed fluence of 1 x 10^{15} ions/cm^2 at 85 K. The data are determined from colloid deformation after Xe irradiation with energies in the range between 300 keV and 4.0 MeV. The solid line is a fit to the data using a viscoelastic thermal spike model. The dashed line represents extrapolation of this model to small F_e. The inset shows an SEM image of a 305 nm diameter silica colloid irradiated with 300 keV Xe ions (projected ion range = 136 nm) to a fluence of 1 x 10^{15} ions/cm^2 at 85 K. (Adapted from[20] with permission. © 2003 American Institute of Physics.)

average electronic energy loss F_e calculated for each ion energy using SRIM, a Monte Carlo simulation program[21]. The measured transverse plastic strain (solid squares) gradually increases with F_e. The solid line is a fit to the data using the mesoscopic viscoelastic thermal spike model[10] with typical thermal properties for silica. More details have been reported[11,20]. From the data in Fig. 3 and the model calculation extrapolated to lower energies (dashed line in Fig. 3), it follows that anisotropic deformation is a general phenomenon that must be taken into account even in the tens to hundreds of keV energy range commonly used in many experiments and technological applications. To illustrate what happens when the ion range is smaller than the colloid diameter, we irradiated 305 nm diameter colloids with 300 keV Xe ions (Xe ion range ~136 nm). The inset in Fig. 3 shows an SEM image (perpendicular to ion beam) of a colloid after irradiation. Only the ion-modified top part of the colloid has deformed, resulting in a nonellipsoidal shape.

Finally, for studies of self-assembly and phase behavior, colloidal particles must be put in suspension. We have shown that, by using ultrasonic treatment, ion-irradiated colloidal particles can be removed from the substrate. A stable suspension of deformed silica particles is obtained and light scattering confirms that the spheroids are redispersed as single entities. Preliminary self-assembly experiments show indications of a nematic colloidal liquid crystalline phase of oblate colloids[7]. The typical particle yield in our experiments is on the order of 3 x 10^8 colloids (0.3 mg) per hour.

Irradiation of other colloidal materials

Fig. 4 shows SEM images of colloidal particles of several different materials, all irradiated with 4 MeV Xe ions at 77 K. A side view image of microcrystalline ZnS particles[22] irradiated at a fluence of 5 x 10^{14} ions/cm^2 is shown in Fig. 4a. The size aspect ratio of these particles is 2.2, similar to that observed for silica particles. Fig. 4b shows single-crystalline Al_2O_3 colloids[23] after irradiation with 4 x 10^{14} ions/cm^2. Although less easy to identify in the SEM image because of particle clustering, we find no evidence for anisotropic deformation. Similarly, microcrystalline Ag colloids[24] (4 x 10^{14} ions/cm^2, Fig 4c) show no deformation. The absence of deformation is consistent with earlier work on the deformation of thin foils[25]. Within the thermal spike model, a crystalline material does not deform because there is a large resistance to deformation as a result of the absence of 'shear sites' (regions containing local free volume)[26]. The molten region in the spike recrystallizes so rapidly that no deformation would occur. We note that the deformation of microcrystalline ZnS colloids (Fig. 4a) may seem inconsistent with the argument that crystalline materials do not deform. However, these particles amorphize under the ion beam, as concluded from X-ray diffraction measurements after irradiation.

We have irradiated SiO_2/Au core/shell particles consisting of a silica core with a radius of 205 nm and a closed Au shell with a thickness of 63 nm. These particles were made as

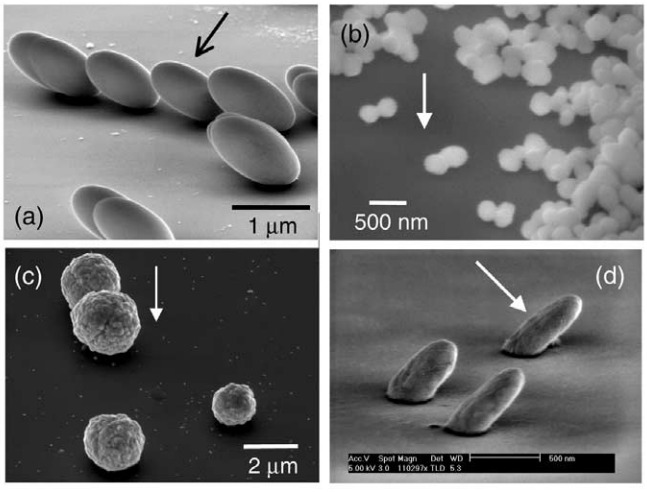

Fig. 4 SEM images of ion irradiated colloids of various materials: (a) microcrystalline ZnS, (b) single-crystalline Al_2O_3, (c) microcrystalline Ag, and (d) SiO_2/Au core/shell colloids. The colloids in (d) have an original silica core radius of 205 nm and a 63 nm thick Au shell. The direction of the ion beam is indicated by arrows. Images (a,d) taken from the side at 15° and 10° tilt angles, respectively, and (b,c) taken as in Fig. 1c. (Adapted from[47]. © 2001 Elsevier Ltd.)

described by Graf *et al.*[27]. The size polydispersity of the colloid distribution is 3-5%. Fig. 4d is a side view SEM image (10° tilt) of these colloids after irradiation with 4 MeV Xe ions to a fluence of 1 x 10^{15} ions/cm^2. The core/shell particles have deformed during ion irradiation. Since no deformation is observed for pure Au nanoparticles[28], the induced deformation of the Au shells is brought about by the deformation of the silica core. This indirect deformation of Au shells makes it possible to fabricate anisotropic metallic shells. Optical spectroscopy shows a distinct anisotropy of the surface plasmon resonance in these shells[29].

Applications of anisotropic colloids

Photonic crystals of shape-anisotropic colloidal silica particles

Colloidal photonic crystals have been fabricated from 220 nm diameter SiO_2 colloids (relative polydispersity ±3%), synthesized using a microemulsion method followed by seeded growth[30]. Thin colloidal crystals, comprising eight to ten layers, were grown on glass substrates using a controlled drying method[31-33] and annealed at 600°C for four hours in air[34]. The colloidal crystals were irradiated with 4 MeV Xe ions to a fluence of 1.0 x 10^{15} ions/cm^2 at 90 K, with the sample surface at 45° to the ion beam. Samples were coated with a 5 nm Pt/Pd layer before analysis by SEM.

Figs. 5a-c show SEM images of a colloidal crystal after ion irradiation. The different viewing directions are shown in the schematic inset. After irradiation, all particles deform into

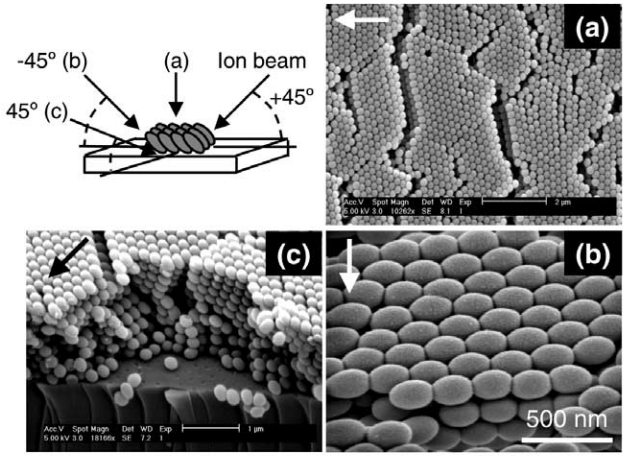

Fig. 5 SEM images of a planar photonic crystal of close-packed SiO_2 oblate ellipsoids obtained after irradiation with 4 MeV Xe ions to a fluence of 1.0 x 10^{15} ions/cm^2 at an angle of 45° at 90 K. (a) Top view showing the (111) crystal plane. (b) Image taken perpendicular to the ion beam direction. The average size aspect ratio L/D image is 1.65 ± 0.09. (c) Side view image (45° tilt) of a broken crystal showing the depth of the deformation caused by the irradiation. The arrows show the direction of the ion beam. (Adapted from[35] with permission. © 2002 American Institute of Physics.)

(almost) oblate ellipsoids, as seen in Fig. 5b. The particles expand relatively undisturbed in the plane perpendicular to the ion beam. From SEM images taken at -45° (Fig. 5b), the size aspect ratio *L*/*D* of the deformed colloids can be measured and amounts to 1.65 ± 0.09.

From Fig. 5c, one can see that the anisotropic deformation extends throughout the depth of the crystal, including the layer in contact with the substrate. However, particles close to the substrate are less deformed as a result of the reduced ion energy at that depth. The layer thickness (~1.8 μm) is close to the penetration depth of the 4 MeV Xe ions, taking the angle of irradiation and SiO_2 filling fraction into account. Higher energies could be used to deform thicker crystals (or other colloidal assemblies) more uniformly. It is apparent that there is a deviation from the ellipsoidal shape caused by deforming spheres touching in the crystal. Most likely, this increases the packing fraction and, consequently, the effective refractive index of the composite. Optical transmission spectra show that, because of a change in the lattice structure and particle form factor of the photonic crystal, the photonic stop band exhibits a clear blue shift[35].

Aligned Au nanorods in silica made by ion irradiation

Core/shell colloidal particles composed of a 14 nm diameter Au core surrounded by a 72 nm thick silica shell were prepared in solution as described elsewhere[36]. A few drops of a dilute solution were dispersed on a 10 nm thick Si_3N_4 membrane, which allowed transmission electron microscopy (TEM) of individual particles. The particles were irradiated with 30 MeV Se ions to a fluence of 2 x 10^{14} ions/cm^2 at 85 K and an angle of 45°.

Fig. 6a shows a TEM image (200 keV electron beam) of an Au/SiO_2 core/shell particle before irradiation. It is spherical with a 14 nm diameter Au core centered inside. Fig. 6b shows a TEM image taken after irradiation along the normal. The arrow indicates the ion beam direction projected onto the surface. Clearly, neither the silica shell nor the Au core is spherically shaped. The deformation of the silica shell is consistent with the anisotropic deformation described above with a relative transverse expansion of ~20%. The Au core has also deformed, but in an entirely different manner: a major axis is now observed along the ion beam and a minor axis perpendicular to the beam. The 14 nm diameter Au core has deformed into a rod with apparent dimensions of 6 nm by 38 nm. Correcting for the 45° projection of the image relative to the ion beam direction, the major axis is as large

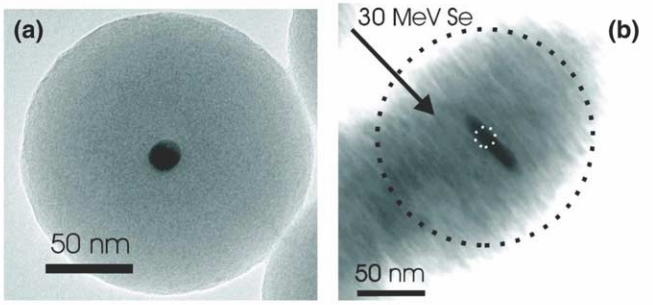

Fig. 6 TEM images of core/shell colloids composed of a 14 nm diameter Au core and a 72 nm thick silica shell (a) before irradiation and (b) after ion irradiation. The ion beam direction projected onto the surface is indicated by an arrow. The original spherical perimeter is indicated by the dashed circle. (Reprinted with permission from[37]. © 2004 Wiley-VCH Verlag.)

as 54 nm (size aspect ratio ~9). No deformation is observed for 14 nm diameter Au colloids without a surrounding silica shell. The deformation of the Au core must, therefore, be related to an effect imposed by the silica shell. The Au deformation is attributed to the in-plane mechanical stress in the silica shell acting on the radiation-softened Au core[37]. Optical extinction measurements[37] show that aligned anisotropic Au nanorods made by high-energy ion irradiation have red-shifted surface plasmon absorption resonances with respect to isotropically shaped Au nanoparticles.

Colloidal metal particles embedded in a *bulk* silica glass environment also show changes in size and shape upon irradiation. We have found that Ag nanoparticles embedded in soda lime silica glass form arrays aligned in directions along the ion tracks[38]. Such arrays may serve as model systems for nanoscale plasmonic energy waveguides[39]. D'Orléans *et al.*[40] have found that Co nanoparticles in silica glass change shape, with an elongation observed in the ion beam direction.

Deformation of colloidal masks

Nanosphere lithography is a well-known technique for fabricating ordered arrays of metallic nanoparticles[41]. In this technique, a metal is evaporated through the holes in a self-assembled colloidal crystal. By using the ion beam deformation technique, the shape of the colloidal mask can be tuned and the lattice spacing and shape of the voids in between the spheres can be uncoupled. Fig. 7a shows a pattern of Ag dots made by evaporation of 30 nm Ag through a hexagonally close-packed colloidal mask composed of 1.0 μm diameter silica colloids. The image was taken after removal of the colloidal mask by ultrasonic treatment.

Fig. 7b shows an image taken after evaporation though a colloidal mask that was irradiated under normal incidence with 4 MeV Xe ions to a fluence of 6 x 10^{14} ions/cm^2 at 90 K.

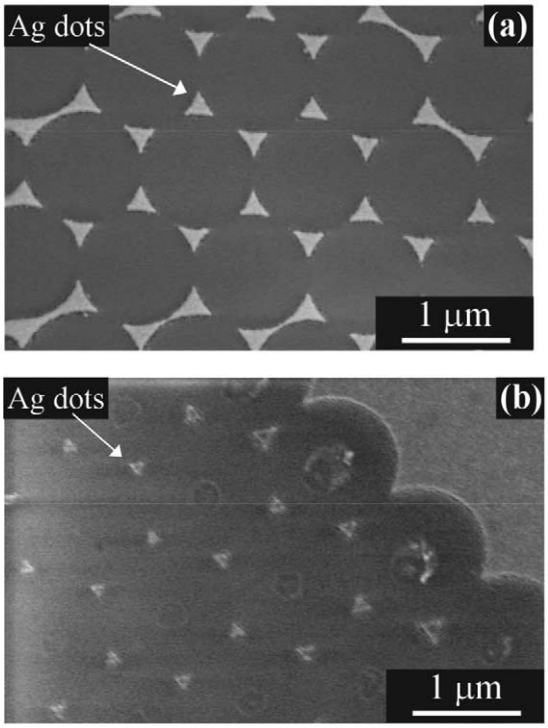

Fig. 7 Ag patterns (thickness 30 nm) on a glass substrate made by thermal evaporation through a self-assembled colloidal mask that was (a) unirradiated and (b) deformed with 4 MeV Xe ions at 90 K to a fluence of 6 x 10^{14} ions/cm^2 at normal incidence. Images were taken at normal incidence after removal of the colloids. The bright spots are the Ag features.

This experiment shows that using a deformed colloidal mask produces a major reduction in the feature size of the Ag dots: feature size is decreased from 234 ± 15 nm (Fig. 7a) to 125 ± 15 nm (Fig. 7b). More recent work by Vossen *et al.*[42] demonstrates further reduced mask features down to 30 nm. Such metal nanoparticle arrays could find application in studies of nanoscale plasmon coupling and energy transfer.

Deformation of toroidal microresonators

As a final demonstration of complex deformation behavior, we show the effect of 30 MeV Cu irradiation (2 x 10^{15} ions/cm^2, 77 K) on a toroidal microresonator[43]. This structure, shown in the inset of Fig. 8, is composed of a SiO_2 toroid with a major diameter of 40 μm and minor diameter of 5 μm, supported by a Si post. Such toroids have been used to fabricate Er-doped SiO_2 microlasers on Si with an extremely low pump threshold[44]. The toroid was irradiated with the aim of reducing its thickness in order to enhance the confinement of optical modes that are guided through it. As can be seen in Fig. 8, a highly irregular geometry is found, most likely as the result of stress inhomogeneities in the oxide around the contact with the Si post[45].

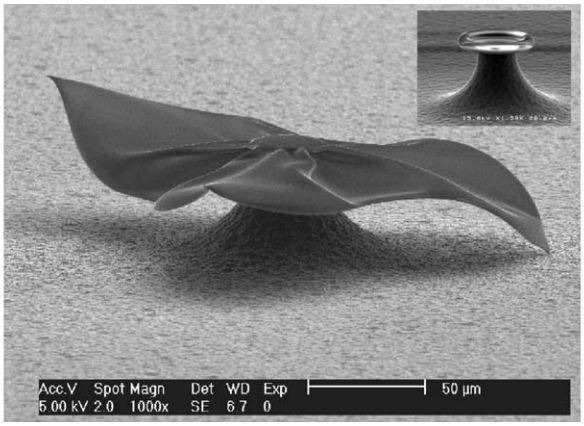

Fig. 8 SEM image of a silica toroid supported on a Si post after irradiation with 30 MeV Cu ions to a fluence of 2 x 10^{15} ions/cm^2 at 77 K. The inset shows the toroid before irradiation[43].

Conclusions

The combination of chemical synthesis and ion irradiation techniques makes it possible to fabricate a new class of colloidal ellipsoids with continuously variable shape. Ion-irradiation-induced anisotropic plastic deformation changes the shape of colloidal silica particles from spherical to (oblate) ellipsoidal. The deformation increases with increasing ion fluence and energy and decreases with increasing temperature in agreement with a viscoelastic thermal spike model for anisotropic plastic deformation. Deformation is also observed for microcrystalline ZnS particles and SiO_2/Au core/shell particles. No deformation is found for single-crystalline Al_2O_3 and microcrystalline Ag particles. The shape and geometry of colloidal assemblies, such as photonic crystals, colloidal masks, and core/shell composites, can be modified by ion irradiation, leading to the formation of nano- or microstructures with distinct optical properties. MT

Acknowledgments

The authors thank E. Snoeks, K. P. Velikov, J. J. Penninkhof, and S. Roorda at FOM-Institute for Atomic and Molecular Physics; D. L. J. Vossen, C. van Kats, C. Graf, and A. M. Vredenberg at the Debye Institute; B. Kooi at Groningen University; and K. Vahala and T. J. Kippenberg at the California Institute of Technology for their contribution to the work reviewed in this article. Research Center Rossendorf is gratefully acknowledged for some of the ion irradiations. This work is part of the research program of the Dutch Foundation for Fundamental Research on Matter (FOM) and was financially supported by the Netherlands Organization for Scientific Research (NWO). This article reviews work reported in the Ph. D. thesis of T. van Dillen[46], which can be downloaded from www.amolf.nl. Printed copies are available upon request by sending an e-mail to library@amolf.nl. For further reference to colloid matter and optical properties related to this work, see: www.colloid.nl (AvB) and www.erbium.nl (AP).

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