

# Synthesis of nanosized silver particles in ion-exchanged glass by electron beam irradiation

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(Received 26 November 1996; accepted for publication 23 January 1997)

Ag particles of 4.2 nm mean diameter have been formed inside a glass matrix, doped with silver by ion exchange, by electron beam irradiation of the glass cut into thin slices by ultramicrotomy. By this treatment, a high concentration of particles which are homogeneously arranged throughout the glass and exhibit a narrow size distribution is achieved (volume fraction of particulate silver:  $3.5 \times 10^{-2}$ ). The interface stress reflecting the particle/matrix interaction is comparable to that of isolated Ag particles. This new route of synthesis will allow to generate materials with strong third order nonlinear susceptibility. © 1997 American Institute of Physics. [S0003-6951(97)01513-1]

Small particles embedded in an insulating matrix are widely studied because of their potential application as resonant-type nonlinear optical materials for photonic devices.<sup>1-3</sup> Glasses containing nanosized metal particles such as gold, silver, and copper exhibit not only an optical absorption originating from the surface plasmon resonance of the metal particles, but also third-order optical nonlinearity.<sup>4-6</sup> The optical absorption depends on particle size, surrounding medium as well as particle shape and spatial distribution.<sup>7,8</sup> Such materials may be synthesized by a variety of methods like ion exchange,<sup>9,10</sup> sol-gel,<sup>11,12</sup> or ion implantation.<sup>13,14</sup> Mostly they exhibit a wide size distribution of particles which is often inhomogeneous with respect to the location inside the matrix. Usually, only small values of the third-order nonlinear susceptibility  $\chi^{(3)}$  are achieved because of low particle concentrations (typical volume fraction:  $10^{-6}$ – $10^{-3}$ ).

Here we introduce a new method to generate high concentrations of metal particles inside a glass matrix having a narrow size distribution as well as a homogeneous arrangement throughout the glass volume. This promising material property is obtained by electron beam irradiation of glass doped with silver by an ion-exchange procedure. High resolution electron microscopy (HREM) is used to study the nanoparticulate composite and the particle/matrix interaction as reflected by the interface stress. For comparison, nonembedded Ag particles synthesized via a sol-gel route are studied as well.

Soda-lime glass (main constituents: 72 mol %  $\text{SiO}_2$  and 13.8 mol %  $\text{Na}_2\text{O}$ ) was subjected to an ion-exchange procedure for 2 h at 400 °C in a mixed  $\text{AgNO}_3$  (2 wt %)/ $\text{NaNO}_3$  melt by which a well defined amount of silver was incorporated. The glass was cut by ultramicrotomy<sup>15</sup> to thin slides of constant thickness (30 nm) to allow a uniform interaction with the electron beam. Inside an EM 10 CR electron microscope operating at 100 kV, these glass slides mounted on a copper microgrid were irradiated by electrons

with a beam current density of 6.4 A/cm<sup>2</sup>. This irradiation being considerably more intense than that usually applied in electron microscopy induced precipitation of Ag particles within a few seconds. The temperature increase of the glass during irradiation was monitored by the melting of defined metal islands to not be above 300 °C.

The sol-gel samples synthesized for comparison are obtained by hydrolysis at 75–90 °C of tetraethoxysilane in ethanol solution, to which  $\text{AgNO}_3$  in ethanol solution was added, followed by drying at 150 °C. The resulting material was ultrasonically agitated in propanol to transfer Ag particles formed at the surface of the  $\text{SiO}_2$  gel to the carbon supporting film of copper microgrids dipped into the solute.

Characterization of the various specimens was done by transmission electron microscopy (TEM) in a JEM 100C operating at 100 kV to determine particle size, shape, arrangement, and concentration. HREM by means of a JEM 4000 EX operating at 400 kV was used to image lattice plane fringes of (111) and (200) type in the particles. The micrographs recorded near Scherzer focus were subjected to digital image processing for contrast enhancement and quantitative determination of lattice plane spacings.

Figure 1 shows a typical overview of Ag particles contained in the glass which are of nearly spherical shape and mostly single crystalline. Their crystalline nature is revealed by corresponding selected area electron diffraction patterns. They exhibit a narrow size distribution with a mean particle diameter of 4.2 nm (see Fig. 2). By the ion exchange procedure, an exchange rate of about 70% was achieved, i.e., 9.7 mol % of the 13.7 mol %  $\text{Na}_2\text{O}$  are replaced by  $\text{Ag}_2\text{O}$  corresponding to a concentration of  $4.8 \text{ Ag}^+$  ions/nm<sup>3</sup>. By assuming a spherical particle shape and with the dimensions of the glass slides known, the amount of silver precipitated could be established to about  $1.353 \times 10^4 \text{ nm}^3$  which means not only a high amount of conversion of  $\text{Ag}^+$  ions (~44%), but also a volume fraction of particulate silver as high as  $3.5 \times 10^{-2}$ .

The conventional precipitation of silver in ion-exchanged glass requires the action of reducing agents

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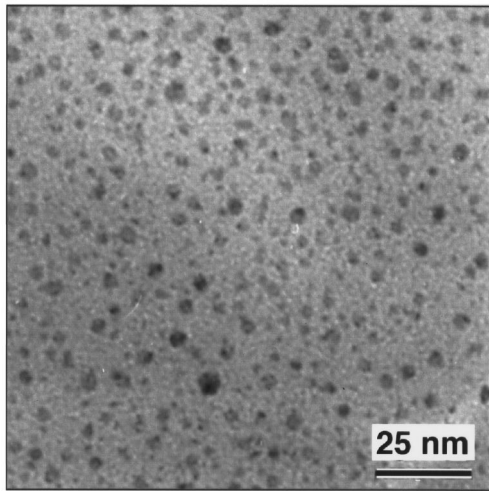


FIG. 1. Ag particles in a thin slide of ion-exchanged glass subjected to electron beam irradiation.

present in the glass and enhanced diffusivity which is achieved only by thermal treatment at temperatures well above 450 °C. By this procedure, only a few percent of the  $\text{Ag}^+$  ions introduced are converted to particulate silver.<sup>16</sup> The formation of crystalline Ag particles under irradiation, however, is induced by electron energy deposition in the glass leading to secondary electron emission. The radiation enhanced diffusivity being some orders of magnitude larger than the corresponding thermal one<sup>6</sup> together with bond breaking and defect creation inside the glass network favor the precipitation of silver not only at distinctly lower temperatures, but also at considerably higher rates.

At small sizes (< about 10 nm), the surface stress causes isolated metal particles to be in state of compression such that the internal pressure is inversely proportional to the particle radius  $r$ . Likewise, the interface stress works in embedded particles if there is no strong particle-matrix interaction. The corresponding effect may be measured as a lattice contraction. For spherical particles, the surface or interface stress  $f$  is determined by:  $f = 3r\Delta a/2a(r)\kappa$ , where  $r$  denotes the

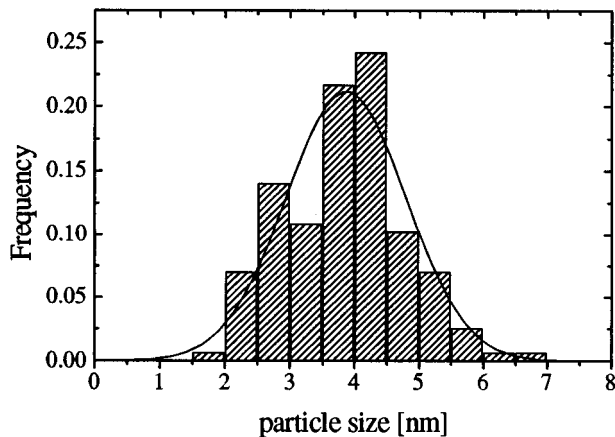


FIG. 2. Size distribution of the Ag particles embedded in glass with a gaussian curve fitted to the data.

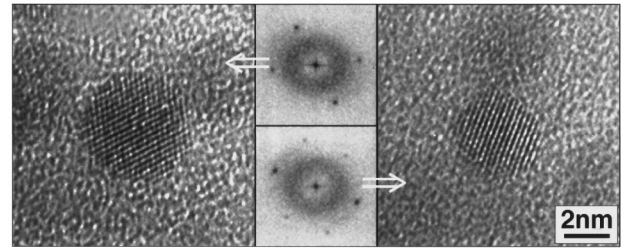


FIG. 3. HREM images of Ag particle in glass and corresponding diffractograms (FFT).

particle radius,  $a(r)$  the size dependent lattice parameter,  $\Delta a$  the deviation from the bulk lattice parameter, and  $\kappa$  the compressibility of the particle material. Since HREM imaging allows to measure lattice plane spacings with fairly good accuracy<sup>17</sup> this is an appropriate means to characterize the particle/matrix interaction of embedded particles. The lattice spacings are determined from HREM images as shown in Fig. 3 together with the corresponding optical diffractograms (Fourier transforms) for the electron beam irradiated glass. From these data plotted in dependence on the particle radius for (111) spacings in Fig. 4, the interface stress of Ag particles inside the glass was estimated to 4.7 N/m from the slope of the straight line obtained by regression calculation. In the same manner, the surface stress of the nonembedded Ag particles is determined to 6.3 N/m which agrees fairly well with the above mentioned value indicating that different from particles in thermally treated ion-exchanged glass<sup>18</sup> no additional stresses are present there. The obtained results are comparable to the surface stress of 5.1 N/m reported earlier for isolated Ag particles.<sup>19</sup>

Whereas conventional Ag precipitation in ion-exchanged glasses requires long enduring thermal treatment at temperatures around the glass transformation point  $T_G$ , the effect of which is limited (by the presence of reducing agents) to only a very few percent of the  $\text{Ag}^+$  ions, electron induced formation of nanosized silver particles in glass is superior in: (i) yield and concentration, (ii) speed and reproducibility, (iii) homogeneous arrangement of particles, (iv) narrow distribu-

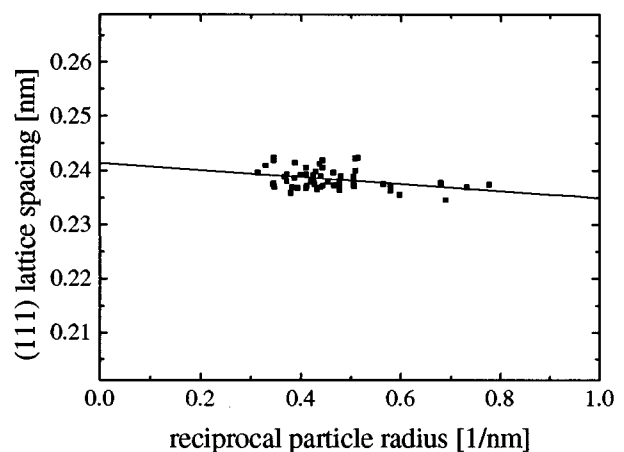


FIG. 4. (111) lattice spacing in dependence on the reciprocal radius of Ag particles in glass with corresponding regression calculation (straight line).

tion of sizes, and (v) absence of additional stresses resulting from thermal treatment. This new route of synthesizing particulate metal-glass composites will allow to produce materials with well defined nonlinear properties if applied on large scale to bulk specimens of ion-exchanged glass.

- <sup>1</sup>D. Ricard, P. Roussignol, and C. Flytzanis, *Opt. Lett.* **10**, 511 (1985).
- <sup>2</sup>E. Heolweil and R. M. Hochestrasser, *J. Chem. Phys.* **82**, 4762 (1985).
- <sup>3</sup>I. Tanahashi, M. Yoshida, Y. Manabe, T. Toda, S. Sasaki, T. Tokizaki, and A. Nakamura, *Jpn. J. Appl. Phys.* **33**, L1410 (1994).
- <sup>4</sup>F. Hache, D. Ricard, and C. Flytzanis, *J. Opt. Soc. Am. B* **3**, 1647 (1986).
- <sup>5</sup>F. Hache, D. Ricard, C. Flytzanis, and U. Kreibig, *Appl. Phys. A* **47**, 347 (1988).
- <sup>6</sup>I. Tanahashi, Y. Manabe, T. Toda, S. Sasaki, and A. Nakamura, *J. Appl. Phys.* **79**, 1244 (1996).
- <sup>7</sup>K.-J. Berg, A. Berger, and H. Hofmeister, *Z. Phys. D* **20**, 309 (1991).
- <sup>8</sup>A. Berger, K.-J. Berg, and H. Hofmeister, *Z. Phys. D* **20**, 313 (1991).
- <sup>9</sup>W. A. Weyl, *J. Phys. Chem.* **57**, 753 (1953).
- <sup>10</sup>R. V. Ramaswamy, *J. Lightwave Technol.* **6**, 984 (1988).
- <sup>11</sup>B. Breitscheidel, J. Zieder, and U. Schubert, *Chem. Mater.* **3**, 559 (1991).
- <sup>12</sup>I. Tanahashi and T. Mitsuyu, *J. Non-Cryst. Solids* **181**, 77 (1995).
- <sup>13</sup>R. A. Wood, P. D. Townsend, N. D. Skeland, D. E. Hole, J. Barton, and C. N. Afonso, *J. Appl. Phys.* **74**, 5754 (1993).
- <sup>14</sup>P. Mazzoldi, G. W. Arnold, G. Battaglin, R. Bertinello, and F. Gonella, *Nucl. Instrum. Methods Phys. Res. B* **91**, 478 (1994).
- <sup>15</sup>O. Becker and K. Bange, *Ultramicroscopy* **52**, 73 (1983).
- <sup>16</sup>M. Dubiel, R. Schmitz, K. Scheerschmidt, and H. Hofmeister, *J. Non-Cryst. Solids* **192/193**, 632 (1995).
- <sup>17</sup>P. Fraundorf, *Ultramicroscopy* **22**, 225 (1987).
- <sup>18</sup>H. Hofmeister, M. Dubiel, H. Goj, and S. Thiel, *J. Microsc.* **177**, 331 (1995).
- <sup>19</sup>R. A. Montano, G. K. Shenoy, T. I. Morrison, and W. Schulze, *Phys. Rev. B* **30**, 672 (1984).