

Dissolution of Silver Nanoparticles in Glass through an Intense dc Electric Field

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Glasses containing metal nanoparticles are very promising materials for photonics applications due to their unique linear and nonlinear optical properties. In this letter, it is shown that silver nanoparticles within a glass matrix can be destroyed and dissolved in the glass in the form of silver ions by applying a combination of an intense direct current (dc) electric field and moderately elevated temperature. The nanoscopic processes leading to this unexpected effect are discussed, and it is demonstrated that this technique allows us to produce optical structures down to the submicron scale, making it suitable for the design of various optical and optoelectronic elements.

Glasses and other dielectrics containing metal nanoparticles are very promising materials for photonics applications due to their unique linear and nonlinear optical properties. These properties are dominated by the strong surface plasmon resonances (SPRs) of the metal nanoparticles. Since the spectral position and shape of these SPRs can be designed within a wide spectral range throughout the visible and near-infrared spectra by choice of (the electronic properties of) the metal and the dielectric matrix^{1,2} or by manipulation of the size,³ shape,⁴ and spatial arrangement⁵ of the metal clusters, these compound materials are very promising candidates for a great number of applications in the field of photonics.^{6–8} One of the main issues in this context is to structure the optical properties of such materials on a micro- or even nanometer scale. While current research on the latter is often aiming at future optical subwavelength structures such as plasmonic waveguides based on metal nanoparticles,^{9,10} the micrometer scale is appropriate for a lot of standard and advanced optical elements (gratings, segmented filters or polarizers, etc.). In the work reported here, we demonstrate a technologically simple, but physically very interesting, way to create optical structures in dielectric composite materials containing metal nanoparticles: applying a combination of an intense direct current (dc) electric field and moderately elevated temperature, the particles can be destroyed and dissolved in the glass matrix in the form of silver ions, leaving a transparent area.

A prototype of these materials is glass containing silver nanoparticles prepared by Ag–Na ion exchange.^{11,12} The originally spherical Ag particles can, for example, via a macroscopic thermomechanical deformation process, be transformed into uniformly oriented ellipsoidal ones, accompanied by the formation of a strongly dichroitic optical extinction,¹³ which makes these materials well suitable as polarizers. In the last years, it was shown that also the interaction of ultrashort laser pulses with silver nanoparticles in glass can lead to

modifications of the particles' shapes; this effect depends on the polarization state of the laser beam and can macroscopically be observed as optical dichroism.^{8,14–16} However, in contrast to supported nanoparticles, which can be selectively evaporated from the substrate surface directly by the absorbed laser energy,^{17,18} glasses with embedded Ag metal particles cannot be made transparent by laser irradiation. More generally, it would be highly desirable to have comprehensive control on the shape, size, and fill factor of nanoparticles in dielectrics for the design of optical elements from these materials.³ In this report, we describe a method for performing such manipulations by the application of a strong dc electric field.

The samples used in our experiments (provided by CODIXX AG) were prepared from soda-lime float glass by Ag–Na ion exchange and following annealing in H₂ reduction atmosphere.¹¹ This technique results in the formation of spherical Ag nanoparticles of 30–40 nm mean diameter in a thin surface layer of ~6 μm thickness. For the experiments described here, single-sided samples were used, made by removing a sufficiently thick surface layer from one side by etching in 12% HF acid. The volume fill factor ($V_{\text{Ag}}/V_{\text{total}}$) of Ag nanoparticles, estimated from scanning electron microscopy (SEM), starts at ≈0.7 near the glass surface and decreases to zero within a few microns (see the SEM picture of the cross section in Figure 1a). This gradient allowed us to produce samples with a very low Ag fill factor removing the upper particle layer of ≈5 μm. Some of the samples were additionally subjected to tensile deformation with simultaneous heating, which results in strongly elongated, ellipsoidal nanoparticles and a reduction of the thickness of the particle-containing layer to ≈1 μm; see Figure 1b (in this form, the samples are commercially available as high contrast optical polarizers).

These materials were subjected to an electric field using a technique that is known as thermal poling of glass in the field of optoelectronics.^{19,20} The samples were equipped with two electrodes pressed on the surfaces, with the anode facing the layer containing nanoparticles; then, the samples were heated to a temperature of 280 °C, and a dc voltage was applied. The voltage was increased stepwise (typical values of 1 kV maximum voltage in steps of 0.2 kV within a total time of 50 min) in a way that the current was <250 μA at any time. This

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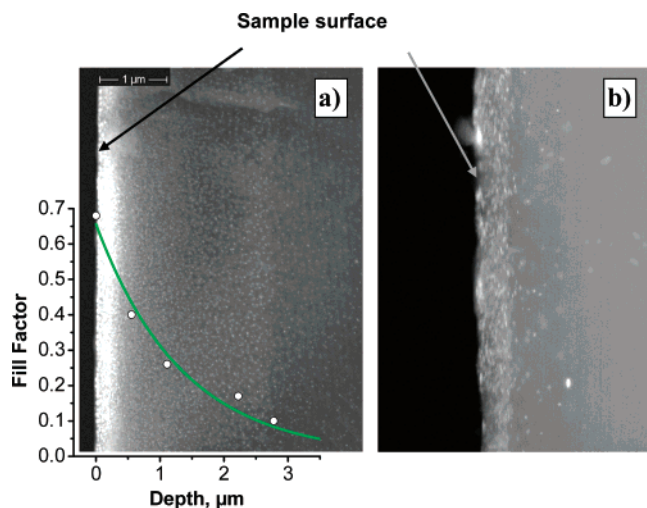


Figure 1. SEM pictures of cross sections of glass samples containing (a) spherical and (b) elongated silver nanoparticles (the Ag particles are reproduced as white spots). The fill factor gradient of the spherical nanoparticles is given by the inset, where the x -axis was adjusted to the length scale of the picture. The ellipsoidal nanoparticles in part b, obtained by mechanical deformation of the sample, are located in a very thin surface layer of $<1 \mu\text{m}$, with only very few large particles remaining deeper below the surface.

approach, which is similar to previous poling experiments on soda-lime glasses,²¹ is necessary to avoid electric breakdown of the material; finally, the temperature was reduced down to ambient temperature again. Depending on the type of sample, this procedure can bleach the area subjected to the electric field up to complete optical transparency. Figure 2 gives optical spectra and SEM pictures of a sample (thickness $200 \mu\text{m}$) containing ellipsoidal silver nanoparticles before and after total bleaching. The optical extinction spectra in Figure 2a (dashed curves, before treatment; solid curve, after treatment) show that the strong SPR bands of elongated Ag nanoparticles in glass have totally disappeared after the procedure. This effect is caused by dramatic changes of the sample nanostructure: as is easily seen in the SEM pictures presented in Figure 2b and c, the densely packed, uniformly oriented silver ellipsoids characterizing the original sample (reproduced in white or light gray in Figure 2b) are no longer present in the optically transparent area after dc electric field treatment. Instead, a number of dark spots in Figure 2b indicate the presence of holelike structures (probably residual nanoholes) in the upper layer of the sample after treatment. Obviously, the particles have been destroyed during the procedure without any (micro)damage of the glass matrix or surface, as was verified by optical microscopy.

Additionally, a cross section of the sample was prepared and subjected to a SEM X-ray spectral analysis, the results of which are shown in Figure 3 (left-hand side, original sample; right-hand side, modified sample). Taking the Si curves as an indicator for the position of the sample surface, it is seen that both Ag and Na content have decreased close to the surface and increased in the depth of a few microns (the Ag peak at $\approx 2.5 \mu\text{m}$ in Figure 3a is caused by a single, large nanoparticle). The silver distribution after treatment has a maximum at a distance of $\sim 2.5 \mu\text{m}$ from the sample surface. Since Ag and Na atoms or ions cannot be distinguished in the X-ray signal, it is an obvious conclusion that these changes are due to a field-driven diffusion of Na and Ag ions, and correspondingly, the Ag nanoparticles have been converted to Ag^+ ions. Therefore, this process will in the following be denoted by “electric field assisted dissolution” (EFAD) of the nanoparticles.

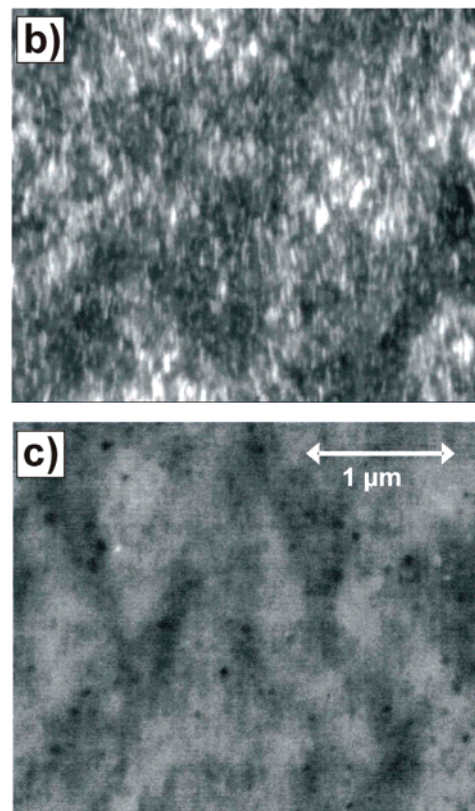
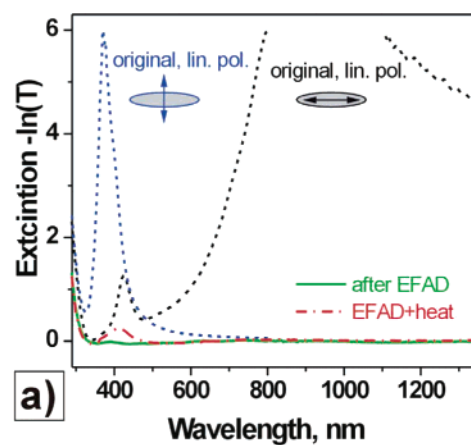


Figure 2. (a) Extinction spectra of a sample containing elongated Ag nanoparticles, before (dashed curves, observed with light polarized parallel and perpendicular to the long axis of the silver clusters) and after (solid curve, directly after process; dash-dotted curve, after additional heating) electric field-induced modification. SEM pictures of the surface of a sample with ellipsoidal Ag nanoparticles (b) before and (c) after dc electric field treatment.

Some additional experiments gave further hints on the physical processes leading to EFAD of silver nanoparticles. (i) After modified samples are annealed at $500 \text{ }^\circ\text{C}$ in air atmosphere, an absorption band at a wavelength of 410 nm occurs (dash-dotted curve in Figure 2a), which is characteristic for spherical Ag nanoparticles in glass. Thus, obviously, the silver is still in the glass and can form nanoparticles again. This is consistent with the X-ray results shown in Figure 3, confirming that silver has not been removed from the sample but is still dissolved within the glass. (ii) The bleaching effect was also observed on samples containing spherical silver nanoparticles; we studied an original sample with a depth gradient of the silver fill factor, as shown in Figure 1a, and an etched one having only a very thin layer containing Ag clusters at a low fill factor

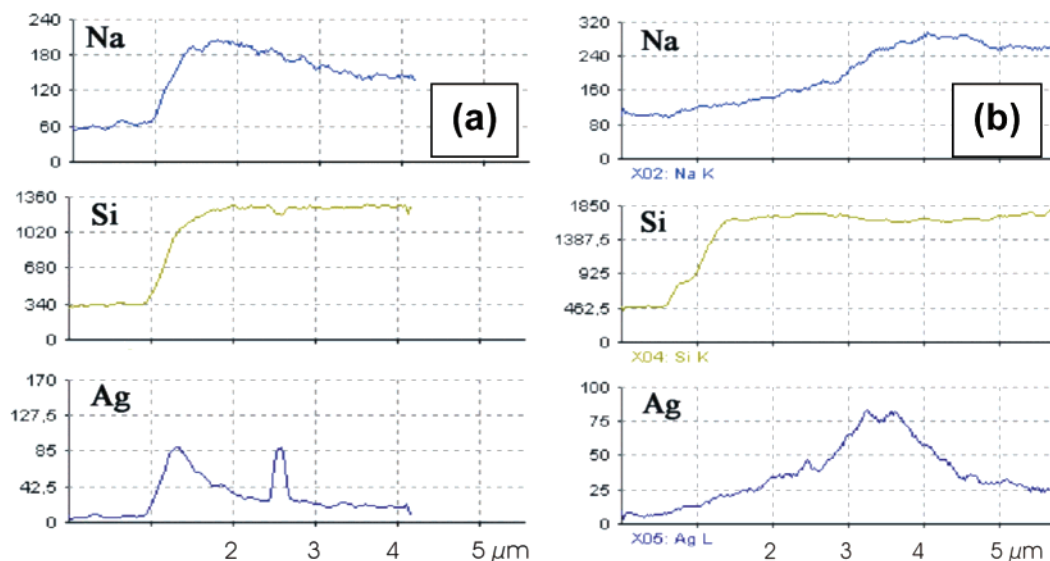


Figure 3. Na, Ag, and Si distributions as a function of sample depth by local X-ray element analysis of vertical cross sections of samples (a) before and (b) after the electric field treatment; the horizontal length scales are identical. The Ag peak found in part a at $\sim 2.5 \mu\text{m}$ corresponds to a single large silver particle seen in the SEM picture (not shown).

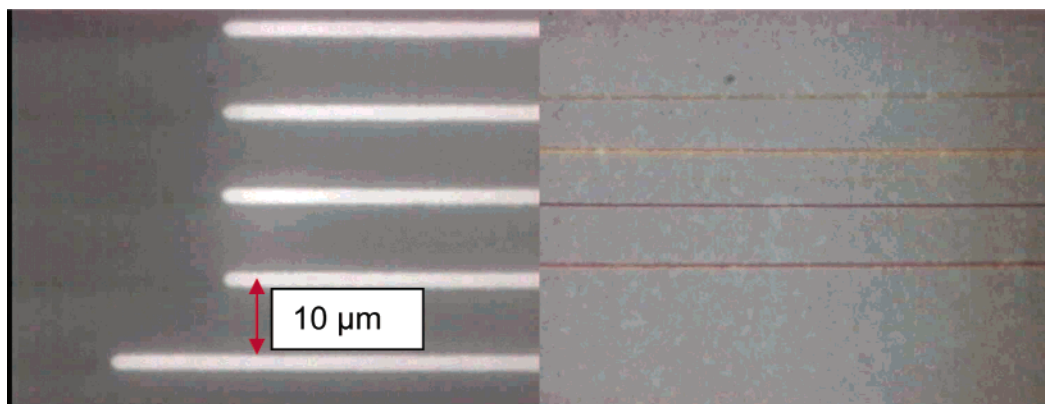


Figure 4. Microscopic photography of sub-micrometer lines made by EFAD using an electrode scratched with a diamond marker (right-hand side) and calibrated length scale with same magnification (left-hand side).

of <0.01 . To achieve complete transparency in these samples, a higher voltage of up to 3 kV was needed. (iii) In contrast to glasses with a thin nanoparticle-containing layer close to the surface only, samples with a nearly homogeneous distribution of silver clusters throughout the whole volume¹⁴ could not be bleached up to the electrical breakdown. This indicates that EFAD of silver nanoparticles only occurs when the particles have a considerable spatial gradient, that is, are restricted to a thin layer close to the surface.

The technique allows optical microstructures to be produced very easily, as is demonstrated by the dark horizontal lines shown on the right-hand side of Figure 4, which is the reproduction of a microscope picture; the left-hand side gives a $10 \mu\text{m}$ scale photographed with the same magnification. The dark lines, which clearly have a thickness of $\leq 1 \mu\text{m}$, were produced by simply making scratches in the steel anode with a diamond marker before the EFAD procedure and then pressing the electrode with the scratched side onto the glass surface containing silver particles. After the treatment, the whole area under the anode was transparent, with the exception of the scratches, where obviously the Ag particles have not been destroyed. Thus, clearly, EFAD of silver clusters requires direct contact between sample and anode.

On the basis of the experimental results, the most probable scenario for the physical processes leading to EFAD of Ag

clusters in glass can be set up. It is well-known that, in contrast to pure soda-lime glass, where the conductivity at $\approx 300 \text{ }^\circ\text{C}$ is dominated by the migration of Na^+ cations in the matrix,²⁰ in composite materials containing metal nanoparticles, the contribution of conduction electrons plays the primary role for the electric current.^{2,22–27} In particular, the conductivity of these materials approaches that of bulk metal with increasing fill factor of the metallic nanoparticles in a given dielectric matrix.^{23,24,27–29} The usual picture to describe generation of electric current in such systems is that of a heterojunction of metal and insulator,³⁰ where the energy of conduction electrons in the metal clusters has to exceed the potential barrier formed by the interstitial insulator layer. In case of a high fill factor of Ag nanoparticles, the potential barrier between two neighboring metal clusters is so low that thermally activated electron tunneling is possible, leading to the repeatedly observed rise of conductivity upon an increase of temperature.^{22–25} This is consistent with our observation that no bleaching at all could be observed at room temperature. An additional increase of conductivity can be expected in the presence of trapping centers in the glass in the form of interstitial cations or positively charged anion vacancies,³¹ via reduction of the height of the potential barrier for electron tunneling.

Over all, glass with Ag nanoparticles incorporated in a near-surface region constitutes a composite material with a high

electronic conductivity in the cluster-containing layer, and (much lower) cationic conductivity throughout the remainder of the material (glass). When an electric field is applied to such a sample in a way that the anode is facing the particle-containing layer, there will be a current due to electrons tunneling from the silver clusters toward the anode. Due to the high electron mobility, this process will leave the silver particles in a positively charged state. Since there is a considerable field enhancement in the vicinity of Ag nanoclusters,³ it is highly probable that they will be further ionized, until silver ions are being ejected from the metal clusters due to strong Coulomb forces and then diffuse away from the anode. An additional field enhancement could be present due to a cation depletion zone, which plays an important role for thermal poling of glass.²⁰ This Ag⁺ ejection increases the fading electronic conductivity, because now again there will be uncharged silver clusters having electrons of high mobility. Additionally, as long as the Ag ions have not yet diffused out of the particle-containing region, they may further increase the probability for electron emission by decreasing the height of the tunneling potential barrier. These processes can go on until the Ag nanoparticles are completely destroyed and the produced silver cations have been dissolved in the glass matrix.

The central point of this scenario is the electronic current and thus the height of the potential barrier for tunneling of electrons, which decreases strongly with the average distance from cluster to cluster. This explains easily the experimental observation that samples with a low Ag fill factor require a much higher voltage to be bleached. The presented picture of the physical processes also explains that no changes were observed with exchanged electrodes (i.e., cathode placed on the layer with Ag nanoparticles), because then a thick layer of insulating (with respect to electrons) glass between the anode and the layer containing silver nanoparticles prevents the electronic current and ionization of the clusters.

In conclusion, we have investigated the effect of a high dc electric field applied to glass samples containing silver nanoparticles in a thin surface layer of a few micrometers. At an elevated temperature of ~300 °C and using samples with a sufficiently high Ag volume fill factor, the silver clusters can be destroyed completely into Ag ions, which are being dissolved in the glass matrix and diffuse into deeper layers of the sample. This approach opens up the opportunity for the manufacturing and microstructuring of various optical devices. Additionally, it is known that silver ions can be redistributed within ion-exchanged glass by the application of an electric field. If this modification is done before particle formation, in principle, arbitrary 3D optical structures can be produced with the technique described in this work.

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References and Notes

- (1) Kreibitz, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, 1995.
- (2) Shalaev, V. M. *Optical Properties of Nanostructured Random Media*; Springer: Berlin, 2002.
- (3) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.
- (4) Jin, R.; et al. *Nature* **2003**, *425*, 487.
- (5) Gudiksen, M. S.; Lauhon, L. J.; Wang, J.; Smith, D. C.; Lieber, C. M. *Nature* **2002**, *415*, 617.
- (6) Chakaraborty, P. *J. Mater. Sci.* **1998**, *33*, 2235.
- (7) Gonella, F.; Mazzoldi, P. *Handbook of Nanostructured Materials and Nanotechnology, Vol. 4*; Academic Press: San Diego, CA, 2000; p 81 ff.
- (8) Seifert, G.; Kaempfe, M.; Berg, K.-J.; Graener, H. *Appl. Phys. B* **2001**, *73*, 355.
- (9) Krenn, J. R. *Nat. Mater.* **2003**, *2*, 210.
- (10) Maier, S. A.; et al. *Nat. Mater.* **2003**, *2*, 229.
- (11) Berg, K.-J.; Berger, A.; Hofmeister, H. *Z. Phys. D* **1991**, *20*, 309.
- (12) Miotelo, A.; DeMarchi, G.; Mattei, G.; Mazzoldi, P.; Quaranta, A. *Appl. Phys. A* **2000**, *70*, 415.
- (13) Borek, R.; Berg, K.-J.; Berg, G. *Glass Sci. Technol. (Frankfurt/Main)* **1998**, *71*, 352.
- (14) Kaempfe, M.; Rainer, T.; Berg, K.-J.; Seifert, G.; Graener, H. *Appl. Phys. Lett.* **1999**, *74*, 1200.
- (15) Seifert, G.; Kaempfe, M.; Berg, K.-J.; Graener, H. *Appl. Phys. B* **2000**, *71*, 795.
- (16) Kaempfe, M.; Seifert, G.; Berg, K.-J.; Hofmeister, H.; Graener, H. *Eur. Phys. J. D* **2001**, *16*, 237.
- (17) Wenzel, T.; Bosbach, J.; Goldmann, A.; Stietz, F.; Träger, F. *Appl. Phys. B* **1999**, *69*, 513.
- (18) Stietz, F. *Appl. Phys. A* **2001**, *72*, 381.
- (19) Mayers, R. A.; Mukherjee, N.; Brueck, S. R. J. *Opt. Lett.* **1991**, *16*, 1732.
- (20) Kazansky, P. G.; Russel, P. St. J. *Opt. Commun.* **1994**, *110*, 611.
- (21) Garcia, F. C.; Carvalho, I. C. S.; Hering, E.; Margulis, W.; Lesche, B. *Appl. Phys. Lett.* **1998**, *72*, 3252.
- (22) Heilmann, A.; Kiesow, A.; Gruner, M.; Kreibitz, U. *Thin Solid Films* **1999**, *343–344*, 175.
- (23) Snow, A. W.; Wohltjen, H. *Chem. Mater.* **1998**, *10*, 947.
- (24) Doty, R. C.; Yu, H.; Shih, C. K.; Korgel, B. A. *J. Phys. Chem. B* **2001**, *105*, 8291.
- (25) Wuelfing, W. P.; Murray, R. W. *J. Phys. Chem. B* **2002**, *106*, 3139.
- (26) Chen, S. *Anal. Chim. Acta* **2003**, *496*, 29.
- (27) Kiesow, A.; Morris, J. E.; Radehaus, C.; Heilmann, A. *J. Appl. Phys.* **2003**, *94*, 6988.
- (28) Kirkpatrick, S. *Phys. Rev. Lett.* **1971**, *27*, 1722.
- (29) Last, B. J.; Thouless, D. J. *Phys. Rev. Lett.* **1971**, *27*, 1719.
- (30) Sutton, A. P.; Balluffi, R. W. *Interfaces in crystalline materials*; Oxford University Press: New York, 1995.
- (31) Shulman, J. R.; Compton, W. D. *Color centers in solids*; Pergamon Press: New York, 1962.