

SHAPE TRANSFORMATION AND TOTAL DISSOLUTION OF METALLIC NANOPARTICLES IN GLASS BY STRONG ELECTRIC FIELDS

G. Seifert, H. Graener, S. Wackerow, A. Stalmashonak
Martin-Luther-Universitaet Halle-Wittenberg, Physics Institute, 06099 Halle, Germany
gerhard.seifert@physik.uni-halle.de

SUMMARY

Silver nanoparticles embedded in glass were transformed from spherical to ellipsoidal shapes by irradiation with ultrashort laser pulses; applying strong dc electric field, the particles could also be dissolved leaving nanovoids in the matrix. The key processes at the glass-metal interface leading to these structural changes and the application potential of the techniques are discussed.

Keywords: glass-metal nanocomposites, femtosecond laser pulses, nanostructuring

INTRODUCTION

The interest on synthesis and controlled manipulation of composite materials containing metal nanoparticles (NPs) has grown considerably since the 1980s, mainly driven by the prospect of various potential applications in different fields of science and technology [1-3]. For instance, the linear and nonlinear optical properties of such materials, being dominated by surface plasma (SP) oscillations of the metal clusters, let metallodielectric nanocomposites appear as promising media for development of novel nonlinear materials, nanodevices and optical elements. Spectral position and shape of the SP resonance is characteristic for an individual metal, but furthermore depends strongly on size, shape, distribution and concentration of the nanoparticles, as well as on the properties of the surrounding dielectric matrix. To date a large number of laser-based techniques have been developed, which allow modifying shape and arrangement of the metal clusters [3-10]. These methods provide a very powerful and flexible tool to control and optimize the optical properties of metallodielectric composites. In this paper we concentrate on a special technique discovered in our group: almost ten years ago we first observed that a permanent transformation of initially spherical metal nanoparticles embedded in soda-lime glass into ellipsoidal (or more general, non-spherical) shape is possible by irradiating these nanocomposites with intense fs laser pulses at a wavelength near the SP resonance [11-15]. Macroscopically, this effect is seen as optical dichroism along an axis defined by the polarization of the irradiating laser. Some very recent studies [16-20] provided new insight into the physical mechanisms leading to this shape transformation. In particular, we found evidence that field-driven electron ejection (and capture in the matrix) during the ~ 100 fs laser pulse interaction time is the key process defining the anisotropy of the reshaped NPs, although the shape transformation takes much more time (at least a few nanoseconds). An overview will be given in the results section below.

Interestingly, very similar processes on the nano-scale are at work when the Ag nanoparticles are locally removed by the so-called EFAD (electric field – assisted dissolution) process. This acronym stands for treating the glass-metal nanocomposites by a strong dc electric field at elevated temperature: choosing the correct parameters, this procedure can lead to a total bleaching of the contacted regions caused by dissolution of the nanoparticles [21]. It was also observed that by this process the patterns of micro-structured electrodes can be transferred to the nanocomposites, leaving NPs below the non-contacted regions of the sample [22, 23]. We will compare the physical mechanisms of EFAD to those of the fs-laser induced effects, and then give an outlook towards applications of our techniques to manipulate the nanostructural properties of glass-metal nanocomposites.

EXPERIMENTAL

For our experiments we used samples prepared from soda-lime glass by $\text{Ag}^+\text{-Na}^+$ ion exchange followed by annealing in hydrogen atmosphere as reducing agent [24]. After this procedure a thin surface layer of 6-10 μm thickness contains spherical silver nanoparticles of 30-40 nm mean diameter. For the fs irradiation experiments the samples were etched leaving a 1-2 μm thick subsurface layer with embedded silver nanoparticles at a typical Ag volume filling factor of 0.001.

The irradiations were done with linearly polarized femtosecond laser pulses (pulse duration $\sim 100\text{fs}$, different wavelengths, repetition rate 1 kHz), focused to a maximum laser peak pulse intensity of 3 TW/cm^2 . Irradiating successively rectangular areas at different conditions (intensity, wavelength, number of pulses per spot, laser polarization), we could prepare quite different dichroic absorption spectra. After annealing all irradiated samples in order to remove color centers and other laser-induced defects in the glass matrix, optical absorption spectra were recorded with polarization resolution. When linear laser polarization has been used for irradiation, we denominate the spectra as p-polarized if the light in the spectrophotometer is linearly polarized along the direction of the laser polarization; s-polarized denotes the perpendicular case. Some experiments have also been conducted using circular laser polarization prepared by an appropriate quarter-wave plate.

For the dc field (EFAD) technique, two electrodes were pressed on opposite sides of the samples, the anode facing the particle-containing layer. Applying a voltage of typically 1kV at a temperature in the range of 250°C – 300°C for several minutes, the contacted area could be bleached up to total transparency. We also used macroporous silicon as regularly structured anodes; these were covered with chromium before use to avoid anodic bonding. EFAD of NPs was also conducted on samples containing spheroidal silver NPs. These samples have been prepared by a thermo-mechanical stretching procedure yielding uniformly oriented spheroids with quite high aspect ratio (ratio c/a of long to short axis of spheroid). These were actually fabricated by CODIXX as polarizers.

RESULTS AND DISCUSSION

Nanoparticle shape transformation by femtosecond laser pulses

The persistent shape transformation of Ag nanoparticles by fs laser pulses displays a very strong dependence on the actual irradiation parameters. The results shown in Fig. 1

give a first impression on two of several important parameters. The data refer to experiments with a laser wavelength of 400 nm and linear polarization; all spectra shown in the Figure refer to p-polarization only. Clearly, upon irradiation the original isotropic SPR absorption at ~ 415 nm has changed to a red-shifted and broadened band for polarization along that of the laser, whereas the band observed at s-polarization is only slightly blue-shifted (not shown in Fig. 1 for clarity). The general trend is that the red-shift of the p-polarized band increases when the peak pulse intensity increases (Fig. 1a) or a larger number of pulses is applied on average to one sample spot (Fig. 1b). Such a spectral behavior can be explained on the basis of Mie theory when one assumes that spheroids are produced by the laser irradiation; in that case larger red-shift would be caused by increasing aspect ratio c/a of the NPs.

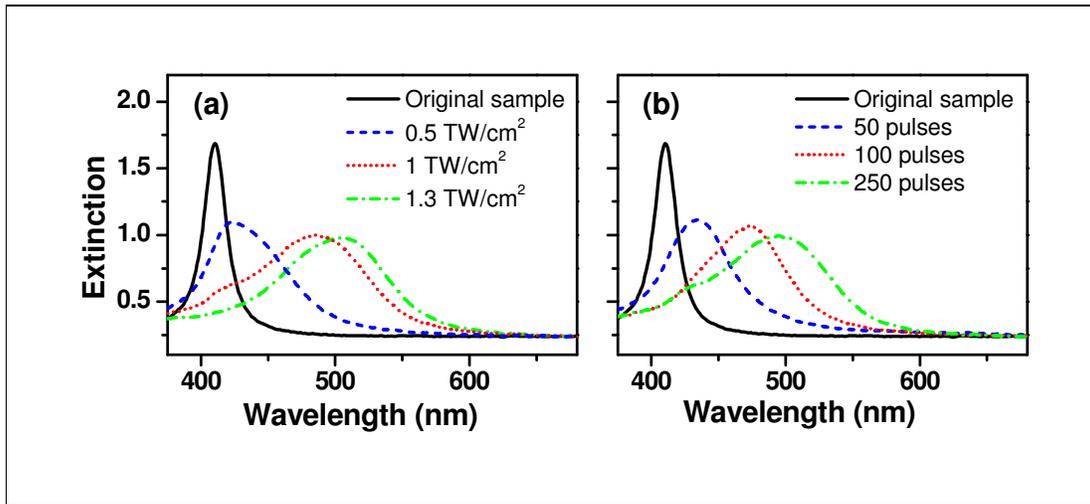


Figure 1: P-polarized extinction spectra irradiated sample: a) 250 pulses per spot, peak pulse intensity: dash – 0.5, dot – 1, dash dot – 1.3 TW/cm^2 ; b) dash – 50, dot – 100, dash dot – 250 pulses per spot, peak pulse intensity 1 TW/cm^2 .

Electron microscopy elucidated that this is indeed the case: under the abovementioned conditions the original spherical NPs are transformed into elongated spheroids with their longer axes being more or less uniformly oriented parallel to the laser polarization. Fig. 2 presents TEM images of individual particles in a reversed contrast, i.e. the dark background here is the glass matrix, whereas the Ag nanoparticles appear as white. It is clearly seen that the original NP is in good approximation a sphere, while a particle after fs laser treatment in the so-called multi-shot regime (center image) exhibits a cigar-like cross section surrounded by a shell of smaller Ag fragments. By optical absorption spectroscopy from orthogonal directions it could be proven that the central elongated objects have a distinct rotational symmetry axis (i.e., they are approximately spheroids) given by the laser polarization [16].

To achieve particle shapes like those shown in the image in the center of Fig. 2, a sufficiently high number of successive pulses in the peak intensity range from 0.2 to $\approx 1.5 \text{ TW}/\text{cm}^2$ has to be applied. Therefore we call this type of reshaping the multi-shot regime. If the intensity is increased above $2 \text{ TW}/\text{cm}^2$, already a single pulse can create a remarkable dichroism in the irradiated spot. That is why this situation was termed

single-shot regime. Irradiating only a few pulses of such high peak intensity to the same spot, the NPs are almost completely destroyed, easily observed by bleaching of the spot. The dichroism found after only one shot in this regime, however, is different from the multi-shot case: in single-shot mode, the band observed with s-polarization after laser treatment exhibits the larger red-shift; furthermore, also the other p-polarized band is red-shifted, but only by a smaller amount. The explanation for this problem could also be found by ‘3D’ optical spectroscopy [16]: like in multi-shot mode, the NPs are transformed into spheroids with their rotational axis given by the laser polarization; only they are now not prolate, but oblate. In other words, the TEM image on the right-hand side of Fig. 2 is a side view onto a disk-like Ag nanoparticle. Together with the pronounced halo of silver fragments, which causes an increased effective refractive index around the NP, this finding is again perfectly compatible with descriptions of the optical absorption bands based on Mie theory [16].

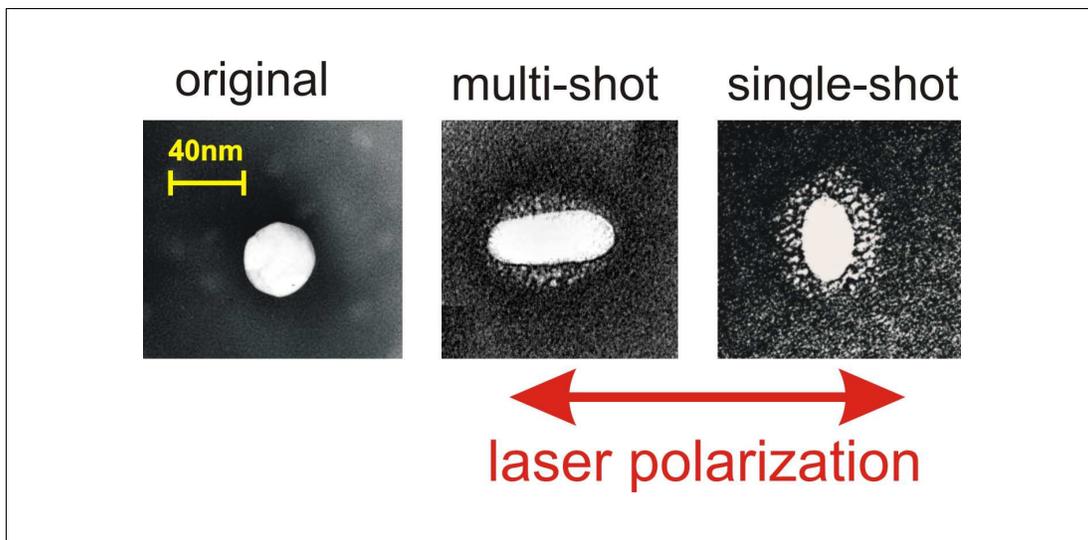


Figure 2: Transmission electron microscope images of individual Ag NPs before and after fs laser irradiation. Left: spherical shape before irradiation; center: NP after multi-pulse irradiation at relatively low intensity; right: NP after high-intensity, single-shot irradiation.

Very recently [20], we managed to show that disk-like spheroids can also be prepared by irradiation with circularly polarized laser pulses (in multi-shot regime), where the symmetry axis is given by the laser propagation direction. This indicates very clearly that electron emission initiated directly by the strong electric field of the laser pulses is the crucial process defining the anisotropy of the reshaped NPs. These recent findings are a very nice confirmation of our model proposed for the sequence of mechanisms after irradiating metallodielectric nanocomposites with linearly polarized femtosecond pulses [16-18].

Summarizing the important steps in chronological order, this model comprises the following processes for the multi-shot case: First, upon absorbing the laser-pulse energy, the conduction electrons of the NP gain very high temperatures up to 10^4 K [18]. Due to the Fermi distribution, such high electron temperatures produce a

considerable number of electrons at energies $\geq 2.7\text{eV}$ above the Fermi energy, where they are already matching the energy of the glass conduction band. Together with the strong electric field enhancement by the NP, these electrons can quite effectively be emitted into the glass by the electric field of the laser pulse, apparently with an anisotropy given by the polarization of the laser pulse. Shortly after emission, part of these electrons may be trapped in the glass. Meanwhile, e-phonon scattering heats up the Ag nanoparticle to $\approx 2000\text{ K}$ [18]; such a high energy density must make an already positively charged NP unstable, leading to a, most probably isotropic, ejection of Ag ions. These ions will be stopped within a few nanometers, and by dissipating their kinetic energy contribute to create a very hot shell (being above the glass transition temperature of $\approx 850\text{ K}$) around the NP. At this stage, which is reached only a few picoseconds after the laser pulse, there is an anisotropic distribution of electrons and an isotropic, positively charged shell of silver cations around the particle. Where electrons and ions meet, they can recombine to Ag atoms, which then diffuse back to the nanoparticle and precipitate at its surface. In contrast, the 'isolated' ions are less mobile and preferentially form small aggregates locally, leading in the end to the 'halo' of silver fragments. As the hot matrix shell is quickly cooled by heat transfer away from the NP, this high temperature enabling fast diffusion lasts only a few hundred picoseconds typically. After that time the situation is 'frozen' again, and the anisotropy of electron emission should be reflected in the probability of Ag precipitation at the particle surface. At typical intensities in the multi-shot regime, a few hundred ions can be emitted after one laser pulse; comparing this to approximately 10^6 Ag Atoms per NP, it is obvious that a single pulse creates only a weak NP shape change, so that at least 50 to 100 pulses are needed to achieve a remarkable anisotropy (aspect ratio $c/a > 1$).

This model is well suited to explain the step-by-step formation of prolate spheroids in the multi-shot regime, and is conform to all previous studies [11-20]. For the single-shot regime, however, the explanation has to be extended. Since the symmetry of the oblate NPs is the same as that of the prolate ones in multi-shot regime, obviously again processes driven by the electric field of the laser pulse are decisive. The quantitative difference lies in larger field peak amplitude; this high field will primarily emit more electrons (and ions), and they should also on average be trapped at locations further away from the NP. Secondly, the NP achieves a still higher energy density, and subsequently the hot shell enabling fast diffusion will have an extended radius and an extended time window for staying above glass temperature. This alone might be sufficient: considering the higher number of electrons and ions emitted into the matrix along the laser field, their local density may be so high that they recombine and precipitate locally, forming the small halo fragments rather than diffusing back to the NP poles. Whereas around the equator the lower concentrated, recombined Ag atoms rarely find partners for nucleation and preferably precipitate at the NP. It could not be proven up to now if these effects are sufficiently strong to explain the oblate shapes, or if further processes like field-driven ion emission or even plasma formation at the NP poles may occur.

Electric field – assisted dissolution (EFAD) of Ag nanoparticles in glass

If glasses containing Ag nanoparticles in a thin surface layer are subjected to a dc voltage of the order of 1 kV at temperatures in the range $200\text{--}300^\circ\text{C}$ for several minutes, the contacted areas can be bleached considerably. Using the correct

parameters, which depend mainly on particle concentration and layer thickness, the sample regions under the anode can even be made transparent [21]. The nanoscopic background of this effect is dissolution of the Ag NPs into silver ions which are driven into the glass by the applied electric field.

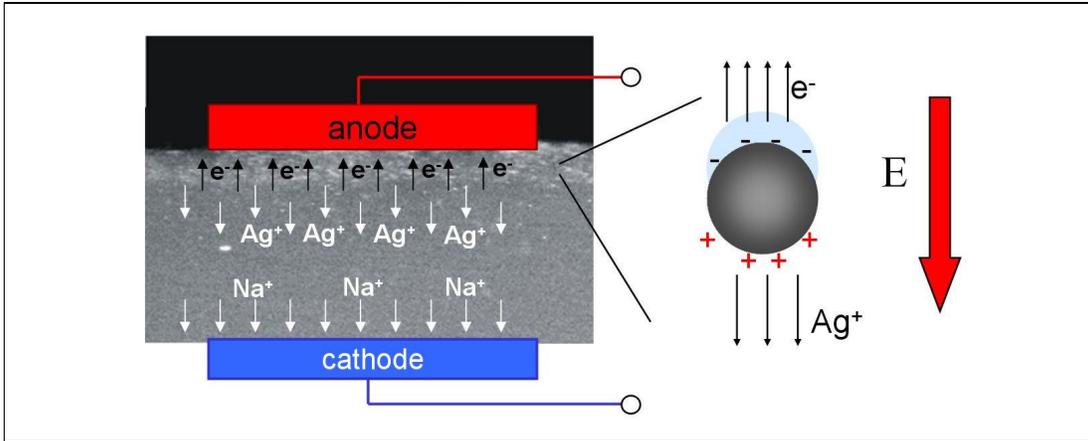


Figure 3: Schematic of EFAD setup (see text for details).

Figure 3 shows a schematic of the setup and a simplified picture for the main processes: at the elevated temperature the dc electric field immediately starts to move the sodium ions in the glass away from the anode, leaving an ion depletion zone; this decreases the conductivity there and lets most of the voltage drop across this ion depleted zone. This in turn enhances the electric field at the NPs, which can then be ionized by electrons tunnelling into the glass conduction band and being drawn into the anode. Since the field is further increased in the vicinity of the NPs, the ionized nanoparticles start to release ions into the glass, which are then also drifting towards the anode.

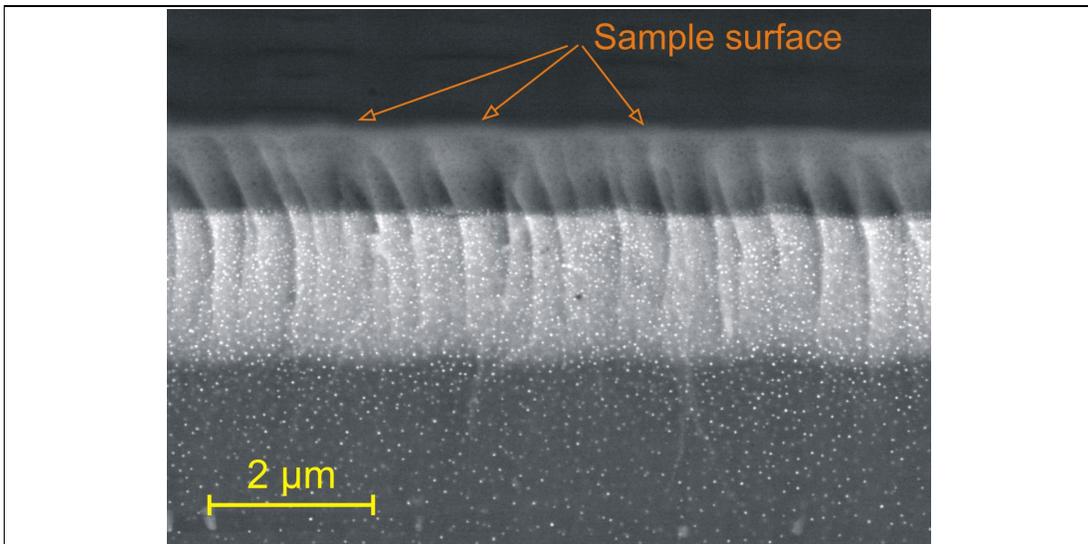


Figure 4: REM image of sample cross section after EFAD stopped in a situation of partial bleaching.

It depends on the actual processing parameters how far these effects are moving on. The electron microscope image of a sample cross section given in Fig. 4 is a very illustrative example of an intermediate state: this sample was treated at 220°C for ~20 minutes, increasing the voltage slowly up to 800 V. Clearly the silver NPs (white spots) have been removed from the uppermost layer of approximately 1 μm thickness. Below one observes a ~ 2 μm wide bright stripe indicating Ag ions; this is apparently the silver from the already dissolved particles which has been drifting towards the anode. Looking very close into the uppermost layer, dark spots can be recognized indicating nanovoids in the glass. Very recently we could unambiguously prove the existence of the nanovoids by small-angle X-ray scattering (SAXS) experiments [25]. In particular, a totally bleached region of a sample which initially contained spheroidal NPs revealed that even the shape of the voids is nearly conserved: removing NPs with an average aspect ratio of $c/a \approx 4.7$ left nanovoids with $c/a \approx 3.8$.

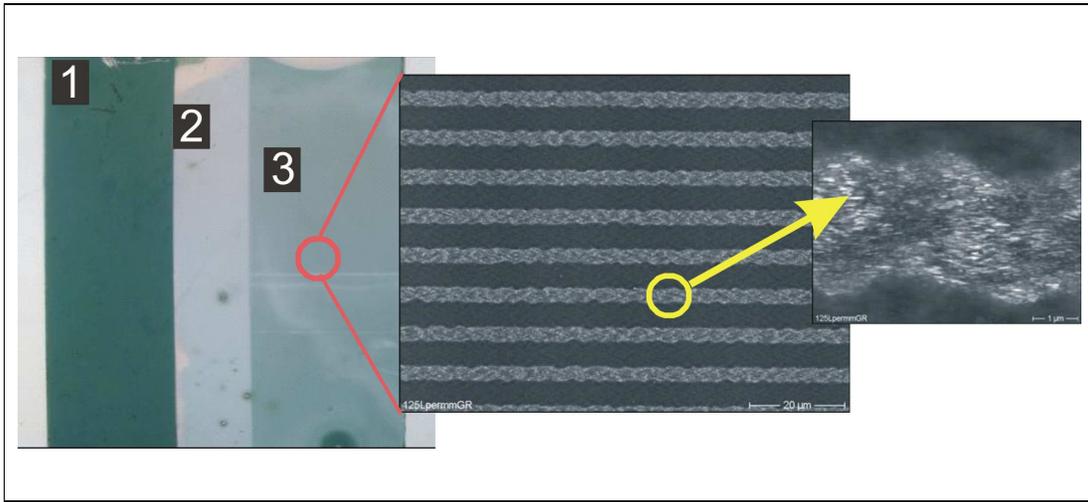


Figure 5: optical and electron microscope images of sample containing spheroidal nanoparticles, bleached by EFAD with a flat (area 2) and a grating anode (area 3).

Figure 5 shows a sample of the type used also for the SAXS study [25]. The dark green region '1' is the original polarizer, the transparent region '2' was produced with a flat anode, and region '3' has been prepared using a metallic reflection grating as anode. Already the microscope image shows that region 3 is only partially bleached. This is, however, in this case not due to a vertical profile by stopping the process too early; as the REM images reveal, the light green colour comes from NPs remaining below the grooves of the grating electrode, whereas the contacted regions are completely free from particles (and thus transparent).

This finding paves the route to a simple micro- and nanostructuring of metal-glass nanocomposites by the EFAD technique. It has already been shown that this 'imprinting' technique allows reproducing the patterns of structured electrodes down to the submicron length scale [22,23]. One of the fascinating ideas connected with this technique is that one can prepare easily regular photonic structures with the plasmonic properties of the metal nanoparticles as an additional degree of freedom for the design of linear and nonlinear optical properties of these structures.

CONCLUSION AND OUTLOOK

We have introduced two, on the first glance vastly different, techniques to manipulate the nanostructural properties of glass-metal nanocomposites in a controlled way. One technique is the fs laser induced shape transformation of the NPs allowing to prepare from initially spherical NPs oblate or prolate spheroids, whose orientation can be controlled by the laser polarization state. The other technique is the local dissolution of nanoparticles in glass by applying a strong dc electric field at moderately elevated temperature. In both cases the removal of electrons from the nanoparticles by a strong electric field, be it oscillating at optical frequencies or nearly constant in time, is the starting process of the nanostructural changes. For the fs laser irradiation, the electrons trapped in the matrix represent the directional memory which causes the anisotropic particle shapes evolving long after the interaction with the pulse, whereas in the EFAD process an enduring field is necessary to dissolve the ionized NP and let its removed ions drift through the glass towards the cathode.

Apart from this interesting parallelism in the fundamental physical mechanisms, the two techniques offer a broad of opportunities for technological applications, each individually as well as in combination. Our fs laser method to produce local dichroism is limited in minimal size only by the diffraction limit (and nonlinearity may even allow to come across it to some extent); the local axis of dichroism can be varied freely during laser writing, so that in principle arbitrarily shaped, sub-micrometer polarizing optical structures can be prepared. Accordingly we think that this novel procedure will find its way into the production of various future optical elements or optoelectronic devices, because it allows the creation of very specialized optical elements which so far can not be produced with any other technique available. The EFAD procedure in combination with properly structured electrodes is in particular attractive for production of regular photonic patterns. Their special aspect of plasmonic features which may be useful for tailoring desired optical properties may be further extended when an optical microstructure prepared by EFAD is locally modified by fs laser irradiation. Such a combined approach opens the way to novel polarization and wavelength selective microdevices such as polarizers, filters, gratings, devices for optical fibre communication, and high density, optical data storage devices with a very good long-time stability.

ACKNOWLEDGEMENTS

The authors are very grateful to M. Leitner and B. Sepiol (University of Vienna, Austria) for the SAXS measurements; to H. Hofmeister and F. Syrowatka for Electron microscope images; and to CODIXX AG for providing samples.

References

1. U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, Springer Series in Materials Science, Vol. 25 (Springer Berlin 1995).
2. V. M. Shalaev, *Optical Properties of Nanostructured Random Media* (Springer Berlin 2001).

3. J. Tominaga, D.P. Tsai, *The Manipulation of Surface and Local Plasmons*, Topics in Applied Physics (Springer, Berlin, 2003).
4. T. Wenzel, J. Bosbach, A. Goldmann, F. Stietz, F. Träger, Appl. Phys. B **69**, 513 (1999).
5. F. Stietz, Appl. Phys. A **72**, 381 (2001).
6. R. Jin, Y.W. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz, J.G. Zheng, Science **249**, 1901 (2001).
7. M. Kaempfe, H. Graener, A. Kiesow, A. Heilmann, Appl. Phys. Lett. **79**, 1876 (2001).
8. A.L. Stepanov, D.E. Hole, A.A. Bukharaev, P.D. Townsend, N.I. Nurgazizov, Appl. Surf. Sci. **136**, 298 (1998).
9. I. Zergioti, S. Mailis, N.A. Vainos, P. Papakonstantinou, C. Kalpouzos, C.P. Grigoropoulos, C. Fotakis, Appl. Phys. A **66**, 579 (1998).
10. E.J. Bjerneld, F. Svedberg, M. Kaell, Nano Lett. **3**, 593 (2003).
11. M. Kaempfe, G. Seifert, K.-J. Berg, H. Hofmeister, H. Graener, Eur. Phys. J. D **16**, 237 (2001).
12. M. Kaempfe, T. Rainer, K.-J. Berg, G. Seifert, H. Graener, Appl. Phys. Lett. **74**, 1200 (1999).
13. G. Seifert, M. Kaempfe, K.-J. Berg, H. Graener, Appl. Phys. B **71**, 795 (2000).
14. G. Seifert, M. Kaempfe, K.-J. Berg, H. Graener, Appl. Phys. B. **73**, 355 (2001).
15. A.V. Podlipensky, V. Grebenev, G. Seifert, H. Graener, J. Lumin., **109**, 135 (2004).
16. A. Stalmashonak, G. Seifert and H. Graener, Opt. Lett. **32**, 3215 (2007).
17. A. Stalmashonak, A. Podlipensky, G. Seifert, H. Graener, Appl. Phys. B **94**, 459 (2009).
18. A. A. Unal, A. Stalmashonak, G. Seifert, and H. Graener, Phys. Rev. B **79**, 115411 (2009).
19. A. Stalmashonak, G. Seifert and H. Graener, J. Opt. A: Pure Appl. Opt. **11**, 065001 (2009).
20. A. Stalmashonak, H. Graener, G. Seifert, Appl. Phys. Lett. **94**, 193111 (2009).
21. O. Deparis et al., Appl. Phys. Lett. **85**, 872 (2004).
22. A. Abdolvand et al., Adv. Mater. **17**, 2983 (2005).
23. A. A. Lipovskii, M. Kuittinen, P. Karvinen, K. Leinonen, V. G. Melehin, V. V. Zhurikhina, and Y. P. Svirko, Nanotechnology **19**, 415304 (2008).
24. Berg, K.-J., Berger, A. and Hofmeister, H., Z. Phys. D. **20**, 309 (1991).
25. M. Leitner, H. Peterlik, and B. Sepiol, H. Graener, M. Beleites, and G. Seifert, Phys. Rev. B **79**, 153408 (2009).