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IN-SITU FORMATION OF Ag-CONTAINING NANOPARTICLES IN THIN POLYMER FILMS

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Abstract — A polymeric material containing Ag nanoparticles was formed by thermal annealing of silver nitrate dissolved in a polymer. Polyvinylalcohol and polyvinylpyrrolidone were used as polymer matrix. The composite material was prepared as thin films by spin coating. UV/ VIS spectroscopy was used to monitor the preparation. The formation of a sharp band at ~425 nm in the UV/VIS-spectra and ultrastructural changes (as revealed by SEM and SFM) indicated the generation of nanoparticles. ©1998 Acta Metallurgica Inc.

INTRODUCTION

Nanocomposites of inorganic materials in organic matrices are of a particular interest. They combine typical properties of organic polymers (*e.g.*, elasticity, transparency or specific absorption of light, dielectrical properties) with the advantages of nanoparticles, particularly, the high specific surface and the high ratio of surface atoms to innersphere atoms.

The specific properties of nanoparticles could be used in technical preparation methods which are compatible to microtechnology if they can be embedded in thin films. Typical preparation schemes included simultaneous plasma polymerization and metal evaporation (1). Gold nanoparticles were formed by deposition of metal vapor with low-temperature organic solvents followed by controlled/limited atom accretion (2). Here, we report the *in-situ* formation of nanoparticles in the matrix of a water-soluble polymer film prepared by spin-coating. The obtained films show very interesting spectral properties, which can be explained by the formation of homogeneous distributed metallic particles with diameters below 10 nanometers.

EXPERIMENTAL

Film Preparation

Polyvinylalcohol (PVOH) and polyvinylpyrrolidone (PVP) were used as film forming materials. Aqueous polymer solutions with concentrations between 5 and 20% were prepared with deionized water. Silver nitrate was p.a. graded. A spin coater for photolithographic film

preparation was used for spinning of the polymer films onto quartz substrates. The rotation speed was varied between 2000 and 6000 rpm. Films of different thickness (50-200 nm) were realized by variation of the polymer concentration and the rotation speed. Thermal annealing was carried out in a convection stove. Water extraction experiments were conducted by immersing the sample in water (4 h at room temperature), prior to extensive rinsing in water and air drying.

Spectral Photometry

The spectra were recorded by the double ray spectralphotometer (UV/VIS) M 40 (Zeiss). The quartz substrates were positioned perpendicularly to the measurement ray. No disturbing interference pattern was observed, what can be explained by the similar refractive indices of the thin film and the substrate.

Scanning Electron Microscopy

Scanning electron images of PVP film samples were obtained by a digitized scanning electron microscope DSM 960 (Zeiss). A homogeneous thin gold film (thickness ~10 nm) was sputtered over a part of the polymer surface to avoid imaging artifacts from electrical charging. Comparison of coated and uncoated regions of the same sample revealed no changes of the texture of the investigated films. Both secondary electron signals and backscattered electron signals were used for sample characterization. The images were obtained with an acceleration voltage of 30 kV, a magnification of 50 0000, and a working distance of 5 mm.

Scanning Force Microscopy

PVP film samples with different curing temperatures were investigated with an AFM Autoprobe CP 100 (Park Scientific Instruments) in contact mode with a 5 x 5 x 1 (x, y, z) μm scanner and etched Si-tips (Ultralever, Park Scientific Instruments) with a scan rate of 1 Hz.

A BioScope (Digital Instruments (DI), Santa Barbara, CA) equipped with an 100 x 100 x 5 (x, y, z) μm scanner and etched Si-tips (Nanoprobe, DI) was used in the tapping mode for imaging PVP films with different concentrations of $AgNO_3$. The obtained images were exported in TIFF-format and imported into NIH Image 1.59 (NIH, Bethesda, MD) for further image processing. For the determination of particle height classes a threshold was set at different heights (20, 40, and 60 nm) prior to counting of the particles reaching this threshold. The peak in the height distribution (*cf.* Figure 4) was assigned as background level. Areas of 9 μm^2 were investigated for every sample.

RESULTS AND DISCUSSION

Film Formation and Spectral Properties

The polymer films were prepared from an aqueous solution. Therefore, the polymer was dissolved in water, resulting in a completely transparent solution. Subsequently, silver nitrate was dissolved in this polymer solution. The intensity of short wave length light was reduced during the preparation of the solution to minimize photochemical reduction of Ag^+ to metallic silver. The
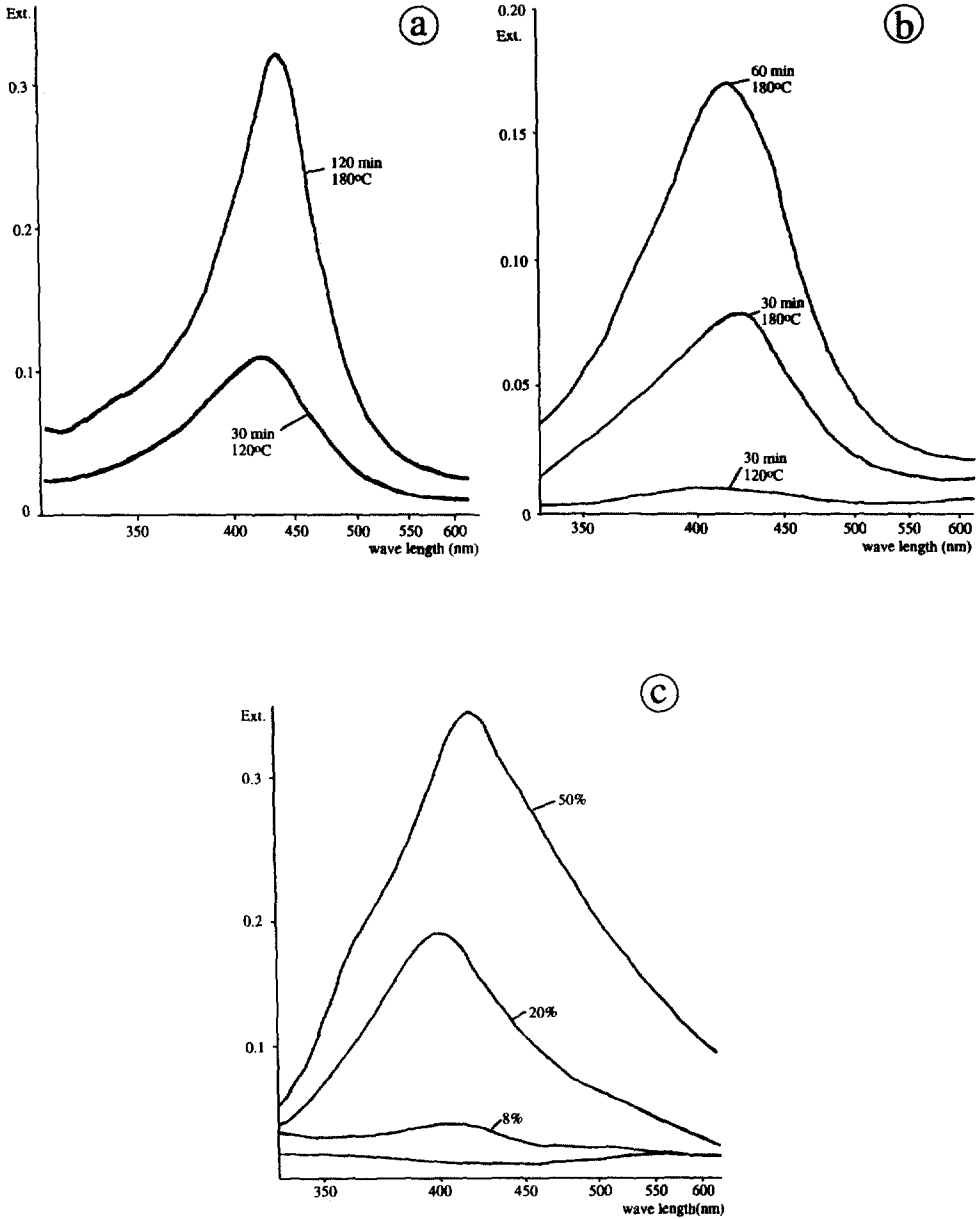
Figure 1. UV/VIS spectra of the cured polymer films in dependence on curing conditions or the silver salt concentration: (a) 30% AgNO₃ in PVOH, (b) 50% AgNO₃ in PVP, and (c) AgNO₃ in PVP cured at 180°C for 4 h.
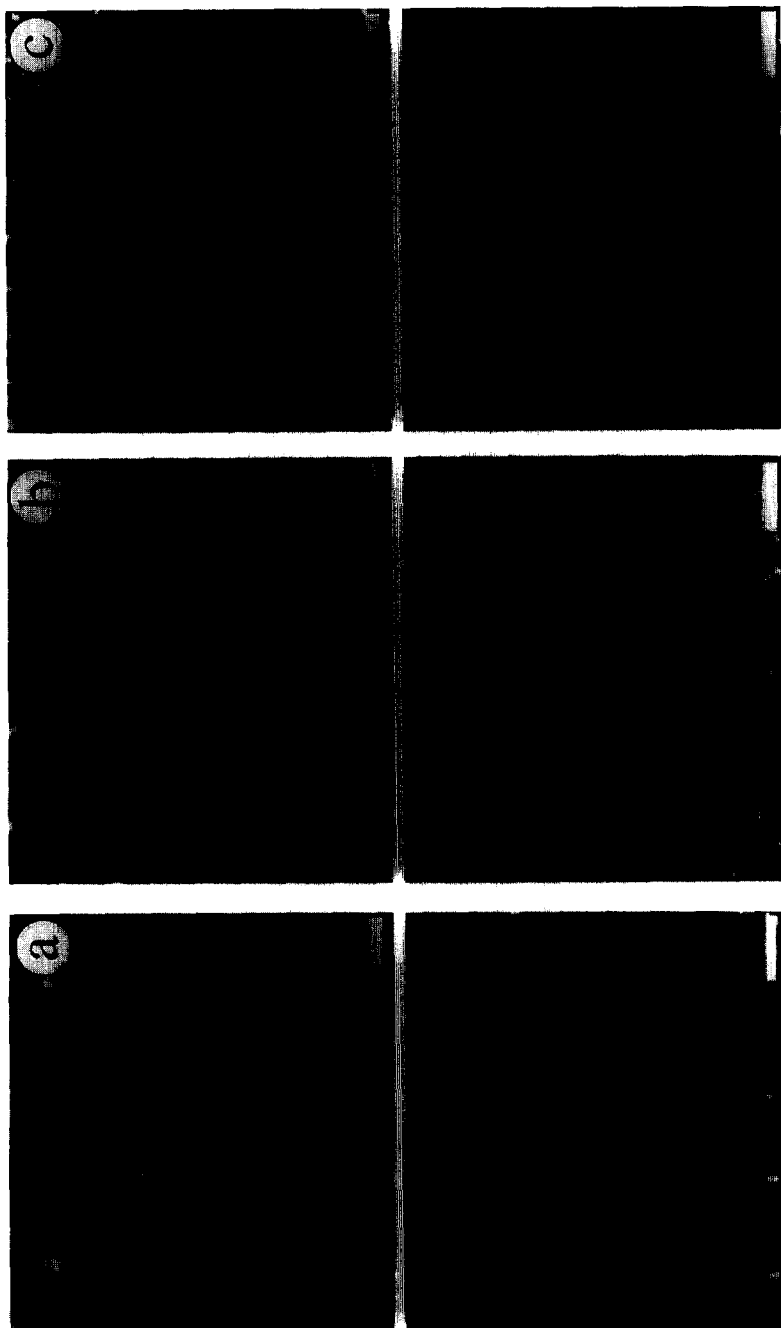
Figure 2. Scanning electron micrographs of PVP films with 8% (a), 20% (b) and 50% (c) $AgNO_3$ in secondary electron (upper row) and backscattered electron (lower row) contrast. The samples were cured for 4 h at 180°C. Topviews. Scale bars = 200 nm.

solutions were kept dark. Spinning of the solution resulted in a transparent and completely uncolored film. The high transparency in the visible region was stable over weeks for films stored at room temperature.

The films remained completely clear during curing. Curing at temperature above 400 K resulted in changes in the UV-VIS spectra. An absorption band with a sharp maximum in the range of 425-435 nm arose (Figure 1a). The intensity of this band correlates with increasing curing temperature and longer curing time (*cf.* Figure 1a, b). A saturation effect in the absorbance band growth was observed after a curing time of 2 hours. Even films with a thickness of less than 80 nm exhibited an intensive absorption.

We compared the formation of the absorption band in a polyvinyl alcohol matrix (Figure 1a) with the same procedure in a $AgNO_3$-containing polyvinylpyrrolidone matrix (Figure 1b). The optical absorption was found at nearly the same position and exhibited a similar shape. This observation suggests that the thermal formation of the high spectral absorbance is not caused by a thermally formed specific chromophor of the polymer matrix, but by the behavior of the added salt. The formation rate of the absorption band correlates strongly with concentration of $AgNO_3$ in the polymer films (Figure 1c).

The increase of spectral absorbance during curing corresponds very well with the known spectral behavior of nanoparticles. Such small metallic particles exhibit a high optical absorbance due to the existence of discrete energy levels of electron and particularly of specific surface states. The smallest particles of Ag with diameters below 5 nm have a rather high absorbance band with a maximum at about 400 nm (3). This band is broadened and shifted toward higher wave lengths with increasing particle diameter (4). Ag particles with diameters of ~10 nm exhibit bands at 430-450 nm in dependence on the used solvent (5). We believe, based on the maximal absorbance at *ca.* 425 nm in both investigated polymers, that small spherical particles of silver with a diameter of 10 nm or less are formed by a redox reaction with the polymer matrix during the annealing procedure. Larger diameters as well as elongated shapes should be clearly revealed in the spectra by shift and broadening of the absorption band (6, 7).

In some experiments with high $AgNO_3$ concentrations (50 mass-% in the matrix) the appearance of shoulders and bands at higher wavelength (between 550 and 650 nm; data not shown) was observed. The bathochromically shifted absorbance indicates metallic silver particles with diameters of 10-20 nm. We assume that the particle size increases with very high salt concentration and high curing temperature.

The suggestion of small metallic nanoparticles as source for the observed absorption is supported by analogous experiments with copper salts. A maximum at slightly lower wavelengths was observed (manuscript in preparation).

Ultramicroscopy

Neither material nor topographic contrast was found in scanning electron microscopy of uncured films. This result agrees with the observed transparency of the films. In contrast, cured films exhibited a significant texture, which is marked by nearly round shaped structures with diameters up to about 50 nm (Figure 2). Their density and size distribution depended on $AgNO_3$ concentration in the film, curing temperature and curing time. The density is generally higher in the cases of high $AgNO_3$ concentration and intensive thermal annealing. These density differences correspond with the increase of spectral absorption of the films at 425 nm. The round structures,
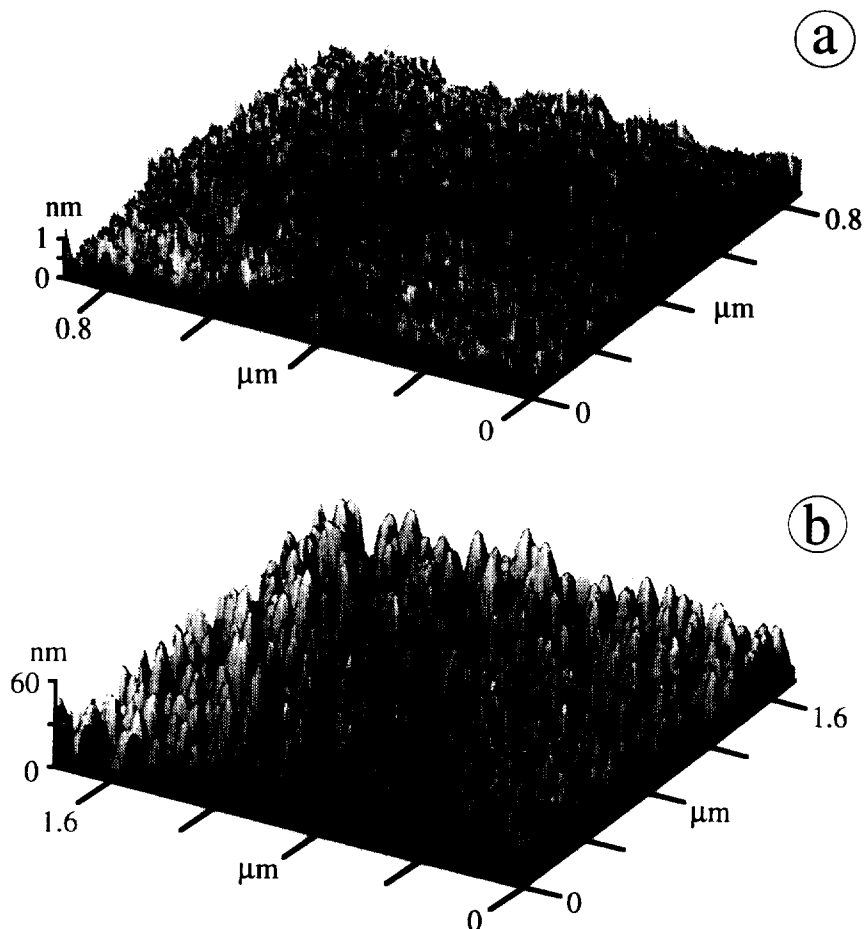
Figure 3. Scanning force micrographs (perspective views) of PVP films containing 5% AgNO₃ cured at 120°C (a) and 180°C (b). Note the different lateral and height scales for each image.

which were embedded in a homogeneously imaged matrix, exhibited a nanotopography with highest point at the center of every region. This observation points to a particle character of the structures observed by the secondary electron signal of SEM (Figure 2, upper row).

The image of backscattered electrons (BSE signal of SEM) reveals significant differences in the atomic composition of the material of the embedding matrix compared to the spherical structures (Figure 2, lower row). This result supports the assumption that these structures are particles which are formed during the thermal curing.

Comparative information about the topography of the nanoparticles was gained by scanning force microscopy. Films with 5% AgNO₃ cured at 120°C (393K) revealed a smooth surface with RMS-roughness smaller than 0.5 nm (Figure 3a). Films of similar composition cured at 180°C (453K) exhibited a nanotopography (Figure 3b). Structure heights of 25 nm to 68 nm were
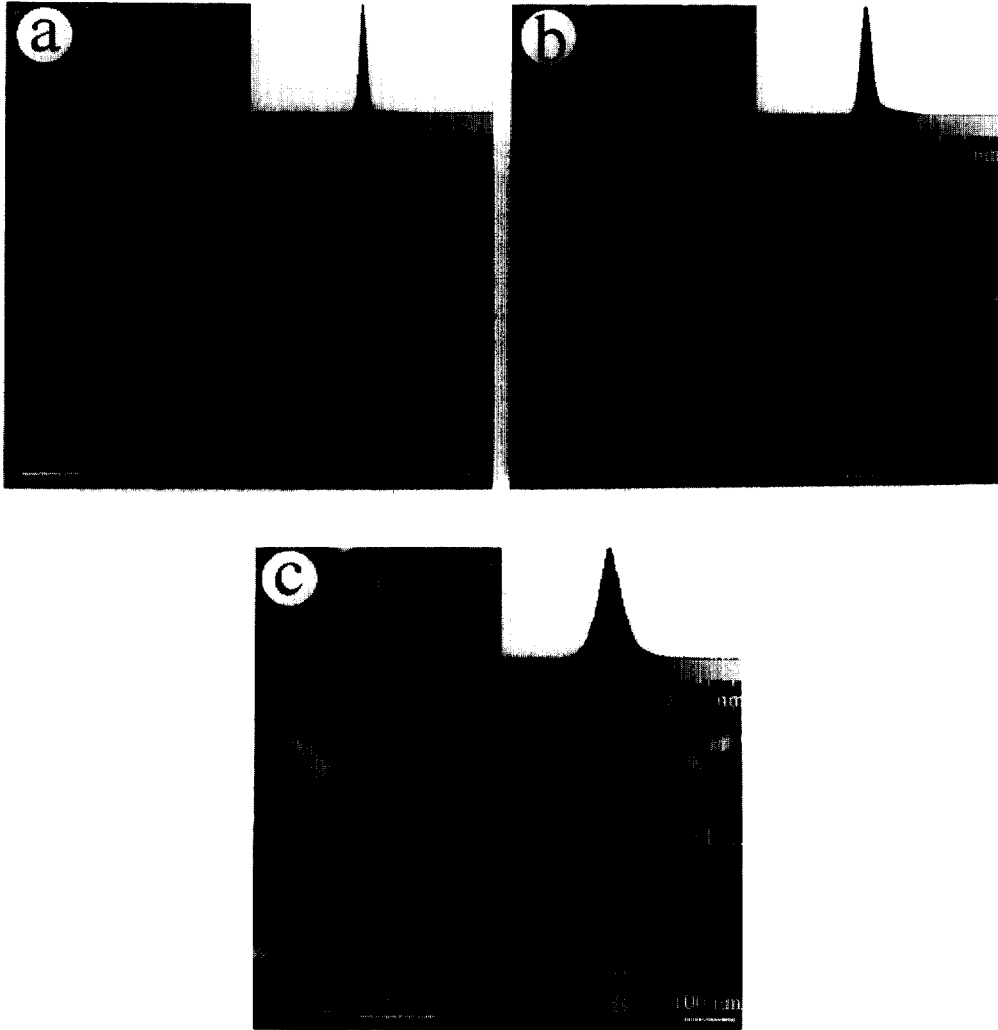
Figure 4. Scanning force micrographs of the PVP films from Figure 2 with 8% (a), 20% (b) and 50% (c) AgNO$_3$. The height is brightness-coded according to the inserted brightness bar, the lateral scale is given by the scale bars. The inserts in the lower right are zooms of the surface, and the histograms in the upper right show the distribution of the brightness (height) values in each image.

observed. The mean particle height is 45±7 nm. The height distribution is broad and corresponds very well with the distribution visible in the SEM image (cf. Figure 2). The area density of particles is 100-160 particles per μm^2.

Scanning force microscopy of PVP samples with a low $AgNO_3$ concentration (8%) revealed a smooth surface, as demonstrated by a sharp peak of the height distribution in the accompanying histogram (Figure 4a). Particles with heights of 20-40 nm exhibited a density of 15 per μm^2, the density of particles with heights of 40-60 nm was 7 per μm^2. No particle higher than 60 nm was observed. At higher $AgNO_3$ concentration (20%) the particle height as well as the particle number increased (Figure 4b). Now more than 25 particles per μm^2 were observed with a height of 20-40 nm, and the density of particles 40-60 nm high was ~2 per μm^2. Again, no particle higher than 60 nm was visualized. An increase of the $AgNO_3$ concentration to 50% resulted in significant changes in the surface topography (Figure 4c). Whereas the number of particles in the 20-40 nm height range was rather similar to the previous $AgNO_3$ concentration, an increase in the 40-60 nm range to ~3 particles per μm^2 was observed. Additionally, the height of 60 nm was ~2.5 times exceeded per μm^2, which was caused by comparatively large particles.

Size of Particles

The particles observed by SEM and SFM are larger as expected from spectral photometry. Additionally, lower absorption intensity would be expected in the case of such large metal particles. Therefore, we assume that the particles seen in all ultramicroscopical studies are not solely responsible for the high absorption at 425 nm. On the contrary, we think that at least two types, but probably three types of nanoparticles, are formed simultaneously during the curing procedure. Only the smallest of them are responsible for the absorbency band. This class is hardly observable in SEM and SFM, because its topography at the surface of the embedding polymer film is too small compared to the surface roughness and the resolution of the SEM did not allow a sufficient material contrast signal. The observed particles with greater diameters (20-150 nm) contained an enhanced concentration of Ag atoms. It is not clear if the silver in these particles occurs in ionic or atomic state. The comparatively large size of these particles and their high density points to the ionic state. Water extraction experiments resulted in a slight decrease in the surface density of the particles, whereas the size of the remaining particles remained apparently unchanged. This observation could be explained by particle removal due to mechanical forces during the rinsing step, and a high stability of the particles against the solution by water. Explanations for this stability could be a high concentration of atomic silver compared to the ionic state and/or a protective layer of the polymeric matrix.

CONCLUSIONS

1. Nanoparticles embedded in polymeric (PVOH, PVP) films can be produced *in-situ* by thermal annealing of polymer films containing metal salt.

2. The formation of nanoparticles was visualized by SEM and SFM. SEM shows a strong material contrast between the nanoparticles and the matrix, reflecting the different atomic composition of both film components. A characteristic nanotopography of the particles formed during the annealing is shown in SFM images. The topographic information of SFM is in accordance with the material contrast information of SEM images. This fact proves that the changed topography of the film surface after annealing is caused by a local material transport and a material separation between formed particles (probably $AgNO_3$) and the embedding polymer matrix.

3. The thermal annealing of the salt-containing polymer films results in the formation of a very intensive light absorbance band at 425 nm. This band has a comparatively narrow shape. It corresponds very well with the spectra of metallic nanoparticles of Ag with a particle size of about 10 nm or below. It is assumed that small particles of Ag are formed by a thermal redox process between Ag^+ and the polymer. Such particles cannot be seen by SEM, but their existence can be concluded from the characteristics of the spectra.

Further work will be focused on an increased uniformity in particle size and on the preparation of thin films with a thickness below 30 nm.

REFERENCES

1. Heilmann, A., Werner, J., Stenzel, O. and Homilius, F., *Thin Solid Films*, 1993, 246, 77.
2. Klabunde, K.J., Habdas, J. and Cárdenas-Triviño, G., *Chemistry of Materials*, 1989, 1, 481.
3. Hornyak, G.L., Phani, K.L.N., Kunkel, D.L., Menon, V.P. and Martin, C.R., *Nanostructured Materials*, 1995, 6, 839.
4. Sanchez-Cortes, S., Garcia-Ramos, J.V., Morcillo, G. and Tinti, A., *Journal of Colloid and Interface Science*, 1995, 175, 358.
5. Chumanov, G., Sokolov, K., Gregory, B.W. and Cotton, T.M., *Journal of Physical Chemistry*, 1995, 99, 9466.
6. Creighton, J.A., Metal Colloids, in *Surface Enhanced Raman Scattering*, eds. R.K. Chang and T.E. Furtak, Plenum, New York, 1982, p. 315.
7. Creighton, J.A. and Eadon, D.G., *Journal of the Chemical Society Faraday Transactions*, 1991, 87, 3881.