

# The Effect of Evaporation Temperature on the Structure and Conductivity of Thin Films Obtained by the Moving Meniscus Method from Nanodispersions of Silver Particles

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**Abstract**—The effect of temperature (23–58°C) on the structure and conductivity of thin films obtained by the moving meniscus method from nanodispersions of silver particles with sizes of 6.5–70 nm has been studied. It has been shown that an increase in temperature leads to an exponential decrease in the specific conductivity of the films, with their thickness varying nonmonotonically. In the case of “large” particles, an increase in temperature decreases the efficiency of their deposition onto a substrate. The reasons for the observed regularities have been discussed.

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## INTRODUCTION

In [1], we have studied the effect of temperature on the geometric parameters and conductivity of ring-shaped deposits formed upon evaporation of droplets of dispersions of silver nanoparticles on hydrophilic (glass) and hydrophobic (copper) substrates. It has been shown that an increase in temperature causes significant changes in the deposit profile. Therewith, increasing temperature has different effects on the structures of the deposits formed on glass and copper substrates. For example, as the evaporation temperature approaches 58°C, the lateral conductivity of ring-shaped deposit on the glass substrate increases jumpwise (analogously to a percolation transition). It has been suggested that the reason for this effect of temperature is related to a change in the ratio between the rates of physicochemical processes occurring at different stages of droplet evaporation.

This work may be considered to be a continuation of a series of papers [2–6], in which the formation regularities, structure, and electrical conductivity of nanocomposites, which are formed upon the evaporation of droplets of aqueous dispersions of silver nanoparticles on different substrates due to the coffee ring effect, were studied [7–9]. In the cited works, the effects of the size and concentration of silver nanoparticles [4], degree of substrate hydrophilicity [5], and the volatility and composition of a dispersion medium [6] on the geometric parameters and conductivity of

ring-shaped deposits were studied. Analysis of the results has shown that the presence of components dissolved in an initial dispersion medium plays a significant role in the formation of a deposit. Therewith, silver nanoparticles act as heterogeneous nucleation sites, which significantly affect the crystallization of the dissolved components during droplet evaporation, while the formed crystals change the structural organization and conductivity of a ring-shaped deposit.

We used the moving meniscus method for the formation of a deposit from nanoparticles in [10], where the structure and conductivity of thin composite films based on silver nanodispersions were studied. In this method, a deposit is formed as a result of the transfer of nanoparticles by an advection flow toward an interface, which moves (recedes) due to evaporation. Advection flow arises because of the nonuniform evaporation of a liquid in the meniscus zone: the evaporation rate is maximum near the three-phase contact line, and it gradually decreases with the distance from it to the “background” rate, which corresponds to the planar horizontal surface of the nanodispersion [11].

Nanoparticles are deposited onto a substrate due to the Brownian diffusion, as well as the van der Waals and capillary forces. Therewith, the tangential (with respect to the substrate) component of the capillary forces “pulls” the particles together into a compact structure. In [10], the dependences of the thickness and conductivity of deposits on the weight concentration of a precursor ( $\text{AgNO}_3$ ) and the number concentration (size) of silver nanoparticles were determined.

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It was shown that some of these dependences have a nonmonotonic pattern, while the dependences of the conductivity on the aforementioned parameters have the character of a percolation transition.

It should be noted that, in spite of the apparent simplicity of the moving meniscus method, the processes that accompany its realization are rather complex because of the large number of external and internal factors, which affect both the mechanism of transfer of nanoparticles and the formation of their deposit on a substrate [11]. Obviously, the fact that components dissolved in the dispersion medium may be crystallized in the meniscus region significantly complicates the deposit (composite film) formation from nanoparticles. As has been mentioned in [10], there is a certain analogy between the evaporating droplet and moving meniscus methods. In both cases, a deposit is formed in the meniscus zone due to the advection transfer of particles to the three-phase contact line. However, there are two fundamental differences. The first difference is related to the dynamics of the three-phase contact line, which remains almost quiescent for a long time in the case of evaporating droplet, while, in the case of the moving meniscus method, it, on the contrary, moves upon the evaporation of a dispersion medium. The second difference is closely related to the fact that the solution concentration continuously increases during droplet evaporation, and, at some moment, supersaturation arises and crystallization of the dissolved components may begin due to homogeneous or heterogeneous nucleation on nanoparticles, which leads to the additional "contribution" to the deposit both in the vicinity of and far from the three-phase contact line. In the case of the moving meniscus method (when a relatively small volume of a dispersion medium is evaporated), the formation of a supersaturated solution has a dynamic character and occurs (if possible) only in a small region of the meniscus, in particular, in a precursor wetting film [12].

Since the effect of temperature has appeared to be significant and multivalued in the case of droplet evaporation, it is of doubtless interest to investigate the regularities of the formation of thin nanocomposite films by the moving meniscus method at different temperatures, which is the aim of this work.

## EXPERIMENTAL

Dispersions of silver nanoparticles were prepared by chemical reduction from an aqueous silver nitrate solution. Tannin was used simultaneously as a reductant a dispersion stabilizer. The characteristics of the components and the synthesis procedure of silver nanoparticles have been described in detail elsewhere [13]. Precursor ( $\text{AgNO}_3$ ) concentration was 0.1 wt %. The average size of silver nanoparticles ( $6.5 \pm 0.2$  nm) was determined by dynamic light scattering using a

Zetasizer Nano instrument (Malvern, United Kingdom).

The moving meniscus method was implemented as follows. Degreased glass substrates with a size of  $25 \times 10$  mm<sup>2</sup> cleaned in an ultrasonic bath were placed vertically into a laboratory beaker with a diameter and a height of 30 and 50 mm, respectively, and mechanically fixed. The beaker and a flask containing a silver nanodispersion were preliminarily exposed in a sealed oven for 2 h at a chosen temperature. Then, the beaker was half-filled with the studied dispersion using a syringe. After that, it was exposed at 23, 33, 40, 45, 50, or 58°C for 45, 26, 18, 13, 10, or 6 h, respectively. In order to maintain a constant moisture content in the oven, a tray with a desiccant ( $\text{CaCl}_2$ ) was placed near the substrates.

Over the aforementioned time periods, the level of the nanodispersion in the beaker decreased by 2–3 mm, while strips of a thin composite film with a corresponding width were formed on the two sides of the glass substrate, with the films exhibiting a metallic luster. After that, measuring silver electrodes were applied onto both sides of the substrate by magnetron vacuum sputtering; the interelectrode distance was  $2 \pm 0.1$  mm.

The geometric parameters and structures of the composite films were studied with a scanning electron microscope (SEM) equipped with a Quanta 650 FEG field cathode and an energy-dispersive X-ray analyzer (FEI, Netherlands), as well as a Multimode V atomic force microscope (Veeco, United States).

The electrical conductivity of the films was measured using a Keithley 6485 picoamperemeter equipped with an Akiakom APS-3103 stabilized power supply unit.

## RESULTS AND DISCUSSION

Figure 1 shows SEM images of some characteristic fragments of the obtained composite films. The films of the highest quality were formed at an evaporation temperature of 23°C, although a number of linear threadlike defects were observed in them (Fig. 1a). Similar defects were also formed in ring-shaped deposits resulting from evaporation of dispersion droplets [4–6]. These defects seem to be caused by the fact that nanocomposites shrink at the final stage of moisture evaporation from the deposit bulk and internal stresses arise, which lead to nanocomposite cracking.

Some structures with sizes from a few tens to several hundreds of nanometers were also observed on the surface of the composite films. As the evaporation temperature was elevated, the sizes and number of these structures significantly increased (Fig. 1b). After a temperature of 58°C was reached, these structures coalesced and the films acquired the appearance of randomly connected individual islands. It should be