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Electrophoretic deposition of silver from organic PDADMAC-stabilized suspensions

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Abstract This study on the electrophoretic deposition (EPD) of silver particles illustrates the influence of the electric field strength on the surface morphology of the deposit. Experiments were performed in ethanol- and methylethylketone (MEK)-suspensions under a direct electric field ranging from 50 to 360 V/cm. The charging agent PDADMAC (poly-(diallyldimethyl)-ammonium-chloride) proved to have a good electrostatic stabilizing effect in both systems and led to a positive zeta-potential in EtOH and to negatively charged particles in MEK. The yield of the deposits showed a linear relation with electric field strength which agrees with Hamakers law for the kinetic of EPD. Layers deposited at low electric field strengths exhibited a smooth and plane surface. Values higher than 180 V/cm resulted in the formation of parallel grooves. The morphology changed again at fields exceeding 360 V/cm and exhibited irregularly distributed hillocks.

Introduction

Electrophoretic deposition (EPD) is a forming process starting from particles suspended in liquid media and can be applied to a broad range of particulate matter (metals, ceramics, glasses, polymers, etc.). It is used to create thin or thick films and even three dimensional bodies. It makes use of the surface charge to transport particles toward an oppositely charged electrode and to deposit them in a densely packed layer. The achievable lateral dimensions are only limited by the shape and dispersion of the electric field at the deposition electrode and by the particle size. This feature has raised interest for EPD in micro-electronics, where the need for miniaturization of ever more complex conductive lines and patterns is still a strong driver for innovation. EPD of metallic particles is an attractive alternative to traditional patterning techniques like screen printing. Silver, silver-palladium alloys, nickel, and copper lines are commonly used in electroceramic multilayer devices in layers having thicknesses down to the micrometer range.

One of the most important developments in packaging technologies is the manufacturing of ceramic multilayer circuits with the so-called low temperature co-fired ceramics-technology (LTCC). Due to its electrical and thermal properties pure silver is used for the conductive lines. The process of manufacturing starts with ceramic tapes. Holes are punched into the ceramic tape and filled with silver paste to provide the connection to the next layer. On the surface of the tapes a pattern of silver paste is applied. A LTCC circuit consists of a number of layers with individually patterned tapes. These are stacked and pressed to form the three dimensional network. Subsequently these laminates are de-bindered and sintered. By screen printing, the lateral dimensions of the metallic patterns are limited to a scale at which the silver paste or ink can be treated as a continuous medium. A reduction below 50 μm line width tremendously increases the cost for inks as well as for the required screens. In high frequency applications a proper aspect ratio of the conductive lines (height versus width) has also to be taken into account.

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The potential of EPD of metallic particles in electronic device manufacturing has already been outlined by Van Tassel and Randall [1]. Zarbov et al. [2] demonstrated the patterning by EPD in prototype micro-components. A process for patterning ceramic tapes for LTCC modules using EPD would consist of two steps. The first step is the deposition of silver particles on a patterned electrode. In a second step the deposit will be transferred to the ceramic tape. A high quality of the deposit requires a dense and uniform packing of the particles, unvarying thickness over the whole area, a smooth surface without cracks and voids, and a high lateral resolution of structures. Prerequisite for fulfilling these criteria is a good stabilization of the suspension. A number of authors have contributed to certain aspects of morphology, mostly of non-metallic deposits. Some articles deal with the reduction of voids and pores caused by the electrolytic formation of gases during deposition [3–6]. Other publications discuss the formation of layers with maximum density [7–9] or the influence of process parameters on the morphology [10], particle size distribution [11], and microstructure within the layer [12]. An industrial manufacturing process with high throughput requires an efficient deposition. According to Hamakers law [13] the kinetics of EPD mainly depends on the particle concentration, the electrophoretic mobility, and the electric field. Aim of this study was to find the limits of EPD process conditions for achieving uniform coatings with silver particles and to designate the main parameters, which influence film morphology.

Experimental procedure

The silver powder used in this study was purchased from Heraeus (item Ag06N043). The particles were pure metallic silver of spherical shape with a mean diameter of 1.4 µm (d_{90}: 2.11 µm, d_{10}: 0.93 µm) and monomodal particle size distribution. Examination by SEM proved a low degree of agglomeration. The powder was used as delivered without further washing. The polyelectrolyte PDADMAC was supplied as aqueous solution from Sigma–Aldrich (low molecular weight—M_W: 100.000–200.000; 20 wt% in water).

The ethanol-suspension was prepared by adding 50 g of Ag06N043 to 250 mL ethanol (Merck) into a glass beaker and stirred to distribute the particles in the medium (200 g/L solids content). 0.25 mL of PDADMAC was used as stabilizer (this amount is calculated from the maximum of zeta-potential measured against additive concentration). The suspension was stirred and cooled down to 5 °C in water. The preparation of the methylethylketone-suspension (MEK 99.5% from Roth) was done in the same way except for the addition of 2 mL of PDAMAC calculated again from the maximum of zeta-potential. The suspensions were dispersed ultrasonically at 95% intensity (UP400S, Hielscher, 400 W, 24 kHz) for 10 min, cooled in water during treatment and stirred until the start of the deposition experiment, which was carried out at room temperature. The zeta-potential was measured by the electroacoustics analyzer DT 1201 (Dispersion Technology, USA).

The depositions were carried out from two freshly prepared suspensions. Glass beakers were used as cells for EPD. The deposition- and counter-electrodes (palladium-coated copper, square shape, 5 × 5 cm^2) were mounted vertically 1 cm below the level of the suspension. Applying Stokes law particles with d_{90} of 2.11 µm would need 7.5 min to sink 1 cm. Since this time considerably exceeds the duration of the experiments itself the particle size distribution in front of the electrode could be considered as constant. The electrodes were connected to the power supply (MCP140-2000IE, FUG). The distance of the electrodes was fixed at 1 cm and 2.4 cm. The experiments were performed at constant voltage and variable particle concentration. Direct electric fields in the range of 50–360 V/cm were applied. Each deposition experiment lasted for 6 s. The time-profile of a deposition experiment included 1 s for the rise of the electric field, 4 s for the nominal voltage, and 1 s for the decrease. After each deposition experiment the suspensions were stirred and the cell was prepared for the next run. The layers were dried under ambient conditions. The deposited mass was determined by weighing the electrodes before and after deposition. After deposition residual silver on the back and the sides of the electrode was wiped off with a tissue before weighing. Since for a number of applications it is relevant to achieve a minimum thickness of the silver layer after a subsequent sintering process we calculated a thickness assuming 100% theoretical density (sintered silver electrodes usually exceed 98% theoretical density). The microstructure was analyzed by light microscopy (BX60M, Olympus) and scanning electron microscopy (Jeol JSM 5900).

Results and discussion

The surface charge on the silver powder was weakly negative in pure EtOH and MEK. In EtOH, the addition of PDADMAC led to a positive surface charge and a well stabilized suspension ($\zeta \sim +32.8$ mV). Hence the deposition took place on the cathode. In MEK the silver particles gained an increase of the originally negative charge with PDADMAC ($\zeta \sim -48.6$ mV) and were deposited at the anode. The reason for the opposite charge can be found in the change of the absorption mechanism in the two liquid media according to [14]. In EtOH with a dielectric constant of 25.3 the degree of dissociation of PDADMAC is large enough that specific absorption of the organic cation on the surface of the silver particles occurs. In MEK with a dielectric constant of 18.6 the mechanism changes to the absorption of a neutral species (the undissociated PDADMAC) with subsequent ionization. The more soluble organic cation will then dissolve in the MEK and the chloride will remain on the silver surface resulting in a negative charge.

The silver content was slightly different for each experiment, because of the reuse of the suspension. In the subsequent experiment the silver content of the suspension was lowered by the amount of silver deposited in the preceding experiment. Hamakers law for the kinetic of EPD [13] was applied to normalize the measured deposited mass to the particle mass concentration of the initial suspension. According to this equation the deposit yield depends on the electric field strength (E), the electrophoretic mobility (M_E), the particle mass concentration (c), the surface area of the substrate (A) and an efficiency factor (f) ($0 \leq f \leq 1; f = 1$, if all particles reaching the substrate are deposited).

$$m(t) = \int_{O}^{t} f \cdot M_{\mathrm{E}} \cdot A \cdot c(t) \cdot E(t) \cdot \mathrm{d}t \tag{1}$$

Strictly speaking the particle mass concentration also changed to some extent during each deposition experiment (deposition under variable particle concentration). For simplification it was assumed to be constant during an experiment and was given the value of the starting concentration ($c_x(t) = \text{constant}$).

$$m(t) = c_{\mathrm{X}}(t) \cdot \int_{O}^{t} f \cdot M_{\mathrm{E}} \cdot A \cdot E(t) \cdot \mathrm{d}t \tag{2}$$

The deposit weights (d.w.) are calculated from the measured weights of the silver layers ($m(t)$) and refer to the freshly prepared suspension ($C_0 = 200$ g Ag/L solvent).

$$\text{d.w.} = m(t) \cdot \frac{C_0}{c_{\mathrm{X}}(t)} \tag{3}$$

Figure 1 shows the calculated deposit weights of the experiments from EtOH and MEK as a function of the applied electric field. The graphs reveal a directly proportional relation and can be fitted by linear regression. Considering Hamaker's law (1) this behavior implies that every factor can be regarded as constant (except the electric field) and does not change significantly during the experiment. In this case Eq. 3 simplifies to

$$\text{d.w.} = f \cdot M_{\mathrm{E}} \cdot A \cdot C_0 \cdot t \cdot E = k \cdot E \tag{4}$$

The distance between the electrodes (1 and 2.4 cm) had no influence on the deposit weight. The regression lines indicate a comparable kinetic from both suspensions (k(EtOH) = 0.138; k(MEK) = 0.163). Assuming the density of silver with 10 g/cm^3 (Ag06N043–10.4 g/cm^3), 1 mg/cm^2 means 1 µm thickness of a layer with 100% theoretical density.

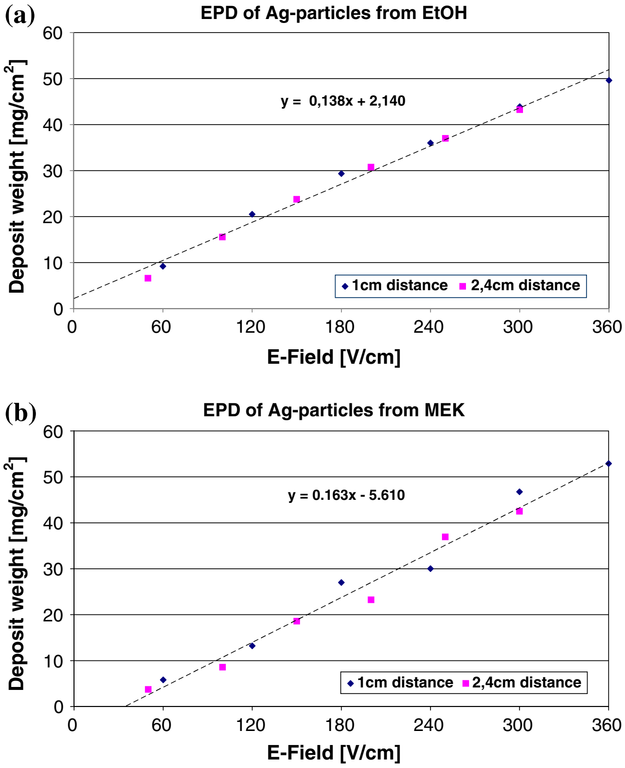

Fig. 1 Deposited weight of silver as a function of applied electric field (1 cm and 2,4 cm distance between electrodes) from ethanol (**a**) and methyl-ethyl-ketone (**b**)

Layers deposited below ≤180 V/cm had a plane, uniform surface. No cracks or other macroscopic defects were found. Analysis by light microscope and SEM proved this observation and revealed a dense microstructure. The surface of the samples from MEK (Fig. 2b) was rougher than that of the deposits from EtOH (Fig. 2a).

At electric field strengths higher than 180 V/cm the morphology of the deposit surface was dominated by significant grooves with linear shape. They ran vertical on the deposition plane, parallel to each other and covered the whole layer. The grooves of layers from EtOH were finer than those of the deposits from MEK. Nevertheless the structures were dense and showed no cracks (Fig. 3, 4, 5, and 6). The existence of grooves on deposits (≥180 V/cm) from both systems proves that their occurrence is independent of the particle charge.

The two suspensions differed significantly in their electric resistivities. From the ratio of the applied electric field strength and the measured amperage the electric resistivity was estimated. For the EtOH-suspension this

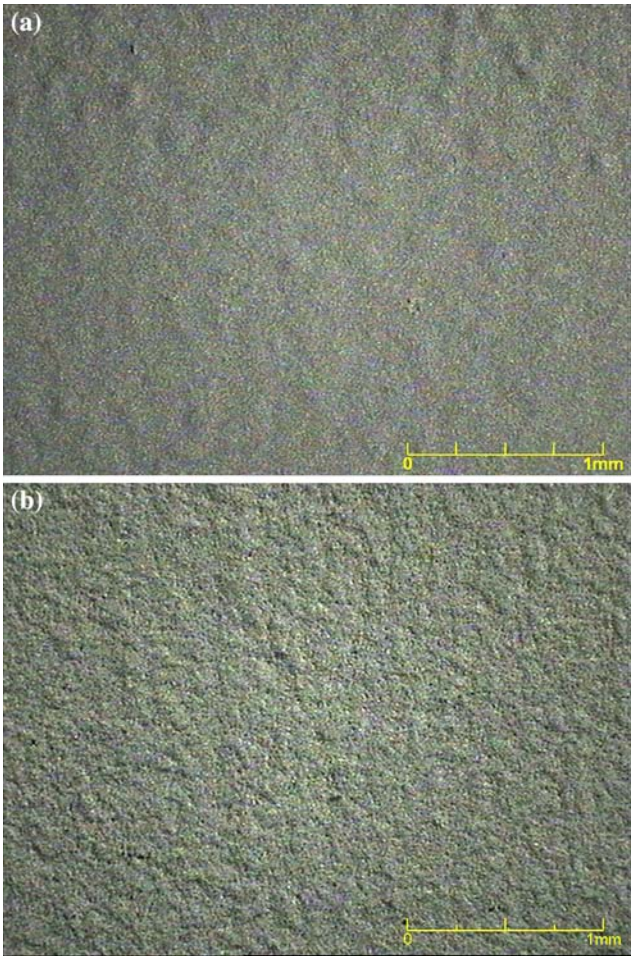

Fig. 2 Deposit of silver particles from EtOH (**a**) and from MEK (**b**) at 120 V, 6 s, and 1 cm distance

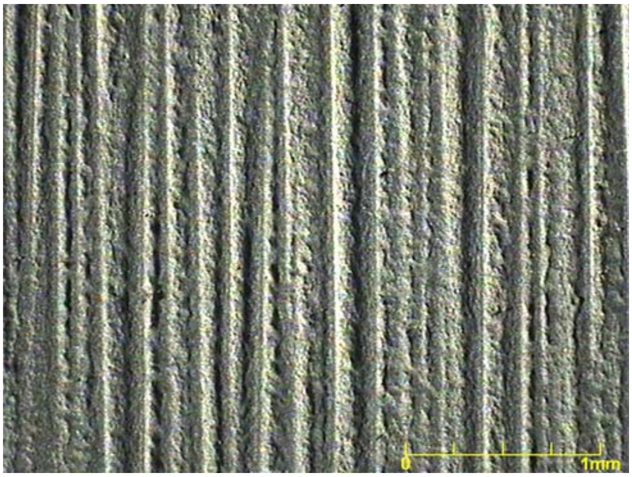

Fig. 3 Deposit of silver particles from EtOH at 240 V, 6 s, and 1 cm distance

yields 6.1×10^3 Ωcm and for the MEK-suspension 76.7×10^3 Ωcm). These values indicate that the resistivity of the MEK-suspension was more than one order of

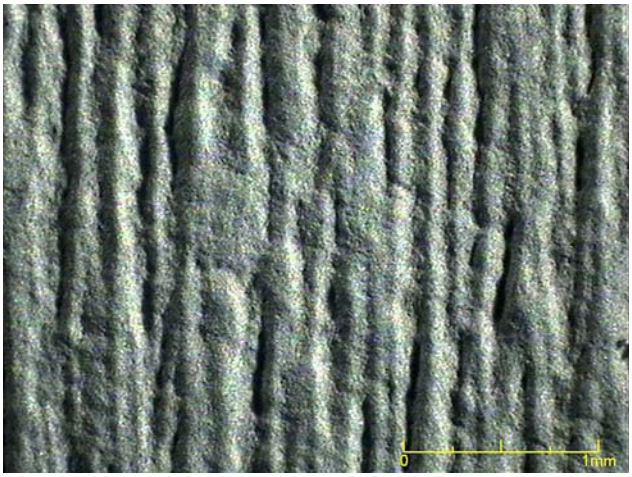

Fig. 4 Deposit of silver particles from MEK at 240 V, 6 s, and 1 cm distance

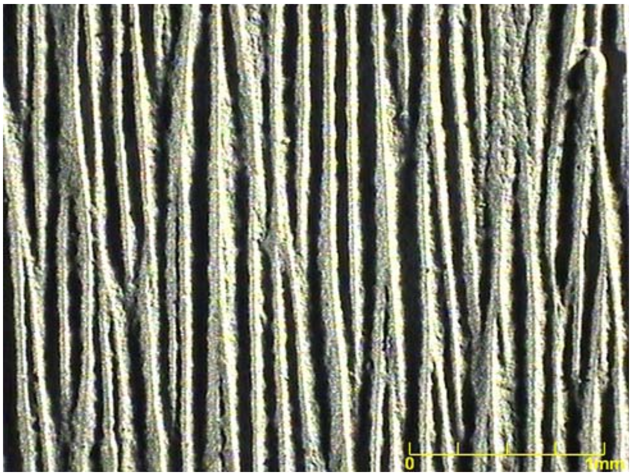

Fig. 5 Deposit of silver particles from EtOH at 360 V, 6 s, and 1 cm distance

Fig. 6 Deposit of silver particles from MEK at 360 V, 6 s, and 1 cm distance

magnitude higher than that of the EtOH-suspension. The electric conductivity and the current flow are obviously not responsible for the formation of grooves. The implication is that these structures are caused by the applied electric field and display the field densities or the field line distribution in combination with convective forces. The root cause for these convective forces is most probably the depletion of particles at the counter electrode, which leads to a downward flow of suspension at the deposition electrode. We exclude thermal convection, because monitoring of temperature did not show any significant changes. At electric field strengths higher than 180 V/cm the driving forces get high enough to create this type of morphology in the given time of deposition (6 s). Further experiments revealed a dependence on the deposition time. If the deposition time was increased, this morphology could also be observed at lower electric field strengths below 180 V/cm (60 s–120 V/cm). This implies that the forming forces exist at any electric field strength, but it depends on their intensity and on the duration of impact, if grooves develop.

At higher electric field strengths (∼>500 V/cm) the grooves on the deposits vanished and hillocks appeared. It is assumed, that this morphology is a consequence in a change of the convective forces in front of the substrate. These convective forces are at least strong enough to suppress the significant appearance of grooves. Figures 7 and 8 show two examples from two depositions from EtOH at 630 and 817 V/cm. The deposited layers are dense and exhibit no cracks.

Conclusion

The influence of the electric field strength on the kinetics and the surface morphology of electrophoretically deposited silver layers was investigated. Silver powder (200 g Ag/L) was suspended in EtOH and MEK with PDADAMAC as electrostatic stabilizer, leading to positive surface charge in EtOH and to negative surface charge in MEK. The electric field strength was varied in the range of 50–360 V/cm (deposition time: 6 s) and resulted in deposit weights below 60 mg/cm^2. The kinetics of the deposition was comparable for both suspensions. The deposit weights revealed a linear raise with the electric field strength and were explained with Hamaker's law. Below 180 V/cm smooth, plane deposit surfaces were obtained. At higher electric field strengths grooves were observed in both systems with a deposition time of 6 s. It is assumed that these grooves refer to the electric field strength and are a mapping of electric field lines in combination with convectional forces. After longer deposition times grooves were also observed below 180 V/cm. At field strength exceeding 500 V/cm this type of morphology vanished and was replaced by irregularly distributed hillocks.

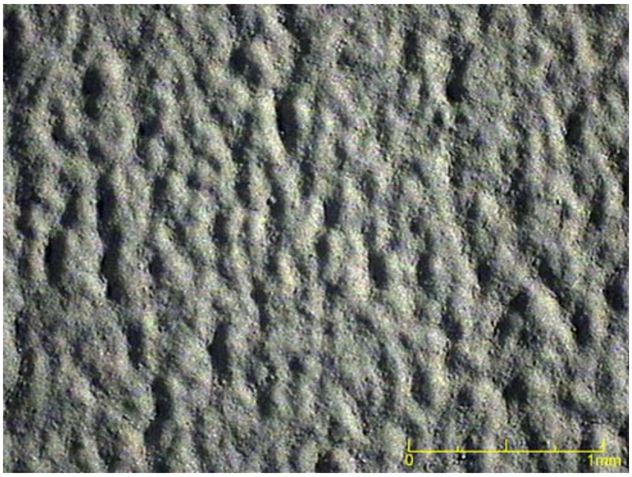

Fig. 7 Deposit of silver particles from EtOH at 630 V, 6 s, and 1 cm distance

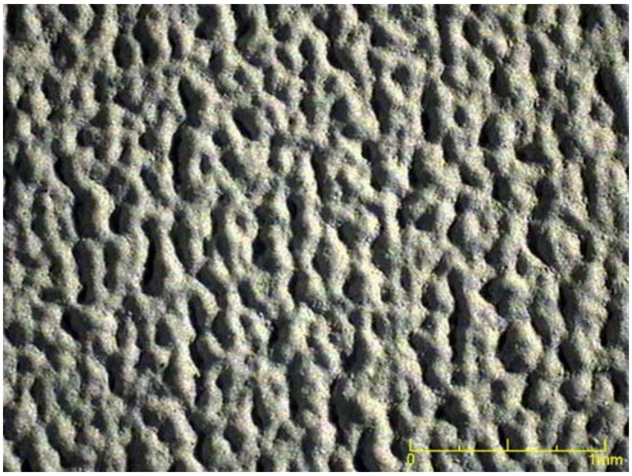

Fig. 8 Deposit of silver particles from EtOH at 817 V, 6 s, and 1 cm distance

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