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Engineering performance in applied EPD: problems and solutions

Martin Zarbov · David Brandon · Nissim Cohen · Liat Shemesh

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Abstract Providing the particle size, shape and size distribution are suitable, appropriate dispersion media and surface-active additives can usually be found for the electrophoretic deposition (EPD) of powder with any chemical composition. The design of the EPD cell is largely dictated by the geometry of the final product and the required dimensional tolerances. The integrity of the microstructure and freedom of the product from process defects commonly depend on the deposition parameters and the dispersion chemistry.

Demonstrations of laboratory feasibility for EPD products may prove straightforward, but developing an EPD process technology that is suitable for mass production can be far more challenging. This contribution reports four examples:

1. The deposition of silver thermal sinks in low-temperature, co-fired ceramic (LTCC) tape vias.
2. The formation and printing of silver-base alloy lines for conducting interconnects.
3. The embedding of passive ceramic components in punched ceramic tape.
4. The production of porous conducting anodes for solid electrolyte capacitors.

In each case, the process parameters have been selected to satisfy the engineering requirements while minimizing the formation of process defects. Observed defects include variations in the particle packing density; loss of adhesion to the substrate, cracking of the deposit and surface roughness or thickness variations.

Introduction

Electrophoresis has been known for a very long time, since 1809, according to Zhitomirsky [1], but even earlier according to some other authors. However, attempts to develop electrophoretic deposition (EPD) as a viable production process have not proved very successful. Randall and Van Tassel [2] have condensed the essence of the process and its potential applications into a succinct and readable encyclopedia article, while a more exhaustive treatment of EPD in the treatise on colloid science by Hunter [3] covers most of the scientific background. Neither text includes significant advances made in the new millennium, for example [4–13], but these more recent scientific contributions demonstrate a renewed interest in EPD, rather than any new paradigm.

This revival of interest followed the publication of an extensive review by Sarkar and Nicholson in 1996 [4] that seems to have stimulated much of the subsequent work on potential applications. Applications outside the field of microelectronics include the work of Van der Biest and his coworkers at Leuven, for example [6], and that of Boccaccini and his coworkers at Imperial college, for example [9]. Of more direct relevance to the present contribution, Randall, Van Tassel and their coworkers at PSU [10–13] have demonstrated that EPD could be a viable process

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M. Zarbov · D. Brandon · N. Cohen · L. Shemesh
Cerel—Ceramic Technologies Ltd., POB 2005,
Tirat Ha'Carmel 39120, Israel

D. Brandon (✉)
Faculty of Materials Engineering, Technion—Israel
Institute of Technology, Haifa 32000, Israel
e-mail: brandon@tx.technion.ac.ill

route in the production of small fuel cells and microelectronic circuit components, and that EPD is possible for ferroelectric particles [13]. Electrophoretic deposition would seem to have significant advantages for several applications in microelectronics. The ability of EPD to follow complex substrate geometries, yielding defect-free deposits in the sub-micron to millimeter range is especially attractive.

Scientific background

Reliable electrophoretic deposition is only possible if the mobility of the particles held in suspension due to an applied electric field exceeds the rate of sedimentation due to gravity. The electrophoretic drift velocity is given by [3]:

$$v_{\mathrm{EPD}} = E\mu = \frac{2E\varepsilon\xi}{3\eta}[1 + f(kr)] \tag{1}$$

where E is the electric field strength, μ is the mobility, ε is the dielectric constant, ξ is the zeta potential, η is the viscosity and κ is the Debye constant. The correction factor *f(kr)* indicates that the mobility is only weakly dependent on the effective particle radius r. The sedimentation rate is given by

$$v_{\mathrm{G}} = \frac{m^{*}g}{6\pi r\eta} \tag{2}$$

where m^{*} is the effective mass of the particle, g is the gravitational constant and r is an average particle radius. The critical parameter for successful EPD is the ratio of these two drift velocities:

$$\left(\frac{v_{\mathrm{EPD}}}{v_{\mathrm{G}}}\right) \approx \frac{4\pi rE\varepsilon\xi}{m^{*}g} = \frac{3E\varepsilon\xi}{r^{2}\rho^{*}g} \tag{3}$$

where ρ^{*} is the effective density (the particle density corrected for the density of the dispersion medium). From equation (3), it is clear that EPD should have distinct advantages over both slip casting and cold pressing in any powder production technology for small components that is based on sub-micron or nanoparticle dispersions, always providing that the dielectric constant of the dispersion medium is sufficient and that sufficient control of the zeta potential is possible. In practice, it has proved possible to adapt EPD to the deposition of particles of widely different shapes and chemical compositions, although the size distribution of the particles must be controlled and the average particle size cannot exceed a few micrometers (dependent on the particle density).

Good control of the green density in an EPD product depends sensitively on the particle shape and particle size distribution (PSD), which can be modified by centrifugal or gravity separation, or by an attrition milling process. Figure 1 compares the PSD for an as-received capacitor anode powder with that obtained after a simple, controlled sedimentation treatment (to eliminate over-size agglomerates) and that resulting after a further, high-shear, micro-fluidizing treatment that yielded a much larger fraction of primary particles and a much narrower distribution of primary particle aggregates.

Most EPD products require a sintering heat treatment, and this post-EPD sintering also demands careful analysis. The growth of inter-particle contacts and the development of grain or phase boundary facets occur rapidly during the first stage of sintering. Shrinkage, on the other hand, is delayed, since it requires diffusion over distances comparable to the separation of the points of contact on the particle surface.

At the onset of sintering the shrinkage rate is zero while the rate of contact growth approaches infinity (and is driven by the nominally infinite curvature at a

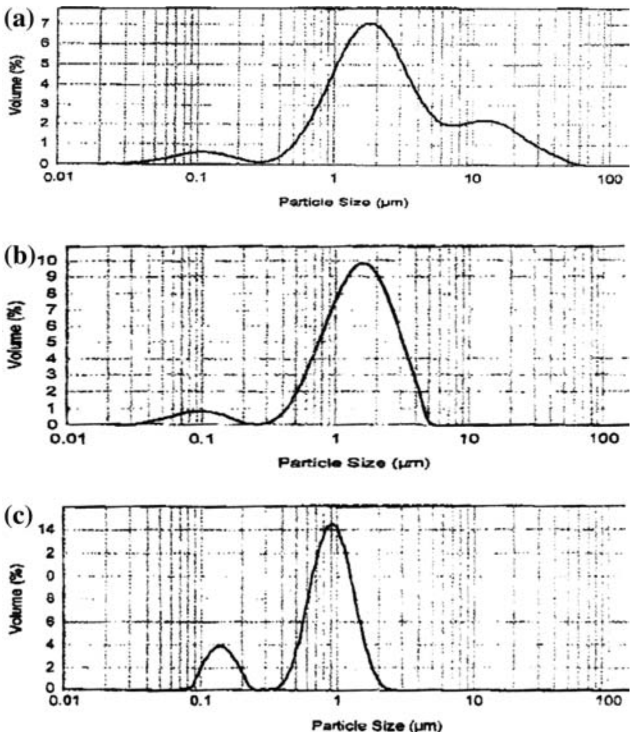

Fig. 1 Modifying the morphology and particle size distribution of a capacitor anode powder: (**a**) As-received powder. (**b**) After removal of coarse agglomerates by sedimentation. (**c**) Increased fraction of primary particles and improved size distribution of agglomerates after micro-fluidizing

point contact). Boundary curvature at contacts destabilizes smaller particles [14, 15], while multiple contacts reduce the shrinkage initiation time and introduce additional torque terms that lead to particle rotation during sintering.

The best powder for a specific application is rarely monodisperse and acceptable powder morphologies vary dramatically. In many cases, the PSD is polymodal, as in Fig. 1, and consists of small assemblies and aggregates. Powders may also contain foreign inclusions, and they may be poly-phase. Some of these features are illustrated in Fig. 2. In developing an EPD process, a narrow size distribution may be an advantage, as in metal interconnects, while an EPD porous anode in a solid electrolyte capacitor may require primary particle aggregates having a very irregular surface topography.

The design of the EPD cell also needs to be optimized. Figure 3a is a 2D simulation showing the beneficial effect of a plastic insert with a low dielectric constant on the cell equipotentials during vertical electrophoretic deposition. In this simulation, the counter-electrode is a vertical coaxial cylinder, while the deposition electrode is horizontal. The plastic insert constrains the equipotentials lines to be nearly horizontal in the region of the deposition electrode. Figure 3b shows a laboratory cell for vertical deposition of patterned silver interconnects on a silicon wafer. By contrast, Fig. 3c is a prototype EPD unit for the batch production of 300 porous anodes using horizontal deposition.

Examples of EPD applications in micro-electronics

Each of the examples that have been selected has resulted in a demonstration of technological feasibility. These prototype products serve to illustrate the flexibility and versatility of the EPD technology in production processing for the microelectronics industry.

Silver thermal sinks in LTCC punched tape

Selection of the metallic silver powder proved to be a key factor in successful electrophoretic deposition for the first two applications. The objective was to apply the EPD process to the commercial production of silver thermal-via heat sinks, to control the heat flux in microelectronic-components.

A major technical problem was that suspensions of commercially available silver powders tend to aggregate, and the aggregation is enhanced by the presence

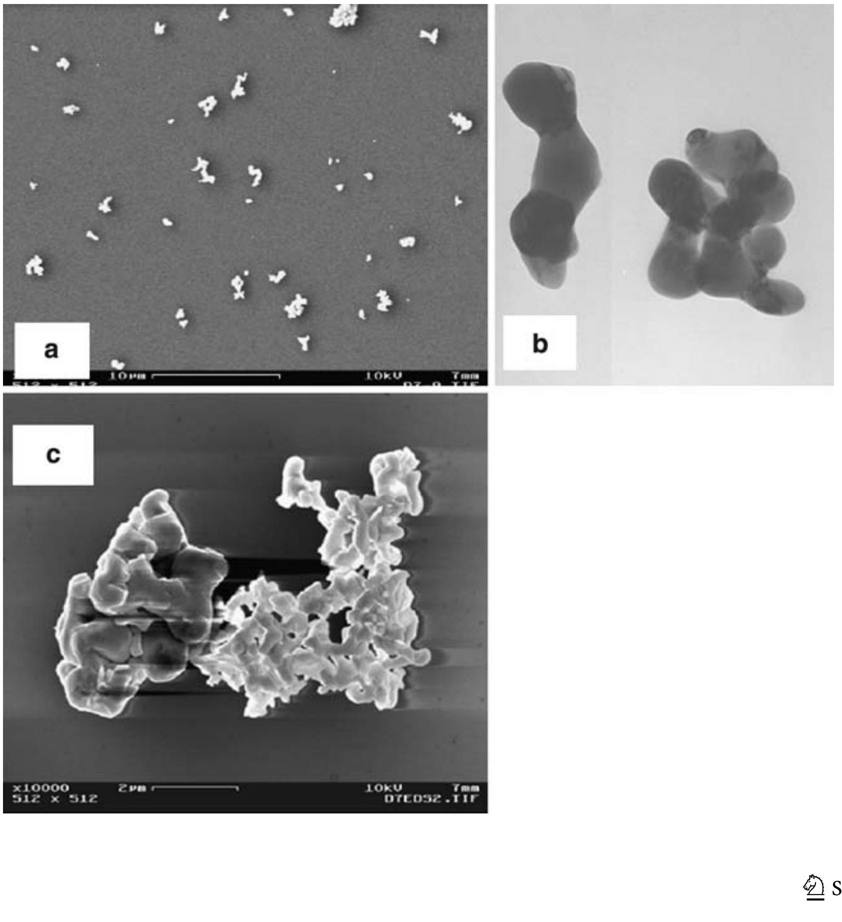

Fig. 2 Observed powder morphologies in an as-received capacitor anode powder: (**a**) Primary particles and small aggregates. (**b**) Aggregate morphology. (**c**) A large, complex aggregate and (left) an impurity particle

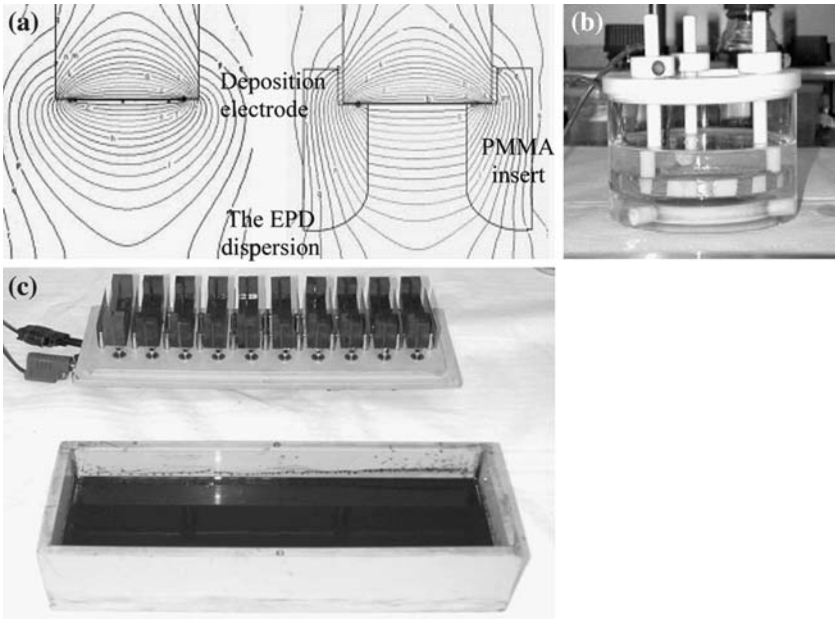

Fig. 3 Design of EPD cells: (**a**) 2-D simulation of equipotentials in a cell using a horizontal deposition electrode with a vertical counter-electrode. On the right, a cylindrical, low dielectric constant, plastic insert helps to smooth the equipotentials. (**b**) A cell for deposition against gravity of silver onto a horizontal, patterned silicon electrode. (**c**) An assembly of deposition electrodes and EPD bath (below), used for EPD of porous anodes in the prototype production of solid electrolyte capacitors

of an electric field. This can lead to sedimentation of a large fraction of the solids loading, and a low green density and rough surface finish for the electrophoretically deposited material. Poor adhesion of the deposit and breakaway from the substrate during sintering; crack formation within the deposited material, and a non-uniform deposit thickness are also common problems.

While nano-technology has developed rapidly in recent years, the availability of ‘‘nano-silver’’ is limited. In addition to particle size and shape, and particle size distribution, the selection of a dispersing medium and the selection of steric and electro-steric additives are no less important for successful silver deposition [16, 17].

Figure 4a–d show the particle shape of four different commercial silver powders with similar particle size. The oval morphology and narrow size distribution of the AgPd powder is quite different from the broad size distributions, aggregated nature and irregular shapes of the other powders. The tap density of the AgPd powder was also the highest of the four powders, suggesting that the green density of any deposit obtained with this powder should also be higher.

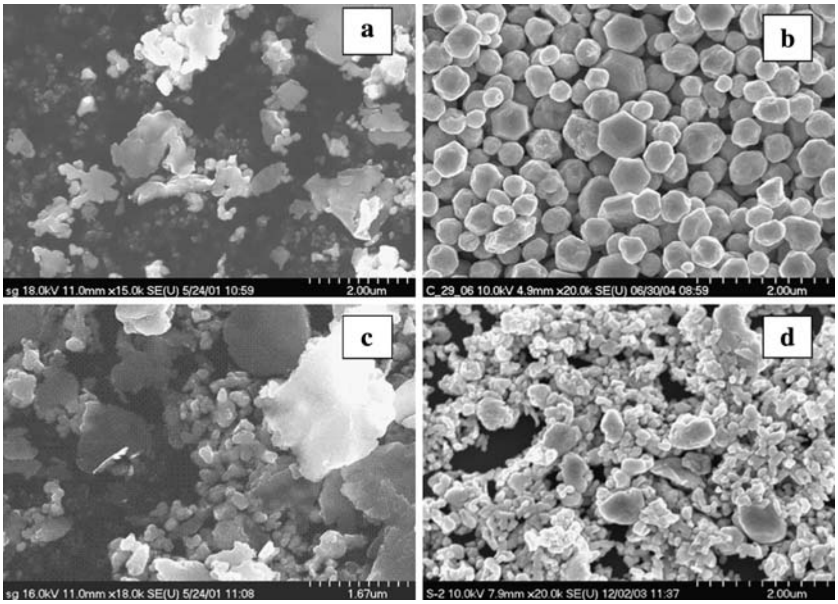

Fig. 4 Four grades of silver powder evaluated for their EPD suitability. (**a**) Ag Cima-nano-tech-440. (**b**) Ag Pd; Cermet 7102FG alloy powder (found to have the best performance). (**c**) Ag Heraues DC100. (**d**) Ag Ferro 11,000–04

Methods for improving the particle size distribution of the as-received AgPd powder (Table 1) that were investigated included: sonication, decantation, air milling and micro-fluidizing. The most effective method for reducing the average particle size and narrowing the size distribution was micro fluidizing; which also provided a high yield with minimal contamination. This commercially available treatment forces the dispersion through a micro-channel array that imposes rheological shear stresses that are high enough to fragment hard aggregates and fracture large particles.

Stable suspensions of the silver alloy powder were obtained in an appropriate dispersion medium (a single solvent or a combination of solvents). The preferred solution (a pure solvent of high dielectric constant and high viscosity) proved to be in conflict with another requirement for the EPD production of thermal vias. The specified LTCC tape proved to be partially soluble in the commonly used aqueous and organic solvents, but was unaffected by immersion in heptane. However, the very low dielectric constant and ionic conductivity of heptane makes it unsuitable for EPD (of silver or any other powder). Modifying heptane with ethanol additions to raise the dielectric constant to above 6, and the ionic conductivity to about 0.4 μS/cm made the electrophoretic deposition of silver possible, while the green LTCC tape was sensibly insoluble in this heptane/ethanol solvent mixture.

A further problem faced in the production of thermal vias using EPD was the loss of adhesion between the silver deposit and the via walls during sintering. However, the addition of a small percentage of a glass powder to the dispersion prevented loss of adhesion by matching the sintering profile of the silver deposit to that of the LTCC tape. Varying proportions of glass powders having acceptable compositions were tested, and the best results were obtained with a commercially available composition, designated SCQ-3, in an addition of 3 vol%. Dilatometer curves, Fig. 5, showed that the sintering temperature was raised by 50 °C when 3 vol% of glass was present and provided a good match of the sintering profile of the silver powder to that of the LTCC tape. Figure 6 compares a glass-free, sintered silver via in LTCC tape (a), with the integrity of a via sintered with an addition of 3 vol% SCQ-3 to the AgPd powder (b). The glass additions were also found to improve the deposition weight and green density under the same EPD conditions, and had no deleterious effect on the thermal properties of the via.

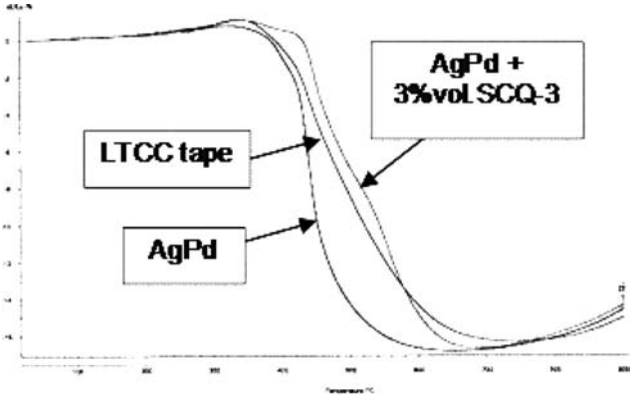

Fig. 5 Dilatometer curves for LTCC tape, AgPd powder deposit and AgPd deposited with a 3 vol% glass addition to help match the sintering profiles

Table 1. Some key properties of the silver alloy powder selected for EPD

Surface area [m2/g]		1.5
PSD [μm]	D10	0.39
	D50	0.70
	D90	1.53
Tap density [g/cc]		3.4

Silver conducting lines for electrical interconnects

Previous work at PSU [10, 13] has demonstrated transfer printing of an EPD silver-interconnect pattern formed on a suitable substrate. The commercial feasibility of this technology has now been explored. This includes the selection of a suitable powder, standardization of the dispersion preparation and composition, EPD onto a patterned silicon wafer, and repeated transfer printing of the silver pattern from the silicon wafer substrate onto a low-temperature co-fired ceramic (LTCC) tape.

A critical issue for successful EPD of silver and silver alloy powders in this application is the design of the EPD cell (Fig. 3a, b). For the deposition of silver interconnects a ‘‘smart’’ cathode has been used with an insulating photolithographic mask of silicon dioxide on a silicon wafer. Selective EPD has been achieved with good resolution and a line-pitch approaching 10 μm. Moreover, as previously reported by Randall and Van Tassel [13], it proved possible to transfer-print the interconnects onto LTCC tape (Fig. 7). The vertical mode of deposition was used (against gravity) to ensure higher green densities, a narrow size distribution for the deposited particles and less contamination of insulating areas.

The final issue to be addressed was the selection of charging agents to control the zeta potential for the dispersion for EPD of silver particles. The methodology

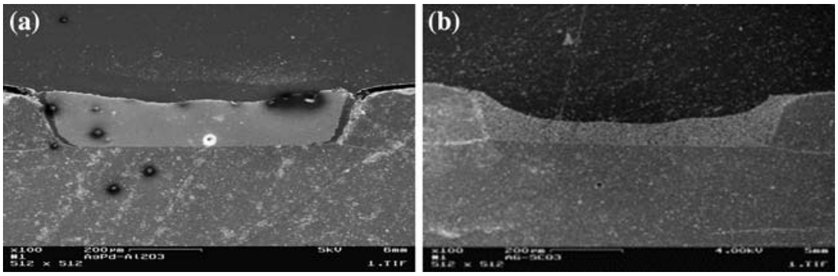

Fig. 6 AgPd embedded thermal vias in LTCC tape after sintering: (**a**) Without glass. (**b**) With 3 vol% glass added to the AgPd powder

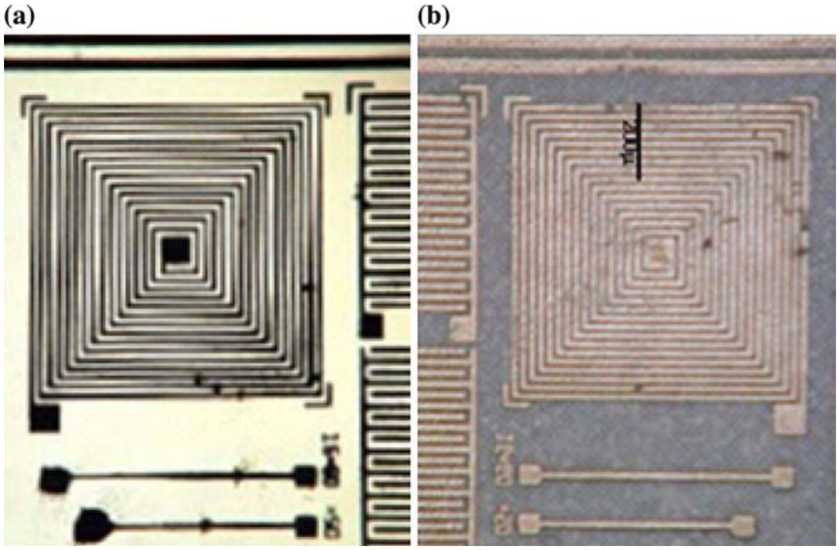

Fig. 7 A pattern of 16 μm EPD silver interconnects: (**a**) As-deposited on a silicon wafer. (**b**) Transfer-printed onto LTCC tape (unsintered)

for selection of the charging agents has been previously described [17]. A standard zeta potential curve for AgPd in 2-propanol was determined and the effect of different charging agents on this zeta potential was investigated. A working range of pH was chosen, based on the conductivity of the dispersion, for additives yielding a zeta potential higher than 30 mV. From the zeta potential curves it is also possible to determine an optimal combination of additives (Fig. 8).

Embedded passive components in LTCC

The challenge here was to reduce the space requirements of a micro-circuit by integrating the passive elements, such as capacitors or resistors, vertically into the multilayer package, placing the component in the vias normally used for conducting elements, The demonstration component was an X7R composition capacitor in a commercial LTCC tape. Three technical problems were to be overcome:

1. The tape had to be stable in the dispersion medium.
2. The multilayer green package had to be free of processing defects.
3. The capacitor element had to remain coherent with the via walls after the sintering cycle.

The first problem was solved by tailoring the dielectric constant of the dispersion medium, as described above for the thermal heat sinks. The second required careful control of the filling of the vias by the EPD process. The final problem was solved by modifying the sintering cycle of the X7R powder by using glass additions (compare the work on thermal vias, above). Figure 9 demonstrates the loss of adhesion of an unconstrained EPD capacitor element (a), and the morphology of an X7R capacitor of modified composition constrained by vertical integration into a sintered LTCC package.

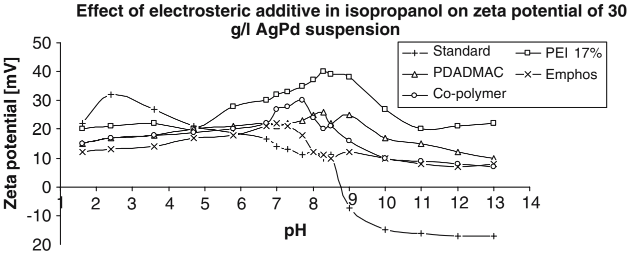

Fig. 8 The pH dependence of the zeta potential for an Ag–Pd alloy powder dispersion for different surface-active additives

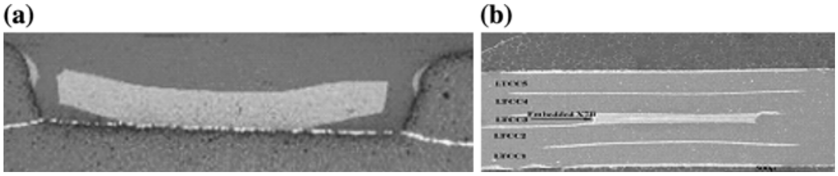

Fig. 9 (**a**) An unconstrained sintered capacitor element in a via and (**b**) a fully constrained sintered capacitor element obtained using EPD deposition of a glass-modified X7R composition

Porous anodes for electrolytic capacitors

Solid state electrolytic capacitors are manufactured in vast quantities and their performance has improved dramatically in recent years, primarily as a result of the optimization of the surface area to volume ratio of the porous anodes. The critical parameter is CV, where C is the expected capacitance for a unit weight of a given powder multiplied by the voltage V used to grow the anodic oxide dielectric film on the porous powder compact. An upper limit to CV of about 200KCV is set by the need to maintain the electrical conductivity of the partially sintered anode. The capacitors are characterized by measuring the direct current leakage (DCL) through the dielectric oxide and their impedance versus frequency response on a logarithmic scale. These curves yield the real and imaginary components of the dielectric constant as a function of frequency. The dissipation factor (DF) was measured at 120 Hz and the equivalent series resistance (ESR) at 100 kHz (the latter is a measure of the inductive losses in the capacitor interconnects).

Cold-pressed pellets of aggregated tantalum or niobium metal powders are currently preferred by the industry, but do not produce reliable capacitors with a total thickness less than 0.5 mm. Cerel has developed an EPD route for the batch production of low-profile (0.3 mm) capacitors. The anodes are deposited from a dispersion of a commercial powder and subsequently sintered before forming the dielectric layer, infiltrating the cathode material and applying insulating and connecting layers. A number of processing defects had to be eliminated in the process of development, most notably gross porosity associated with poor packing of oversize aggregates and wedge formation during deposition due to incipient instability of the dispersion. An array of green anode blanks, micrographs showing the morphology of the process defects and a view of the finished product are all shown in Fig. 10.

Discussion

Integrating EPD into a production process is far from trivial and requires a sound understanding and appreciation of the scientific limitations of the process, as well as a detailed, quantitative analysis of the technological problems and the development of a sound manufacturing methodology. None of the four example given above have yet established that EPD processing can lead to a commercially viable, marketable product that can meet the full range of engineering and economic requirements. The LTCC capacitors embedded by EPD have been shown to be technologically feasible but will require a great deal of additional development before the process can be judged sufficiently reproducible for serious consideration in production. The solid electrolytic EPD anode capacitors, on the other hand, have been put into pilot plant production but will need to find a large and profitable market. The thermal vias have also been found to

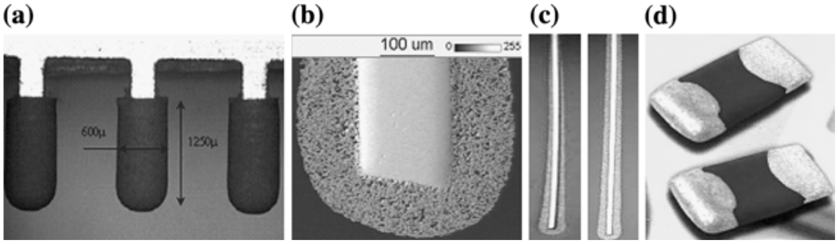

Fig. 10 The EPD route to production of solid electrolyte capacitors: (**a**) Green anode blanks after EPD. (**b**) Gross porosity in a transverse section of an anode blank. (**c**) Wedge formation in different dispersion media: ethanol (left) and iso-propanol (right), and (**d**) The prototype product

satisfy all the technical requirements, but adequate reproducibility and freedom from processing defects has yet to be demonstrated. Finally, the silver conducting interconnects have confirmed that there is no scientific barrier to the development of such patterned EPD products, but the process is still a long way from demonstrating true technological feasibility.

It has proved possible to resolve the technical problems that have made electrophoretic deposition of commercial powders for micro-electronic components a major challenge, but we have yet to solve many of the production problems associated with reproducibility of the product and freedom from process defects. That said, it still remains true that the EPD route is potentially capable of achieving an engineering performance that is beyond the range of current technologies.

Conclusions

1. Electrophoretic deposition (EPD) has the potential for improving the dimensional and engineering tolerances of many components in a micro-electronic circuit.
2. The technical problems to be solved include those associated with powder selection and pre-treatment, choice of dispersion media, selection of steric and electro-steric additives, design of the EPD cell and choice of EPD parameters and their control.
3. In addition, the requirements for the EPD substrate and post-EPD treatment of the product must also be considered.
4. Prototype products have been successfully prepared that satisfy all the engineering requirements:

a. Silver-based thermal vias in LTCC tape.
b. Silver alloy interconnects for transfer printing to LTCC tape.
c. Embedded passive components in LTCC tape.
d. Porous anodes for solid electrolytic capacitors.

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