Particulate dispersion and freeform fabrication of BaTiO$_3$ thick films via direct inkjet printing

Wenjea J. Tseng · S.-Y. Lin · Shin-Ru Wang

Abstract A piezoelectric drop-on-demand inkjet printer was used to print BaTiO$_3$-Ni functionally graded thick films onto porous substrates of computer-defined patterns without the need of prior mold tooling and the use of masks. The inkjet deposits were built up from a sequential delivery of ink droplets expelled from the print-head orifice with a precise location-registration capability upon multiple printings. A uniform dispersion of the particle-filled liquid inks was a prerequisite for a successful printing, and an addition of propylene glycol facilitated the nanoparticles dispersion in evaporative ethanol-isopropanol solvents. Typical line width of the inkjet-printed patterns was as narrow as 200 μm, and a maximum film thickness attainable exceeded 20 μm. A uniform concentration gradient of the dissimilar phases was evident along the thickness direction of the printed functional films.

Keywords Inkjet printing · BaTiO$_3$ · Nickel · Functionally graded materials

1 Introduction

A growing number of applications demands delivery of small quantities of functional materials with specific electrical, optical, biological or structural functionalities into well-defined locations on a substrate [1]. While the nature and properties of the substrate often dictate the selection of process involved, solution-based process becomes favorable when the substrate material is prone to high temperature or is not amenable to vacuum deposition techniques. Inkjet printing of particle-filled liquid, in particular, finds emerging applications that require creation and patterning of fine-scale structures with multi-functionalities in three dimensions [2–11]. The inkjet-printing method in which multiple small volumes of metallic, semiconducting, or insulating materials are deposited at computer-defined positions enables an all-additive fabrication of complex structure devices to be made in a layer-by-layer fashion with a much faster and less expensive basis. Inkjet fabrication of passive electronic components and high-frequency communication devices on low-temperature flexible substrates has been demonstrated recently with a comparable performance to that of conventional thick-film materials [3, 8]. One theme decisive for a consistent ink-droplet formation and positioning is the dispersion quality of functional particles in liquid-ink vehicle [10–12], typically with specially tailored chemistries and rheological properties of the ink that consists of combinations of functional nanoparticles, surface coatings, solvents, organic surfactants and binders. In this regard, particulate dispersion was examined in this study for functional dielectric BaTiO$_3$ and conductive Ni nanoparticles in ethanol-isopropanol solvent mixtures. We demonstrate the first known inkjet printing of BaTiO$_3$-Ni nanoparticles to build functionally graded thick films of different contours on porous substrates by this method.

2 Experimental procedure

Hydrothermally prepared BaTiO$_3$ nanoparticles (Titanex Corp., Taiwan) with an average particle size of 60 nm, and metallic nickel particles (Argonide Inc., U.S.A.) with purity >99% and an average particle size of 90 nm were used

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as the raw material. The nanoparticles were polycrystals, about spherical in shape, and were apparently agglomerated by scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan). Reagent-grade ethanol and isopropanol solvents (both from Sigma Chemicals, U.S.A.) were used as the liquid carrier without further purification. The solvent mixtures were prepared in a 1:1 ratio before addition of the BaTiO$_3$ and Ni nanoparticles to form particle-filled inks with volumetric solids concentrations (ϕ) ranging from 1 to 35 vol.%.

A polymeric surfactant was used to facilitate the particulate dispersion in the solvents. The commercially available, non-ionic surfactant (Hypermer KD-6, ICI Surfactant, U.K.) consists of propylene glycol as its major ingredient. The surfactant concentration was up to 5% of the solids weight. The powder mixtures were all ball-mixed in polyethylene bottles for a period of 24 h before their viscosity (η_s) being determined by a strain-controlled concentric viscometer (VT550, Gebruder HAAKE Gmbh, Germany) at room temperature. The floc size of the nanoparticles inks was carried out by a dynamic light-scattering technique (Zetasizer NS, Malvern Instruments, U.K.) using dilute inks with $\phi \sim 0.0005$. The dilute inks were prepared from particulate dispersions that were first centrifuged at a rotational speed of 10,000 rpm for 20 min. The supernatants were then carefully siphoned out by a glass pipette and then mixed with a small amount of the "original" ink dispersions without centrifuge separation to form uniform dispersions. An additional ultrasonic agitation (Sonicator 3000, Misonix, U.S.A.) was applied with amplitude of 600 Watts operated at 20 kHz prior the zeta measurement.

A desktop piezo-driven inkjet printer (Canon 1000SP, Japan) was used to deposit the nanoparticle inks on flexible, porous acetate sheets. A piezo-based drop-on-demand inkjet print-head allows for the use of solvents from a wide range of selection, and it also has precise controls over the droplet formation at the nozzle orifice consistently [5]. There are total of 64 nozzles in the given print head used. The nozzles are all circular in shape with diameter spans across 20 μm. The raster motion of the inkjet printing was at about 30 mm s^{-1} with the nozzle orifice about 1 mm above the acetate sheets. The BaTiO$_3$ and Ni nanoparticles inks with a volumetric particle loading of 1 vol.% were injected into separate ink reservoirs. Printing took place following the selection of desired contours from computer-graphic software and a maximum of about 100 layers of Ni base droplets were deposited, following then by additional 100 layers of BaTiO$_3$ overprints. The nozzle tips were cleaned periodically with ethanol-isopropanol solvents to avoid the nozzle tips dried and clogged. The elemental distribution of the cross-section of the BaTiO$_3$-Ni films was examined by an energy-dispersive spectrometer (Oxford Inca Energy 400, U.K.).

3 Results and discussion

3.1 Dispersion of nanoparticles inks

Inkjet printing involves deposition of material onto a substrate in the form of liquid. In order to use inkjet printing to build functional thick films, the simplest way is to disperse the required material as a fine powder suspended in a suitable liquid vehicle. The dispersion quality and accordingly the rheological property of the powdered ink are critically important in controlling the fluid behavior during both droplet formation and impingement on a substrate [13]. When a non-polar fluid is chosen as the liquid vehicle for powdered inkjet printing, polymeric surfactants are often used to facilitate the particle dispersion and hence reduce ink viscosity by the modification of interparticle surface forces in liquid in order to match the window of inkjet operability. In Fig. 1, the apparent viscosities appear to decrease pronouncedly as the non-ionic, polymeric surfactant was added in the BaTiO$_3$ nanoparticle inks. The viscosity reduction reaches ca. 95% as the surfactant concentration exceeds 4 wt.% when compared to that of the inks without the surfactant. In Fig. 2, an adsorption isotherm shows that the polymeric surfactant molecules adsorb preferentially on the BaTiO$_3$ surfaces in the ethanol-isopropanol solvents. The adsorption appears to reach a saturation plateau above $\sim$4.8 mg m^{-2}, which corresponds to 4 wt.% of the surfactant concentration. The adsorption behavior hence reveals that a steric-hindrance mechanism was operative in the liquid carrier to prohibit the nanoparticles from direct contact with one another due to Brownian motion. Nonetheless, the exact morphology and conformation of the adsorbed molecules remain unclear at present. It may be interesting to note that the floc size of the BaTiO$_3$ nanoparticles in the liquid solvents decreased with the increasing surfactant concentration, from 375 nm for the inks without
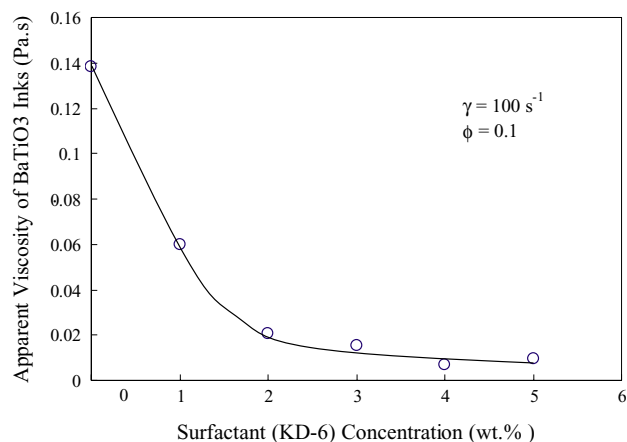

Fig. 1 The apparent ink viscosity (η_s) of BaTiO$_3$ nanoparticle inks at various surfactant (KD-6) concentrations
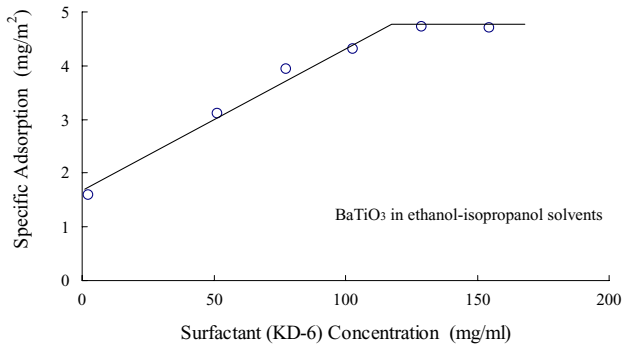
Fig. 2 The adsorption isotherm of surfactant-added BaTiO$_3$ nanoparticle inks
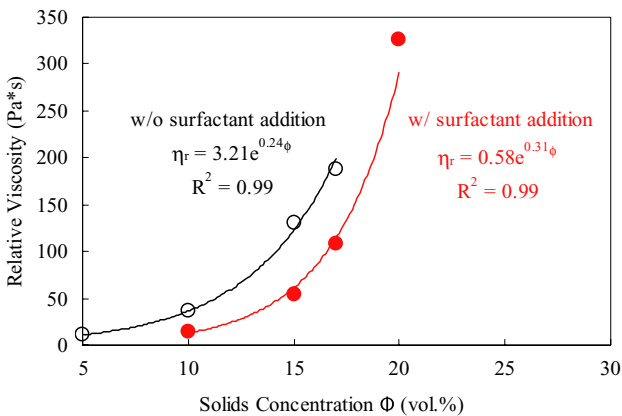

Fig. 3 Relative viscosity—solids fraction dependence as surfactant (KD-6) is introduced in the Ni nanoparticle inks

the surfactant to reach as low as 160 nm as the surfactant concentration exceeded above 4 wt.%. This finding vindicates the surfactant efficacy in particulate dispersion; yet, the BaTiO$_3$ nanoparticles were still flocculated (even though with a lesser degree of flocculation) with the surfactant presence in the carrier liquid. This unfortunately limits the choice of particulate inks to relatively dilute suspensions (typically <2% by volume).

Similar results were found when Ni nanoparticles were dispersed in ethanol and isopropanol mixtures with addition of the polymeric surfactant (KD-6). As shown in Fig. 3, relative viscosities of the inks increase exponentially with the solids concentration, and the Ni inks with the surfactant always result in a reduced viscosity. The same surfactant can be used in the nanoparticles inks of dissimilar compositions, thus avoiding possible interactions between surfactants of different chemistries.

3.2 Inkjet printing of BaTiO$_3$-Ni functionally graded thick films

Trial runs of inkjet printing were carried out on porous acetate sheets using the BaTiO$_3$ nanoparticle inks of 1 vol.% in
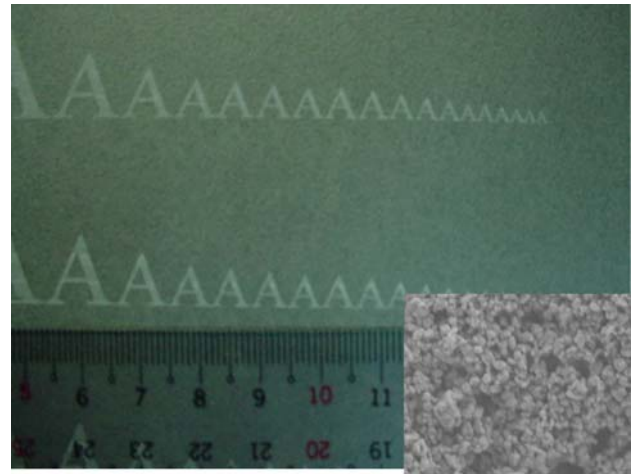

Fig. 4 Inkjet printed BaTiO$_3$ letter "A" of different sizes. The inset shows an SEM micrograph of the particle-packing structure
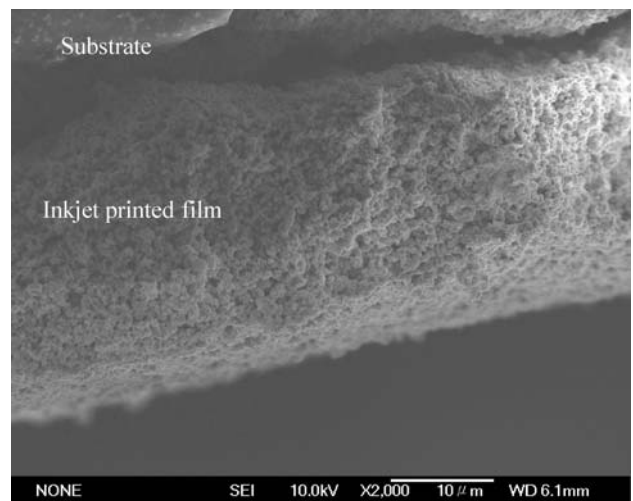

Fig. 5 A cross-sectional view of an inkjet printed BaTiO$_3$-Ni functionally graded film
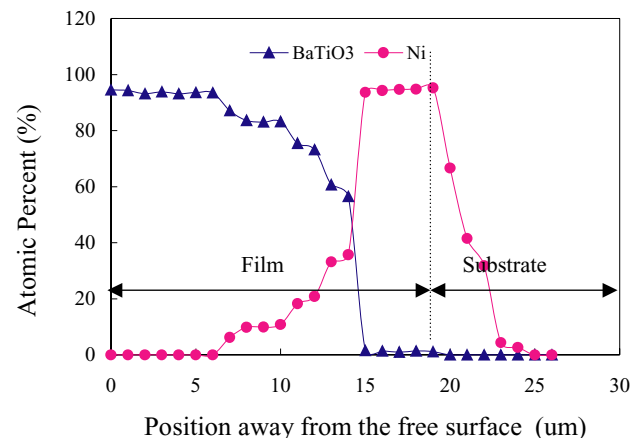

Fig. 6 Elemental distribution along the thickness direction of the functionally graded film

the inkjet reservoir. English letter "A" of different sizes was successfully printed by multiple printing of 10 runs (Fig. 4). The placement repeatability of individual drops was precise enough to give a gap between lines typically as low as 200 μm. A micrograph in the inset of Fig. 4 shows the porous particle-packing structure of the deposit. Thickness of the inkjet deposit increased with the printing cycle. By printing 100 layers of Ni base droplets followed then by additional 100 layers of BaTiO$_3$ overprints, a film thickness of about 20 μm was achievable (Fig. 5). A quantitative elemental analysis employing the ZAF technique reveals a uniformly distributed concentration gradient of the dissimilar phases along the thickness direction of the film (Fig. 6). The formation of functionally graded structure is a result of at least the following reasons. First, the ink droplet bombarded on the porous substrate was not dried completely before the next droplet impinge on the same position; second, the porous structure of the print deposit with a "channel" size greater than the primary particle size (see the inset of Fig. 4) allowed for the following-up droplet to infiltrate into the film interior to a certain extent.; additionally, the liquid droplet would favor to penetrate into the porous acetate paper by the capillary "wicking" force; finally, the multiple printing motion required the substrate repeatedly pass through rollers that lead the printing passage. This leading motion involves compressive forces in a direction about perpendicular to the substrate surface.

4 Conclusion

BaTiO$_3$-Ni functionally graded thick films were inkjet printed onto porous substrates with computer-defined patterns in a layer-by-layer manner without the need of prior mold tooling and the use of masks. A uniform dispersion of the particle-filled liquid inks is critically important for a successful printing, and an addition of surfactant consisting of propylene glycol facilitates the nanoparticles dispersion in evaporative ethanol-isopropanol solvents. The improved dispersion is a result of the preferential adsorption of the surfactant molecules on the particle surface. This provides a steric hindrance which prevents particles from direct contact with one another in the liquid. Typical line width of the inkjet-printed patterns was as narrow as 200 μm, and a maximum film thickness attainable exceeded 20 μm. A uniform concentration gradient of the dissimilar phases was evident along the thickness direction of the printed functional films.

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