CHARACTERIZING METAL NANOPARTICLE FILMS: A METHODOLOGY USING SURFACE MICROMACHINING BY DIRECT PRINTING

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ABSTRACT

We report a methodology for characterizing the mechanical properties of metal nanoparticle films based on microfabricated structures. Structures are mechanically characterized by beam deflection measurements and nanoindentation. Based on a 2-sphere sintering model, and the relationship between particle size and melting temperature, a relationship between the nanoparticle film's elastic modulus and film geometry has been determined to be $\frac{E}{E_0} = \left(1 - \left(\frac{L}{L_0}\right)^3\right)^{0.6982}$, where L/L_0 is the degree of particle fusion. This methodology was used to determine the property-process for silver nanoparticle films but should be transferrable to other nanoparticle films.

INTRODUCTION

Printing-based fabrication methods have emerged as a promising alternative to conventional lithographic processes in a number of applications. These methods are being exploited in display manufacturing [1], flexible electronics [2], and more recently MEMS [3,4]. Unlike applications in printed electronics, MEMS devices require comparatively thick layers, typically on the order of microns. In the micron-thickness regime, nanoparticle-based inks are the preferred means for material delivery, in large part due to the ability to deliver high solids content. However, as we previously reported in [3], sintered nanoparticle films possess unique morphology and hence different properties when compared to bulk material or materials deposited through evaporation or sputtering. In this new work, we report on a detailed study of the process-property relationship for nanoparticle-based films with an eye towards optimizing this material for MEMS applications. Our work will enable prediction of mechanical properties for this class of materials, and will provide guidance for optimization of sintering conditions towards a desired mechanical property. The specific results we will report include: i) detailed data which maps modulus versus process conditions and ii) a semi-empirical model explaining the data and enabling prediction of resultant properties.

PROCESS OVERVIEW

The fabrication process contains eight steps as summarized in Figure 1. An overview is provided here with details of the process in the following sections. We have previously reported using a printed PMMA sacrificial layer [3] but in this work we use a conventionally-deposited amorphous-silicon film for simplicity in the process while still maintaining chemical and thermal compatibility with the silver nanoparticle ink. The amorphous-silicon is deposited by PECVD and patterned by photolithography. Etching of the amorphous-silicon is achieved by XeF₂ dry-etching. The silver nanoparticle ink is jetted onto the sacrificial layer using our previously reported apparatus [3]. The nanoparticle ink is dried and subsequently sintered, forming a self-supporting film. The structures are laser-trimmed to remove edge effects, such as non-uniform thickness due to the

Figure 1. Digital Fabrication Silver Surface Micromachining Process Flow. Laser-trim is optional but results in better defined structures.

coffee-ring effect. The resulting structures are released by another XeF₂ dry-etch to complete the surface micromachining process. Figure 2 is an SEM image of a printed silver cantilever.

Figure 2. SEM image of surface micromachined cantilever. Dashed line highlights boundary of the cantilever beam.

MATERIALS

This process has three layers/materials: substrate, sacrificial layer, and structural layer. Glass was chosen as the substrate material for the process but the process should be compatible with other materials such as polymers, metals, and silicon.

The sacrificial layer was created by depositing amorphous-silicon by PECVD at 200°C. The amorphous-silicon thickness was 1.1µm, but other thicknesses are possible. Patterning of the sacrificial layer consists of ~1µm OCG 825-20CS photoresist etch-mask and five 60s cycles of XeF₂ to etch the amorphous-silicon. The photoresist etch-mask was stripped by cleaning the substrate in a 4:1 H₂SO₄:H₂O₂ solution for ten minutes.

The structural layer consists of a silver film created by depositing, drying, and sintering Cabot Corporation's CCI-300 silver-nanoparticle conductive ink. This ink contains 30-40nm-

diameter silver nanoparticles suspended in an ethylene glycol/ethanol solution. Films made from this ink become electrically conductive after a thermal sintering at temperatures greater than 100°C. The ink's viscosity was lowered by diluting 1:2 volumetrically with ethanol to make it more readily printable with thermal inkjet.

INKJET DEPOSITION

Prior to printing, the droplet diameter for the CCI-300 ink was characterized to improve fabrication reliability and film uniformity. The inkjet printer used a 50pL Thermal InkJet (TIJ) nozzle resulting in a spot diameter of 150µm. Deposition occurred in an air environment while the substrate was isothermally held at 50°C to assist in ink drying and prevent ink running. While the print head and ink reservoir were not heated, proximity to the substrate heated them to 38°C-40°C.

DRYING SILVER FILMS

Silver nanoparticle films were jetted onto the glass substrates and amorphous-silicon steps and then dried immediately after printing. Post-printing, samples are dull and have a purple tint due to the nanoparticles still suspended in ethylene glycol. Samples were considered dry when the ethylene glycol is completely removed by a combination of evaporation or pyrolysis. Upon removal of the ethylene glycol, the films become metallic and reflective. The samples were heated in air to 80°C at 3°C-min⁻¹, isothermally held overnight (12 hours) to ensure the films were completely dried, and then cooled to room temperature at 3°C-min⁻¹. Gradual heating/cooling the samples prevents crack formation by reducing the film's thermal shock. It has also been observed that the gradual heating/cooling improves film thickness uniformity [5]. It is likely that the total drying time could be reduced through process optimization, but this was not the focus of the current work.

LASER TRIMMING

A Resonetics laser milling tool was used to remove non-uniform thickness at the silver film's edges. A 150mW, 248nm laser pulse with 15% attenuation was used to ablate the silver film. The laser spot size and shape was a 100µm square. The laser trimming can be done either after drying or after sintering the nanoparticle film. No discernable differences in mechanical properties have been observed between the nanoparticle films that have been laser trimmed after drying and the films that have been laser trimmed after sintering.

SINTERING SILVER FILMS

After drying, the samples were sintered on a hotplate to fuse the nanoparticles. Two sintering parameters have been explored: peak sintering temperature and dwell time. For the peak sintering temperature, the samples were heated to the peak temperature of 125°C, 150°C, 250°C, and 350°C at 3°C-min⁻¹, isothermally held for 3 hours, and then ramped down to room temperature at 3°C-min⁻¹ in an air environment. To explore the dwell time, the samples were heated to 250°C at 3°C-min⁻¹, isothermally held for 0, 1, 3, and 6 hours, and cooled to room temperature at a maximum 3°C-min⁻¹ in an air environment.

RELEASING STRUCTURES

The final step is releasing the structures by removing the remaining amorphous-silicon. The structures were etched in ten 60s cycles of XeF₂. In a few cases, particularly if the silver structural layer was thinner than 1µm, stiction was observed;

however this stiction could be overcome by mechanical methods. An SEM of a released silver cantilever is shown in Figure 2.

RESULT AND CHARACTERIZATION

As a demonstration of the process, cantilevers of 500µm (length) and 50µm or 100µm (width) were fabricated. The thickness of the silver nanoparticle film was typically 2.8µm. The amorphous silicon was 1.1µm thick. The amorphous-silicon thickness was measured using optical profilometry prior to printing the silver nanoparticle ink. The silver film thickness was determined by contact profilometry of the anchor region after releasing the structures.

Using a Hysitron Triboindenter, two modes are used to determine the film's mechanical properties: beam-deflection and nanoindentation. During beam-deflection mode, known force-loads are applied to the cantilevers and the resulting mechanical deflections are measured. Repeating these measurements at pre-determined spacing between the deflection points, the third-order dependence on the cantilever's beam length is removed and the nanoparticle films' elastic moduli is calculated using the cantilever's width and thickness.

In nanoindentation mode, a diamond tip is used to indent the silver film. While the film mainly experiences plastic deformation, a portion of the indent is elastically deformed. By measuring the elastic rebound when unloading the diamond tip, the mechanical properties of the film can be determined. The nanoindentations are made on the cantilever anchors to avoid erroneous measurements caused by beam deflection. Depictions of both modes are summarized in Figure 3.

Figure 3. Characterization methods and elastic moduli from films sintered at 150°C for 3 hours. The elastic modulus is consistent between both methods of characterization. Error depicted in each characterization represents 1 standard deviation from characterizing 5 cantilevers and 49 indents, respectively.

Samples sintered while varying peak sintering temperature and dwell time respectively are summarized in Figure 4 and 5. There is a monotonic relationship between peak sintering temperature and the resulting elastic modulus. Dwell time when sintering at 250°C does not seem to significantly affect elastic modulus. The beam deflection calculations assume a clamped boundary condition at the anchor and a rectangular beam dimension where the width and thickness of the beam are uniform. Because the results from both measurement modes are

Figure 4. Modulus (beam deflection) vs. Sintering Temperature. Samples were sintered for 3 hours with ramp rate of $3^{\circ}\text{C}\cdot\text{min}^{-1}$. >3 cantilevers per test condition were characterized and error bars represent 1 standard deviation of the measurements. Moduli were also measured using nanoindentation and were consistent with beam deflection results. The grey solid line represents values predicted by sintering model.

consistent with each other, it is assumed the characterization methods can be used interchangeably.

ANALYSIS AND MODELING

Previous silver nanoparticle sintering models have suggested the film's densification corresponds to an increase in cross-sectional area, thus correlating to a monotonic increase in electrical conductivity [6]. Similarly, it can be inferred that an increase in cross-sectional area is proportional to the reduction of the void volume inside the film, which is consistent with SEM microscopy previously presented [3]. As suggested in previous reports, two sintering parameters dominate the process-property relationship of sintered metal nanoparticle films: sintering temperature and dwell time [6].

Sintering Temperature

Sintering models in powdered metallurgy suggest the relationship between elastic modulus and void volume is

$$\frac{E}{E_0} = \left(1 - \frac{p}{p_0}\right)^f \quad (1)$$

where E_0 is the elastic modulus of the bulk material, p is the pore concentration, p_0 is the initial pore concentration, and f is a parameter constant dependent on the grain morphology and pore geometry [7]. In this case, p is defined as the fractional void volume between the nanoparticles. As such, if the particles are initially packed in a simple cubic formation, $p_0 = 1 - \frac{\pi}{6} \approx 0.477$; similarly, if the particles are packed in a face-centered cubic arrangement, $p_0 = 1 - \frac{\pi}{3\sqrt{2}} \approx 0.260$. As mentioned in [3], it is believed that material and sintering process are directly related to the sintered nanoparticle film's nanostructure and therefore directly affects f . Using the standard 2-sphere sintering representation [6,8] and particle melting temperatures, a correlation between the distance between the sphere centers L and melting temperatures can be established. Using equations relating particle size to melting temperature as reported by Buffat *et al.* [9], it can be assumed that:

$$\frac{L}{L_0} = 1 - \alpha_1 r_l(T) \quad (2)$$

where $r_l(T)$ is the fractional thickness of the liquid shell surrounding the metal nanoparticle at temperature T , L is the distance between the particle centers, L_0 is the original distance between the two particle centers, and α_1 is an empirically-derived constant to account for deviations in particle boundaries

Figure 5. Modulus (nanoindentation) vs. Sintering Time. Samples were sintered at 250°C with ramp rate of $3^{\circ}\text{C}\cdot\text{min}^{-1}$. Dashed line represents average modulus of all samples. 49 indentations per test condition were performed and error bars represent 1 standard deviation. Unlike sintering temperature, sintering time does not significantly affect modulus at the time scale investigated.

caused by conservation of volume. Because pores can be seen as void volume between the spherical nanoparticles, we assume that L and p are proportional:

$$\frac{p}{p_0} \propto \left(\frac{L}{L_0}\right)^3 \quad (3)$$

By substituting (2) and (3) into (1), we obtain

$$\frac{E}{E_0} = \left(1 - \left(1 - \alpha_2 r_l(T)\right)^3\right)^f \quad (4)$$

where α_2 incorporates both α_1 and the proportional constant between p/p_0 and L/L_0 . Fitting the data obtained from varying the peak sintering temperature, α_2 and f have been determined to be 1.76 and 0.6982, respectively. The elastic moduli calculated using this sintering model is represented by the grey solid line in Figure 4.

Time Dependence of Sintering

As shown in Figure 5, no significant relationship between dwell time and resulting elastic modulus has been determined. It is hypothesized that the slow heating and cooling rates used to prevent thermal shock in the silver nanoparticle films causes a quasi-static state in which the film will no longer densify until the sintering temperature increases. As such, it is assumed that the process to date is time-insensitive and dwell time is not a factor in the process-property relationship. This could potentially be different at lower sintering temperatures where silver self-diffusivity is considerably lower [10].

CONCLUSIONS

In summary, we presented a methodology to characterize the process-property relationship for silver nanoparticles. Printed cantilevers were fabricated while exploring peak sintering temperature and dwell time. Using a 2-sphere representation, we hypothesize the silver nanoparticle films exhibit a nanostructure-elastic modulus relationship of

$$\frac{E}{E_0} = \left(1 - \left(\frac{L}{L_0}\right)^3\right)^{0.6982} \quad (5)$$

Furthermore we established that peak sintering temperature significantly affects the film's nanostructure and that they have a relationship of

$$\frac{L}{L_0} = 1 - 1.76 r_l(T) \quad (6)$$

Combining equations 5 and 6, we have established a model explaining the monotonic relationship between peak sintering temperature the sintered nanoparticle film's resulting elastic

modulus. However, exploration of dwell times at 250°C showed no significant relationship between dwell time and elastic modulus, implying dwell time does not play a significant role in the current microfabrication process.

Additional studies will be conducted to further explore the process-property parameter space. One particularly promising investigation is to vary the environment during sintering because increasing partial pressures of oxygen have been shown to change the surface tension of molten silver [11] and thus could potentially affect the melting temperatures of silver nanoparticles. Another proposed study is to explore dwell time at lower sintering temperatures to determine whether the process-to-date remains time-insensitive as silver self-diffusivity decreases. Other studies in consideration include characterizing films made from larger/smaller silver nanoparticles and nanoparticles made out of alternative metals such as gold to validate whether the methodology is transferrable to other metal nanoparticle inks.

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