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Thermal sintering of solution-deposited nanoparticle silver ink films characterized by spectroscopic ellipsometry

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Low-temperature sintering of metal nanoparticle inks is a promising technique in realizing large area and flexible electronics. It is demonstrated in this letter that spectroscopic ellipsometry in the spectral region of 0.75–3.5 eV can be employed to characterize the sintering process manifested by the evolution of film thickness, effective dielectric function, and percolation transition. A two-oscillator model can be used to model the effective dielectric function. The oscillator energy shifts lower and correlates well with the increase in dc conductance as demonstrated by both in situ and ex situ ellipsometric measurements. A simple model based on two-dimensional R-L-C impedance network was adopted to explain experimental results quantitatively. © 2008 American Institute of Physics. [DOI: 10.1063/1.3043583]

Due to its compatibility with jet printing and low-temperature processing required by flexible substrates, nanoparticle (NP) metal inks present a promising candidate for large-area electronic applications. Generally, thermal sintering is required to achieve the ink’s transformation from non-conductive NPs into conductive film. Various devices have been demonstrated using this technique. Especially with the aid of laser, micron and submicron features can be defined. For these applications, it is important to determine the percolation threshold and the sintering conditions, i.e., temperature and time, over which the film transforms from insulator to conductor. Controlling the percolation level is also shown to be critical for avoiding cracking. In this letter, we show the feasibility of using visible-near IR (VIS-NIR) spectroscopic ellipsometry (SE) to probe percolation transition during sintering.

Film under percolation transition has been studied extensively including electroless deposition, evaporation, and plasma growth. It is generally accepted that these percolating systems involving metal growth can be studied by Bruggemann approximation (BA). So far no effort has been paid to study the percolation in NP film sintering. This process is interesting since it cannot be modeled by the BA model. As-deposited NP film consists of densely packed particles insulated by thin surface coating. In this film, metal concentration $P(\geq 0.5)$ is usually higher than the percolation threshold $P_c = 0.5$ (0.33) predicted by BA. Therefore BA is not applicable and numerical calculation is required, which will be demonstrated in this letter.

Silver NP with size of ~30 nm with organic surface coating was purchased from Sumitomo, Inc. Ethanol based NP suspension was then spin coated on a glass slide. Half of the slide’s back surface was roughened to eliminate back reflection during ellipsometric measurement. The other half was left clear to facilitate normal transmission measurement, as illustrated in Fig. 1(d) (inset). Thermal sintering was performed in argon ambient on a hot plate at temperature of 250 °C. Samples with different sintering times were prepared for characterizations.

Optical properties of NP films were characterized by spectroscopic ellipsometry (Spectroscopic Ellipsometry, Woollam Co.). The measured spectra range is from 0.75 to 3.5 eV. The ellipsometric angle ($\psi$) and phase difference ($\Delta$) were recorded at an incidence angle of 75° and normal incident transmission was also measured. By this way, refractive index and thickness can be uniquely determined and direct fitting of $n$, $k$, and thickness is possible. Two methods of fitting were employed. First, the refractive index $n$, $k$, and film thickness were declared as direct fitting parameters. Second, a two-oscillator model was used to model dielectric function

FIG. 1. (Color online) Experimental (solid curves), two-oscillator model fitted (C), and direct fitted (O) ellipsometric data ($\psi, \Delta$) for as-deposited NP film (a) and film sintered for 18 min (b). Normal incident transmission of as-deposited NP film (c) and film sintered for 18 min (d). The inset shows the measurement configuration.
FIG. 2. (Color online) (a) The evolutions of oscillator energy \( i \), the thickness \( ii \), dc conductance \( iii \), and grain size \( iv \) as a function of time. (b) Spectra of dielectric functions \( \varepsilon_1 \) and \( \varepsilon_2 \) for NP films: (□) as deposited, (△) sintered for 4 min, (○) sintered for 15 min, and (+) sintered for 18 min. (c) The AFM images of NP films.

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\varepsilon(E) = \varepsilon_\infty + \frac{A_1}{E_i^2 - E^2 - i\Gamma_1 E} + \frac{A_2}{E_f^2 - E^2 - i\Gamma_2 E},
\]

where \( \varepsilon_\infty \) is the dielectric function at large photon energies, \( \Gamma_1 \) is the broadening, \( A_1 \) is the oscillator energy, and \( E \) is the photon energy, all in units of eV. A two-layer model consisting of substrate and NP layer has been used to represent the sample.

Figure 1 shows the experimental (solid curves) and fitted (symbols) spectroscopic spectra of \( \phi \) and \( \Delta \) as well as transmission. For as-deposited film, a single Lorentz oscillator is sufficient to reproduce experimental and directly fitted results [Figs. 1(a) and 1(c)]. On the other hand, for sintered films two oscillators are required [Figs. 1(b) and 1(d)]. The positions of the two oscillators, labeled as A and B, can be identified in the extracted dielectric function [Fig. 2(b)]. As-deposited film exhibits a Lorentz oscillator A centered at \( \sim 2.2 \) eV. The Lorentz shape A undergoes broadening, reduction in amplitude, and redshift, while the other oscillator B appears in the NIR range upon thermal sintering. The positions of A and B were summarized and plotted in Fig. 2(a)(i). The evolutions of thickness obtained from both direct fitting and two-oscillator model are plotted along with atomic force microscopy (AFM) measured values [Fig. 2(a)(iii)] and reasonable agreement was found. This validates the use of the empirical two-oscillator model to quantify film transition.

A semiconductor analyzer (4155A, Agilent) with two probes separated by 2 mm was used to measure the dc conductance of each sample. The measured dc conductance of the sample sintered for 22.5 min was used to normalize the values measured for other samples. The evolution of the conductance is plotted in Fig. 2(a)(iii). The dc conductance increases abruptly (indicating percolation) at \( \sim 17 \) min. The conductance variation correlates well with the behavior of oscillator B, namely, the normalized conductance reaches the neighborhood of 0.1 when B moves close to zero (\( <0.25 \) eV). The AFM images taken for each sample clearly show the growth of NP size as a result of thermal sintering [Fig. 2(c)].

To furthermore examine the correlation between optical and electrical signals, \( in situ \) measurements were performed.

The NP solution was spun on SiO\(_2\)/Si wafer where Au electrodes with gaps of \( L=6 \) and 20 \( \mu \text{m} \) were lithographically patterned. The two-oscillator model was used to fit the ellipsometric data (without transmission). The oscillator energy and normalized conductance were plotted in Fig. 3. For the smaller \( L=6 \) \( \mu \text{m} \) gap, the system percolates when B \( \sim 0.8 \) eV, while for larger system with the \( L=20 \) \( \mu \text{m} \) gap, the percolation requires lower energy of B.

To explain the observed experimental facts, quasistatic dc and ac calculations based on the network of 2D R-L-C (resistance, inductance, and capacitance) were carried out. In the quasistatic limit, the Maxwell equation for electric field is reduced to the current conservation law \( \nabla \cdot j = 0 \), where \( j \) is the local current. This equation can be discretized on a 2D square lattice so that the NP film can be represented via metallic and dielectric bonds connecting the lattice sites [Fig. 4(b), left inset]. Thus, each NP consists of 24 metal bonds forming a square surrounded by dielectric bonds [Fig. 4(b), right inset]. The NP sintering processes are modeled by randomly replacing dielectric bonds with metal bonds [Fig. 4(b)]. The percentage of dielectric bonds being replaced (filling percentage) indicates the level of sintering. Drude’s formula is used for metal permittivity \( \varepsilon_{\text{dr}}(\omega) = \varepsilon_b - (\omega_p/\omega)^2/(1 + i\omega_p/\omega) \), where \( \varepsilon_b \) is the contribution due to the interband transitions, \( \omega_p \) is the plasma frequency, and \( \omega_L \) is the relaxation rate. For silver, \( \varepsilon_b=5.0, \omega_p=9.1 \) eV, and

FIG. 3. (Color online) \( in situ \) ellipsometric (evolution of oscillator energies A and B vs time) and dc measurement (evolution of conductance for electrode gap of 6 and 20 \( \mu \text{m} \) vs time) results. Note that the indicated time includes the cool-down to room temperature for the ellipsometric measurement.
$\omega_c = 0.021$ eV. For dielectric layers, $\varepsilon_d = 2.25$. The discretized equations were solved numerically using block elimination method.\textsuperscript{12}

Predicted imaginary part of the effective dielectric function $\varepsilon_2$ for an array of $38 \times 38$ NPs with different filling percentages is presented in Fig. 4. Due to the sintering between neighboring NPs, a wide distribution of larger cluster size appears in the film, which gives rise to a collection of plasmon resonances from 0.7 to 2.0 eV [Fig. 4(a)]. Note that $\varepsilon$ in this range can effectively be approximated by single Lorentzian line shape. The line shape peak B moves toward lower energy as the filling increases consistent with the experimental trend. The amplitude of peak A in Fig. 4(b) due to the plasmon resonance of original NPs reduces substantially with filling percentage rises per the experimental observation. It is therefore educed that the empirical two-oscillator model applied originates physically from these two peaks A and B just described.

Finally, the correlation between the position of B and dc conductance was evaluated numerically. The dc conductance was calculated for an array of $75 \times 75$ NPs and an array of $83 \times 83$ NPs, respectively, with filling percentage of 15%. With this filling percentage peak B is located at $\sim 0.8$ eV [0.78 eV, Fig. 4(a)]. dc calculation reveals that $75 \times 75$ array percolates but not the $83 \times 83$ array. This implies that the longest cluster size in the film will be $\sim 80 \times \text{NP size}$. Let NP size be 40 nm, $80 \times \text{NP size} = 3.2$ $\mu$m, which is close to experimental observation that when B $\sim 0.8$ eV, transition occurs with a characteristic size of $L = 6$ $\mu$m.

In conclusion, the sintering of silver NP ink films has been characterized by visible-NIR SE. The parametrization of dielectric functions using a two-oscillator model provides direct connection between optical and dc electrical properties. The percolation in various sample sizes, e.g., from microns to millimeters, can be identified readily from SE measurements.

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\textsuperscript{11}A Short Course in Ellipsometry, J. A. Woollam Co., Inc.