

Low Temperature Sintering Nanoparticle Inks for Printed Electronic Devices

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The organic and printed electronics bares a great potential to become an industry of \$300B in next 20 years. While more and more companies and research institutes around the world are joining into this industry for a large variety of exciting applications, however, there still lack of extraordinarily successful stores in product commercialization. At NanoMas Technologies, Inc., we have been keeping challenging ourselves to bring in more materials that would be better suitable for needs in the development and commercialization of high performance printed electronics on low cost substrates, such as paper and plastics. We have developed a variety of nanoparticle based inks with different electric functionalities. Those truly nano-sized materials (mostly less than 5 nm) have low sintering temperatures, and thus can be processed on most widely used plastic substrates. In this presentation, we also demonstrated using printing technologies to fabricate various patterns as well as OTFTs using conjugated polymers and nanomaterials. Sintering behaviors from metal nanoparticles to conductive metallic films have been further investigated. In addition, we have tested the stretching of printed silver nanoparticle films on PET, and found the films electrically conductive up to 120% elongation.

Introduction

Printable electronics manufactured using roll-to-roll processes will offer the unique opportunities for mass production of large format and inexpensive flexible electronics [1]. A popular choice of the printable conductor precursor is metal nanoparticles (MNPs), which could be printed to substrates from solutions and sintered to conductive films at low temperatures because of the size effect [2]. Particularly, silver nanoparticles (Ag-NPs) are considered by many the most important precursor candidate for printed conductors for the good balance of cost and performance [3]. On the other hand, gold-nanoparticles (Au-NPs) are desirable because Au has better chemical stability and high work function. There have been extensive R&D efforts in developing methods for mass production of high

quality Ag- and Au-NPs and exploring their applications in fabricating flexible devices [e.g., 3-6]. However, the understanding of the sintering process from precursor MNP to conductive metallic film is rather limited. In this paper, we report measurements in order to gain better understanding and better control of the MNP application to conductive film formation. This study is possible because high-quality and large quantities of uniform MNPs particles become available. By applying a range of characterization methods including spectroscopic, thermal, microscopic and scattering techniques, we illustrate details of structures and behaviors of MNPs in both solution suspensions and deposited films. We try to gain fundamental understandings of nanomaterials processing in device applications. The insights in the sintering mechanism would offer guidance in materials design and processing.

Conductive Metal Nanoparticles and Inks

High-quality metal nanoparticles are obtained from NanoMas Technologies, Inc, who has developed synthesis routines for large scale production of silver and gold MNP with ultra-small particle size (2 to 10 nm) and narrow distribution. MNPs are stabilized with a thin layer of surfactant molecules, which also render MNPs soluble in non-polar organic solvents such as cyclohexane or toluene. UV-visible absorption spectroscopy shows narrow absorption peaks centered at ca. 420 and 510 nm for Ag- and Au-NPs in dilute cyclohexane solutions, respectively. X-ray diffraction indicates that both MNPs have the same crystalline structures as the bulk metals. The size and uniformity of particles are examined using electron microscopy and small angle neutron scattering (SANS). Figure 1 shows a SEM micrograph of ca. 5 nm Ag-NPs (a), and a TEM

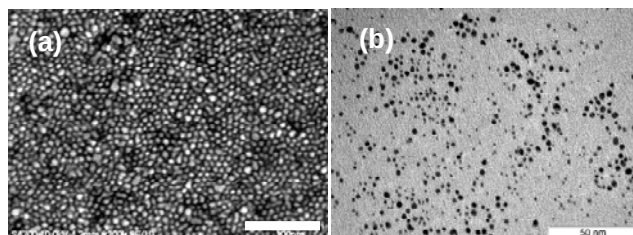


Fig. 1. (a) SEM micrograph of ca. 5 nm silver nanoparticles, and (b) TEM micrograph of ca. 4 nm gold nanoparticles.

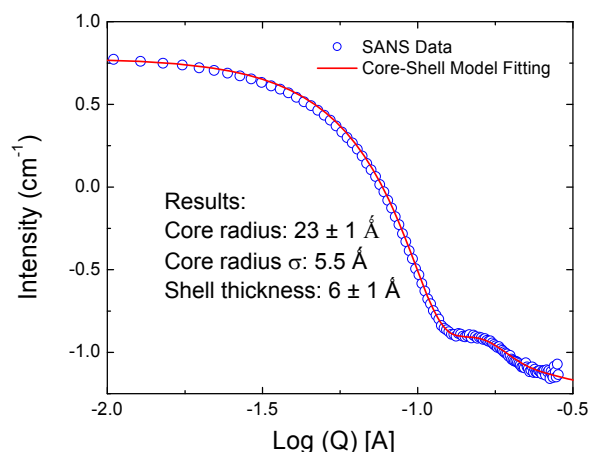


Fig. 2. Small angle neutron scattering of silver nanoparticles in deuterated toluene reveals an ensemble-averaged Ag core diameter of 4.6 nm with 20% dispersion, which is consistent with electron microscopy observation. The thickness of the organic shell is found to be ca. 0.6 nm in solutions.

micrograph of ca. 4 nm Au-NPs (b). SANS measurement of Ag-NP in toluene is shown in Fig. 2, in which the SANS data (open circles) are fitted with a core-shell model to give the average Ag-NP characteristics. The ensemble-averaged Ag-NP core diameter is found to be 4.6 ± 0.2 nm with a standard deviation dispersion of 1.1 nm, or $\pm 20\%$, which is consistent with electron microscopy observation. The thickness of the organic shell is found to be ca. 0.6 nm in solutions and 0.3 nm in the dried state. We emphasize the importance of characterizing bulk properties for achieving better performances in device applications.

Sintering of Nanoparticle Inks

Typical morphologies of sintered films are illustrated in Fig. 3. Sintered Ag-NP films usually are smooth with isolated holes, whereas sintered Au-NP films show long cracks. This could be understood since the volume reduction is larger in Au-NP films than in Ag-NP films. Thermal gravimetric analysis indicates that both Ag- and Au-NPs lose about 10% mass upon fully sintering. Since Au has higher density, the volume fraction of organics is higher in Au-NP films than in Ag-NP films. Upon sintering, larger volume shrinkage in Au-NP films causes higher tendency toward cracking than hole formation. For device application, crack morphology is not desirable since it would greatly deteriorate the electrical transport properties. A simple mending approach

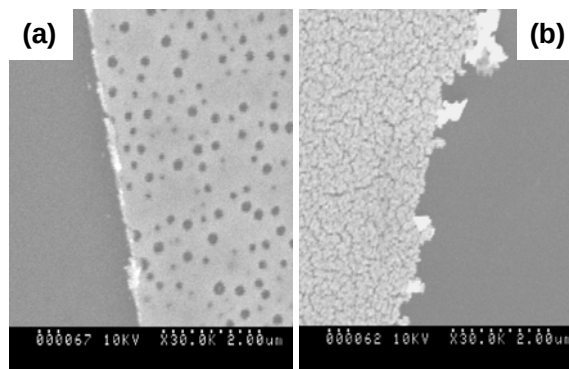


Fig. 3. SEM micrographs of (a) Ag-NP film after 5 min at 100 °C, and (b) Au-NP film after 6 min at 190 °C.

is printing multiple layers with sequential printing and sintering of each layer. Usually a second layer could improve the transport by 4 times to more than one order of magnitude. A challenging task is to control the volume shrinkage to occur normal to the film surface instead of in lateral directions.

Resistance

Electric resistance measurements on sintered Ag-NP films are shown in Fig. 4. The time dependent resistance data as shown in Fig. 7a could be compared to the corresponding residual H content data in Fig. 5a. The comparison indicates that resistance of sintered film is sensitive to both the residual organic content and the sintering temperature. However, films with similar organic content at 80 °C and 100 °C can differ in electric resistance for several orders of magnitude. This observation suggests that morphology of sintered films be critical in determining the transport properties. The morphology is in turn sensitive to particle characteristics and the thermal history.

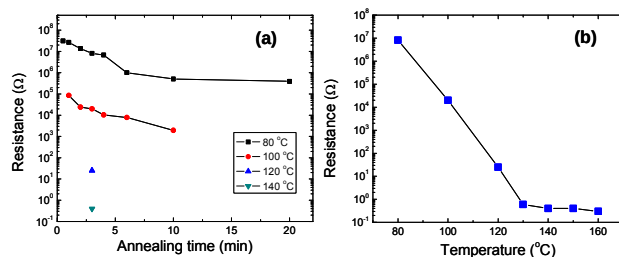


Fig. 4. The electrical resistance of Ag-NP films (a) sintered at various temperatures for various times, and (b) sintered at various temperatures for 3 min.

The effect of sintering temperature is illustrated in Fig. 4b for Ag-NP films after 3 min sintering at various temperatures. The reduction of organic materials is of one decade at low and high temperatures, whereas the resistance varies over more than 7 decades. Furthermore, both residual H and resistance measurements indicate the somewhat optimal processing temperatures, ca. 200 °C for Au-NPs and ca. 130 °C for Ag-NPs, respectively. The conductivity of Ag-NP films sintered at 150 °C was found to be $2.4 \times 10^{-8} \Omega\text{m}$.

Printed Nanoparticle Film Stretching

We have also studied the stretching and electrical behavior of the printed Ag nanoparticle films (Ag-NPFs) on PET with large elongation. As shown in Fig. 5. Ag-NPFs are electrically conductive upon stretching more than 120%, which is the new record for the deposited metal thin films. The resistance depends almost linearly on the elongation, as shown in the fig. 5 (b), which certainly is not due to simple geometrical deformation. Morphology studies using scanning electron microscopy show the development of micro-cracks upon large tensile deformation. Both crack density and dimension increases with the degree of deformation.

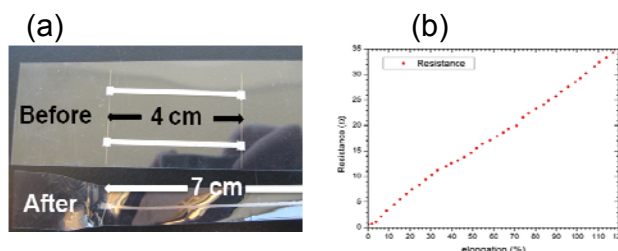


Fig. 5 Ag-NPFs stretching test: (a) photograph of the printed Ag-NPFs before and after stretching with the elongation ~ 120%; (b) electric resistance as a function of elongation.

Printed OTFT Fabrication and Characterization

We have fabricated organic thin film transistors (OTFTs) using conjugated polymers, polythiophene, as the organic semiconductor inks with Optmec M3D aerosol jet printing, as shown in Fig. 6. The evaporated Au and printed Ag as source-drain electrode materials are compared. Figure 7 shows the I-V curve characters: (a) double scan of I_d vs V_{ds} with increasing V_{gs} , there is no significant hysteresis and the saturation appears at applying high V_{ds} ; (b) I_d vs V_{gs} with specific V_{ds} as shown in the figure shows the log scale of I_d and SQRT of I_d vs V_{gs} which would give the carrier mobility at the saturation region. The OTFTs printed on pre-patterned substrate with Au source

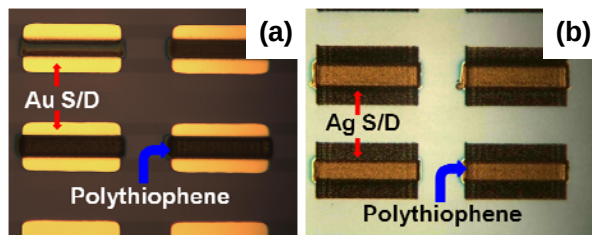


Fig. 6. Optical microscopy of fabricated bottom-gate-bottom-contact polythiophene OTFTs with (a) evaporated Au and (b) printed Ag as the electrode materials, respectively.

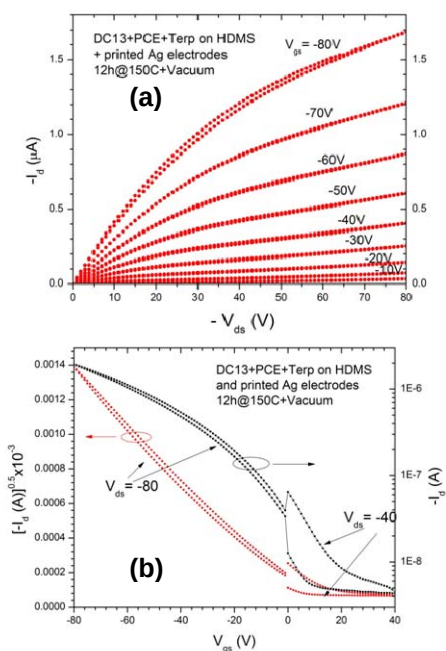


Fig. 7 I-V characterization of OTFT based on polythiophene as the organic semiconductor and printed Ag electrodes. (a) I_d vs V_{ds} with increasing V_{gs} ; (b) I_d vs V_{gs} at specific V_{ds} as shown in the figure, which indicates the on/off current ratio ~ 1000 and carrier mobility $\sim 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$.

and drain electrodes indicated carrier mobility of $0.02 \text{ cm}^2/\text{Vs}$, and on/off ratio of $10^2 - 10^3$. The polymers are shown to be stable in printing without inert gas protection, thermal annealing in air, and subsequent storage of devices in air for months. We also demonstrated the compatibility of polythiophene organic semiconductors with printed Ag nanoparticle electrode. The device performance was similar to that of evaporated Au.

Very small hysteresis and very good Ohmic contacts between electrode and polymers have been verified on several devices. We conclude that the initial test was a success, further improvement are possible.

Conclusions

We have carried out a series of measurements in order to understand processes in sintering uniform metal nanoparticles. The composition, morphology and electric resistance of sintered Ag- and Au-NP films have been revealed. Upon sintering, the organic content in MNP films reduces to less than 10% while the overall film thickness reduces to half. The conductivity of Ag-NP films sintered at 150°C was found to be $2.4 \times 10^{-8} \Omega\text{m}$. The transport properties are due mostly to the morphology of sintered films, which could vary due to particle characteristics and processing conditions. The printed Ag-NP electrodes were found to be suitable materials for fabricating printed OTFTs.

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