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Impact of ink synthesis on processing of inkjet-printed silicon nanoparticle thin films: A comparison of Rapid Thermal Annealing and photonic sintering

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ABSTRACT

Inkjet printing has a high potential for cost reduction in solar cell and thermoelectric industry. This study demonstrates that silicon thin films can be produced by inkjet-printing of silicon nanoparticles followed by subsequent drying and annealing steps. Ink formulation is crucial for the sintering of the silicon nanoparticles and control of the microstructure at low temperature. Upon heating, the microstructure is modified from porous layer made of juxtaposed silicon nanoparticles to denser layer with coarser grains. This evolution is monitored by scanning electron microscopy and by micro-Raman spectroscopy, which offer a fast and precise characterization of the microstructure and chemical composition of thin films. Above a threshold temperature of 800 °C cracks appear within thin film and substrate because of the stress induced by the oxidation of the surface. An innovative sintering method, photonic annealing, is studied in order to reduce both oxidation and stress in the thin films as well as reducing processing time. Evolution of the thermal conductivity is performed by micro-Raman spectroscopy and can be tailored in a large range between ~1 and ~100 $W \cdot m^{-1} \cdot K^{-1}$ depending on the sintering method and atmosphere. Therefore control of the microstructure evolution with applied annealing process allows tailoring of both microstructure and thermal conductivity of the silicon thin films.

1. Introduction

Inkjet-printing has been seen as a very promising way to deposit and pattern a broad choice of materials on large areas for low costs. Nowadays, ink based on metallic nanoparticles and polymers are widely used for flexible electronics [1–4]. Nevertheless, organic semiconductor efficiency and lifetime are clearly behind those of inorganic semiconductors, which limit strongly the field of applications for printed electronics. Therefore, solution-processing of inorganic semiconductors appears as a promising way to fabricate high-performance devices at low costs [5].

Silicon is the most employed semiconductor for electronic applications due to its availability, its useful oxide, its performances and good process know-how developed throughout the years in microelectronics. Deposition of silicon by solution-processing is therefore researched in order to lower fabrication costs without developing new materials and device architectures [6–9]. Furthermore, very specific properties (band gap broadening, photoluminescence…) appear by reducing silicon into nanosized-objects (nanoparticles, nanorods, nanowires…), as well as the possibility to use solution-based processes such as inkjet-printing. Therefore, the control of inkjet-printing of silicon nanoparticles (NPs) opens a way towards the fabrication of low cost electronic devices with tailored properties.

After inkjet-printing deposition and drying of the Si nanoparticle-based inks, thin films ranging from some hundreds of nanometers to some micrometers can be obtained. They are composed of juxtaposed nanoparticles in punctual contact and as a result are very porous. Electrical conductivity of such thin films is very limited [8,10] since the percolation threshold has to be reached [11], especially if the particles are not doped.

An annealing step is therefore needed in order to modify the microstructure (densification or grain coarsening) by sintering [12] to permit charge carrier transport [13]. For example, conductivities ranging between 10^{-8} and 5 $\Omega^{-1} \cdot cm^{-1}$ could be obtained after laser annealing depending on both laser pulse energy and doping level of the silicon nanoparticles [14]. Those values guaranty sufficient carrier transport for thermoelectrics and photovoltaics devices' performance. This paper studies the evolution of the microstructure upon annealing depending on the nanoparticle surface chemistry due to the ink synthesis as well as the impact of the sintering atmosphere and method. Photonic annealing – especially developed for printed electronics – is compared to more classic annealing methods (Rapid Thermal Annealing).

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2. Experimental details

2.1. Materials

Two commercial silicon nanoparticle-based suspensions (inks) were developed for our purposes and purchased from Meliorum Technologies Incorporation (Product #09820). Nonetheless, the supplier kept the synthesis procedure confidential. The undoped nanoparticles obtained from chemical synthesis, the same for both inks, have a diameter ranging between 20 nm and 150 nm (Fig. 1). They were put in suspension in ethylene glycol (reagent grade) with a concentration of ~1 wt.%. Concerning one of the two inks, some trace of water has been identified. This issue will be discussed in the following.

Following inks were studied: ink 1 with addition of 0.1 μM of sodium dodecylbenzenesulfonate and ink 2 with addition of sodium polymethacrylate (NaPMA) in an uncontrolled concentration (Na content of 144 mg/L was measured afterwards by atomic absorption). These components are commonly added in order to improve the stability of the suspension and to protect the nanoparticles against oxidation.

Viscosities (measured with a Brookfield DV1 + dynamic viscosimeter, rotating spindle) and surface tensions (measured through the pendant drop method with OCA 200 goniometer from Apollo Instruments) at room temperature are respectively of 24 mPa·s and 39 mN/m for ink 1 and of 13 mPa·s and 46 mN/m for ink 2.

2.2. Inkjet-printing process

A drop on demand system (Dimatix printer DMP 2800) was used for printing of Si nanoparticle inks using specifically designed waveforms. Silica glass substrates (reference JGS1 purchased from ACM) with average roughness $R_a = 0.62$ nm (measured with a Veeco Atomic Force Microscope SP-II) were used. An initial cleaning was performed with acetone in ultrasonic bath before printing. Surface energy of 47 ± 1 mN/m was calculated from goniometric measurements with three different liquids (water, ethylene glycol & diiodomethane) using the Owens–Wendt–Rabel–Kälble model [15].

Drop spacing of 20 μm between two consecutive drop centers was identified as being optimal. In order to increase the layer thickness two passes printing was applied without intermediate drying or annealing.

The printing step was followed by a two-steps drying process: 1) at room temperature under vacuum (<1 mbar) and 2) drying at 200 °C under nitrogen for 5 min in order to evaporate the ethylene glycol. It resulted in the layer morphology described in Fig. 2 Layers (11×11 mm^2) exhibit a squared coffee ring [16] structure with a flat part (~1 μm thick) at the center.

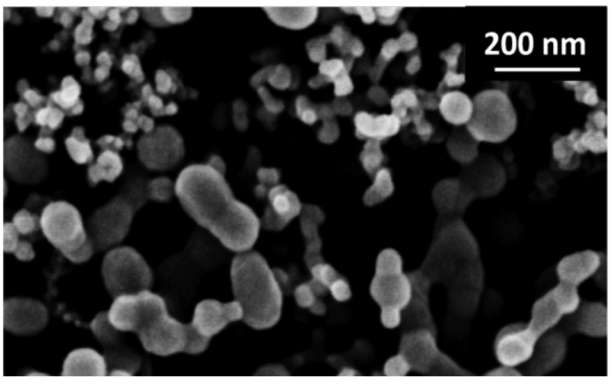

Fig. 1. Scanning Electron Microscope picture of Si nanoparticles after evaporation of the ink solvents at 200 °C.

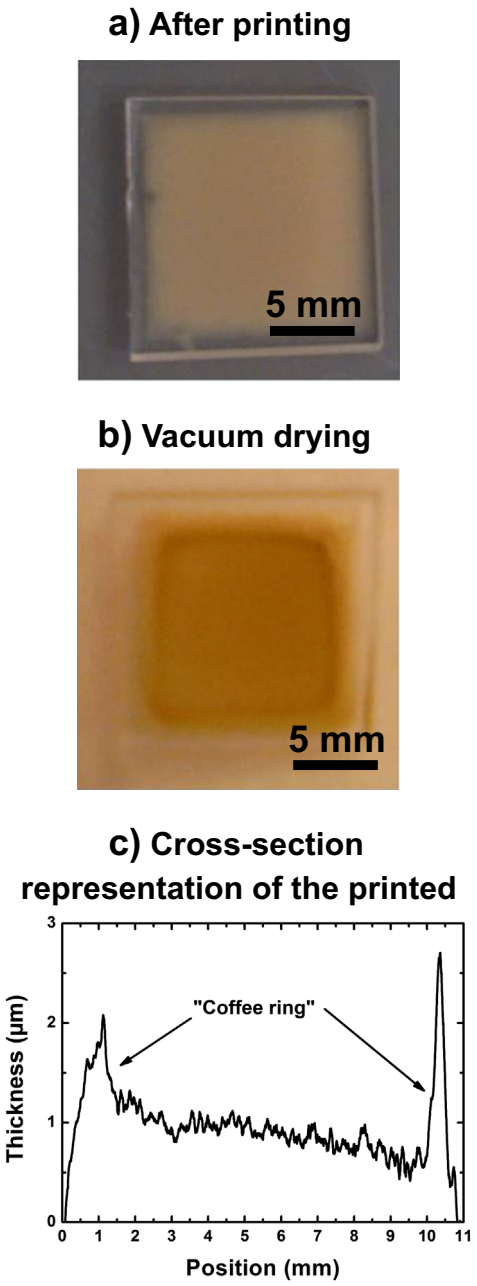

Fig. 2. a, b) Pictures and schematic cross-section representations of a printed layer just before and after vacuum drying at room temperature. c) Cross-section obtained by mechanical profilometry of a Rapid Thermal Annealing (RTA) of the layer at 700 °C for better mechanical behavior.

2.3. Annealing processes

Two types of annealing processes were studied for functional properties recovering of the thin films: Rapid Thermal Annealing (RTA) and photonic annealing.

Concerning RTA, a Jipelec jetfirst furnace equipped with 12 halogen lamps of 144 V–1200 W was used. Temperatures ranging from 600 °C to 1000 °C were applied (dwell times of 5 min and heating rate of 50 °C/s) under two types of atmosphere: inert atmosphere N_2 (99.999% purity) and reducing atmosphere N_2 (H_2 — 5%, 99.999% purity).

Photonic annealing was performed on a PulseForge system (PF3200-X1 from NovaCentrix) equipped with two broad spectrum high-intensity discharge lamps (XP-447 from NovaCentrix). The discharge