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# Silver nanowire networks as transparent top electrodes for silicon solar cells

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ABSTRACT

Losses caused by the metal top contacts still remain as an issue in crystalline silicon (Si) solar cells. One approach to eliminate shading losses is to utilise transparent nanostructure networks synthesised through rapid and low cost processes. In this work, the potential of highly conductive silver nanowire (Ag NW) networks as transparent top electrodes for the elimination of metallisation process in Si solar cells was investigated. Ag NW top contact cells were found to possess enhanced conversion efficiencies with respect to conventional metal contact reference cells. Increase in conversion efficiency was attributed to the elimination of shading losses, preferential scattering of light into the substrate by localised surface plasmon resonances (LSPRs) of the Ag NWs and localised and higher charge collection capability with respect to conventional metal contacts.



## 1. Introduction

Crystalline Si solar cells have dominated photovoltaics (PV) market primarily due to their advantages, such as relatively high efficiency, mature technology and abundant material supply. Screen-printed contact metallisation is the main route for the deposition of electrical contacts in crystal Si solar cells. In particular, optimally designed silver (Ag) narrow grid lines are used for the front contact to minimise shading losses and increase photocurrent and cell conversion efficiency. While screen-printing technique provides economic benefits as a result of high-volume manufacturing, the use of Ag paste increases the cell manufacturing costs. Therefore, many efforts have been conducted in order to reduce Ag paste consumption in screen-printing technology and it is predicted to decrease further down to 40 mg per cell until 2026 (International Technology Roadmap for Photovoltaic (ITRPV), 2016). In addition to cost, toxicity of the glass frits used in pastes and shading losses require development of alternative contact materials and methods. One recent metallisation technique in this context is the use of contacts composed of metal stacks such as electroplated nickel/copper (Ni/Cu). This technique offers low contact resistance, low material costs and low shading losses; but suffers from poor adhesion of contacts to Si (Raval and Solanki, 2013).

Transparent conducting films (TCFs) are important parts of the photovoltaic and many other optoelectronic devices, such as liquid-crystal displays, organic light emitting diodes (OLEDs) and touchscreens (Hecht et al., 2011). Both organic and inorganic materials are used as TCFs in photovoltaic applications. Transparent conducting oxides (TCO) Oxide Thin Films Materion Technical Paper, 2015, such as indium tin oxide (ITO), fluorine doped tin oxide (FTO) and aluminium doped zinc oxide (AZO) are the most popular examples of inorganic TCFs and organic films are polymeric materials like poly (3,4-ethylenedioxythiophene) and its derivatives (Hecht et al., 2011). The most commonly used and industrialised TCO is ITO due to its superior optoelectronic properties. However, ITO is brittle, limiting its application in flexible devices. It also shows degradation with time when it is subjected to mechanical stress. Increase in cost is also an important concern encouraging researchers to look for other alternatives. Recently, new generation TCFs based on nanostructures that include carbon nanotube (CNT) films (Wu et al., 2004; Hu et al., 2004; Ahmad et al., 2006) and graphene sheets (Wang et al., 2008) have been proposed to improve energy conversion efficiencies in photovoltaic devices. Highly conductive metal NW networks were also proposed as flexible, transparent and conducting electrodes (Rathmell et al., 2010; Lee et al., 2008). In addition to flexibility and low fabrication cost, Ag NW networks have comparable

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transparency and sheet resistance values to ITO films, which make them highly attractive alternatives (De et al., 2009; Hu et al., 2010; Morgenstern et al., 2011; Van De Groep et al., 2012). The use of Ag NWs as transparent electrodes has recently been investigated in polymer (Chen et al., 2012; Leem et al., 2011; Guo et al., 2013; Stubhan et al., 2012), dye sensitised (Margulis et al., 2013), thin film (Wang and Choy, 2016; Kim et al., 2014), hybrid (Li et al., 2014; Chen et al., 2012), perovskite (Guo et al., 2015) and crystalline Si (Jarret et al., 2015) solar cells. In addition to its function as conducting electrodes, Ag NWs can also provide plasmonic effect, which can be particularly useful for devices utilising thin active layers. Plasmonic effect of Ag NWs has recently been studied by Jarret et al. (2015). However, they did not show an increase in the efficiency of the cells due to the lack of good quality ohmic contact between Ag NWs and Si as well as due to poor light transmission (53% at 550 nm) resulting from parasitic inclusion of synthesis by-products (i.e. silver nanoparticles (Ag NPs)) in the electrodes used.

The goal of this work is to show the potential of replacing the costly and shading metal top contacts by Ag NW networks as transparent top electrodes in crystalline Si solar cells. With this goal, highly pure and conductive Ag NW networks were deposited onto the fabricated solar cells by a low cost and easy technique, namely spray coating. The effect of heat treatment on the formation of an ohmic contact and the further optimisation of the photovoltaic characteristics were investigated.

## 2. Experimental details

To fabricate Si solar cells, *p*-type single-crystalline Si (1 0 0) wafers (resistivity 1–3 Ω cm), with dimensions of 2 cm × 2 cm × 180 μm (length, width and thickness, respectively) were used. The saw damage removal process was performed on Si substrates using a 20% sodium hydroxide (NaOH) solution at 80 °C for 2 min. Hydrofluoric acid (HF) cleaning, deionised (DI) water (resistivity 18.3 MΩ) rinsing and nitrogen gas drying were carried out subsequently. For the *p-n* junction formation, wafers with flat surface were *n*-type doped by phosphoryl chloride ($POCl_3$) diffusion. The sheet resistance of the doped surfaces was 50 Ω/sq. The back aluminum contacts were screen printed using a standard aluminium paste [Ferro Electronic Materials (Mayfield Heights, OH) AL5130 Aluminium Conductor], which was followed by a short annealing process conducted at 900 °C for the formation of the back surface field. The Ag NWs were synthesised via polyol process as discussed elsewhere (Coskun et al., 2011). In summary, 7 mg of sodium chloride (NaCl, 99.5%) was added into 10 ml of 0.45 M ethylene glycol (EG) solution of polyvinylpyrrolidone (PVP, monomer-based calculation, $M_W$ = 55,000) and heated to 170 °C. Subsequently, 0.12 M silver nitrate ($AgNO_3$, 99.5%) solution in 5 ml of EG was prepared and added dropwise into the PVP solution. During the whole process, the solution was stirred by a magnetic stirrer and was annealed for 30 min following the injection process. In order to separate Ag NWs from PVP, EG and other by-products, the solution was diluted with acetone and centrifuged several times. Another centrifuge process was conducted with the same parameters for ethanolic dilution. The final product was dispersed in ethanol and stored for further processing. NW deposition process was performed by spray coating of the ethanolic solution of the Ag NWs using a simple nitrogen fed air brush. Substrates were placed onto a hot plate, heated to 150 °C for instant removal of ethanol. For reproducibility, the gas pressure and the distance between the air brush and the hot plate were set at 2 atm and 10 cm, respectively (Coskun et al., 2013).

Before spray coating of Ag NWs onto top surface of the Si cells, native oxide on the top surface was removed using diluted HF acid, which was followed by rinsing and drying with $N_2$ gas as described before. Glass substrates were spray coated at the same time as the Si cells in three sets with different Ag NW densities to study the effect of NW density on transparency and resistivity of Ag NWs and to correlate their effect on the photovoltaic conversion efficiency of the solar cells. Spray coating was continued until the desired sheet resistance is achieved as monitored on glass substrates. Density of Ag NWs on substrates can simply be adjusted by the number of spraying cycles. In order to connect probes during electrical measurements, frame shaped Ag paths were deposited using thermal evaporation with the help of a shadow mask. After Ag NW deposition, the cells were annealed at 200 °C for 20 min under $N_2$ atmosphere to burn the residual poly (vinylpyrrolidone) (PVP) layers from the Ag NW synthesis process and fuse the NW junctions. Annealing at a temperature below 200 °C was found not to be sufficient to create ohmic contacts between Ag NWs and n-type Si. Important parameters of the solar cell such as short circuit current ($J_{sc}$), open circuit current ($V_{oc}$), fill factor (FF), conversion efficiency ($\eta$) and series resistance ($R_s$) were measured for each cell with different Ag NW network densities and compared with reference cells without NW network top contact.

Morphologies of the Ag NWs were investigated through scanning electron microscopy (SEM, FEI Nova Nano SEM 430 microscope operated at 10 kV). Optical measurements of the glass and Si substrates with Ag NWs were carried out through a Si photodetector calibrated integrated sphere [Newport (Irvine, CA) 70679NS] capable of resolving the diffuse reflectance and transmittances. A sourcemeter (Keithley (Cleveland, OH) 2440) was used to obtain current-voltage characteristics of the fabricated solar cells and a solar simulator [Newport 94042A, AM 1.5G, 1000 W/m$^2$] was used for illumination during the measurements. EQE measurements were performed using an apparatus equipped with a monochromator, chopper, lock-in amplifier system and calibrated light detector.

## 3. Results and discussion

### 3.1. Morphology and sheet resistance

A photograph of the fabricated solar cell and an SEM image of Ag NW network top electrode is shown in Fig. 1. The area of the cell

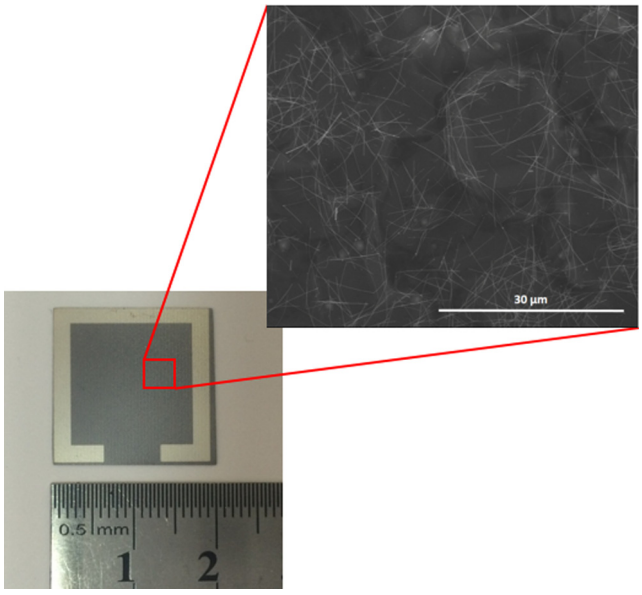


**Fig. 1.** Photograph of the fabricated solar cell with the SEM image of Ag NW network top electrode.