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Effectively Transparent Contacts With Low Temperature Reactive Silver Ink

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Abstract

There is great interest in minimizing the various losses caused by metal contacts in photovoltaic devices, in particular the optical and shadowing losses. In this study, a polymeric Polydimethylsulfoxide (PDMS) mold inscribed with a triangular microchannel pattern is used to deposit front metal contacts using a highly conductive, low temperature reactive silver ink (RSI) via capillary action. Fingers deposited with this technique exhibit a high aspect ratio, are optically narrow and ~ 85 % transparent. The resulting effectively transparent metal contacts (ETCs) can redirect incoming solar radiation to the photo-active area of the solar cell and mitigate parasitic absorption as well as shading losses. The use of RSI for the development of (ETCs) at low processing temperatures makes it possible for optoelectronic devices to include thermally sensitive layers. RSI exhibits conductivity $>10^4$ S/cm which is comparable to that of bulk silver and anneals at ~100°C, making it suitable for devices that require low temperature processing. With the reduction of porosity upon addition of a suitable solvent and increasing compactness of these grid fingers, they have the potential to outperform their low temperature silver paste screen-printed counterparts.

Keywords: solar; photovoltaic; metallization, transparent contacts, reactive ink .

1. INTRODUCTION

Received in abundance by the earth, Solar energy holds great promise for fulfilling the global energy demand, but a few major challenges need to be overcome to make this technology more economically favorable, One such challenge is increasing the overall efficiency of the modules which operate at less than 18%, far below the silicon balance efficiency limit of 29.8% [1]. The overall solar cell efficiency is affected by many factors, among which losses at the front surface metal contacts play a critical role [2]. Losses in output power of the solar cell at the front metal grid are classified into four types i.e. 1) losses attributed to the internal resistance of the metal electrode 2) losses from the contact resistance between the metal grid and emitter 3) losses due to current flowing through emitter causing emitter resistance and 4) shading losses due to aspect ratio of the front metal contacts which are highly reflective in most cases [3]. In silicon solar cells, screen printed silver contacts carry out charge transport but there is an approximate 4% to 10% loss of incident light because of the shading effect from the metal fingers [4]. These losses can be mitigated to some extent by either modifying the cell design, changing the scheme of the front contact, or utilizing light management external to the cell. Metal contact design modifications include use of fractal contacts ,transparent conductive oxides (TCOs) [5]-[6], or triangular contacts with high aspect ratio [7], [8].TCOs mitigate optical losses by ommiting the metal but are expensive and face intrinsic parasitic absorption along with low sheet conductivities. Furthermore, in large scale devices, the high photocurrents require metal grid fingers in order to achieve low resistance. These metal fingers lead to further optical losses due to geometric shading [9]. In conventional solar cells with rear and front contacts, a measurable fraction of the incident solar power is lost immediately at the front contact through either absorption, as in transparent conductive oxides or due to reflection at the metal fingers.

Effectively transparent contacts (ETCs), which are high aspect ratio triangular cross-section contacts, have the ability to reflect incident light directly on to the absorber layer in the solar cell, demonstrating over 99% reduction in reflective losses as well as excellent sheet conductivity [1].

These microscale contacts are placed closely together or apart, according to the diffusion length of the device material. If spaced densely, these ETCs exhibit high lateral conductivity [9] and have the potential to reduce TCO layer thickness, or replace it altogether [8] increasing the short circuit current density and mitigating the losses due to parasitic absorption and reflection. With the conventional techniques, such dense spacing of grid fingers would lead to high shading losses, however, the high aspect ratio and triangular cross-section if the ETCs reflects all incident light to the absorber layer [7], [8], demonstrating >85% effective transparency using the reactive silver ink.

In this study, we explore the possibility of using a low temperature reactive silver ink synthesized by a modified Tollen's method [10] with high conductivity and > 20% silver loading. The ink was used to deposit effectively transparent contacts (ETCs) on bare and FTO coated glass slides. Triangular cross-section microchannel grooves, that are 5.6 µm wide, 9.5 µm deep and ~75 µm apart (Fig. 1) were inscribed on to polydilmethylsiloxane (PDMS) using a silicon master mold developed using two photon lithography [11].

So far, the ETCs have been tested on Silicon heterojunction solar cells, bifacial solar cells and perovskites [4], [8], [9] but not on textured Silicon solar cells. Using this design, the fraction of area required by the macroscopic grid fingers can be reduced further on macroscale solar cells and modules compared to conventional designs. Moreover, the ETCs may be used in tandem solar cell architectures along with other optoelectronic devices [9].

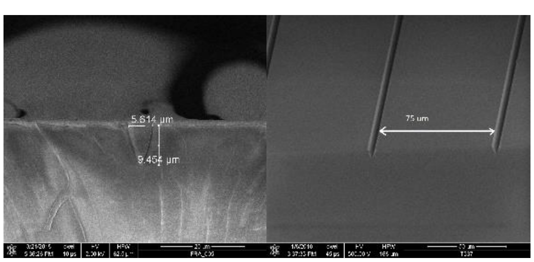

Fig.1. Scanning electron microscope images of a) Cross-section of PDMS stamp with triangular grooves prepared using master mold prepared by two photon lithography b) pitch of the metal finger grid design (~75 µm).

2. Experimental Section

2.1 Synthesis of the Reactive Silver Ink

RSI was synthesized by adding 1g of silver acetate into 2.5 mL aqueous ammonium hydroxide (32%) followed by vortex mixing until the salt was dissolved at room temperature. 0.2 mL of formic acid was then added dropwise with constant vortex mixing after each drop. The change in color of the solution from light brown to greyish black indicates reduction of silver ions to large particles of silver. This solution was kept undisturbed for around 12 hours to allow the larger particles of Ag to settle out and then filtered using a 0.22 µm syringe filter, resulting in a clear ink solution containing 22wt% silver [10], [12]. Thermogravimetric analysis of the ink was carried out at 90ºC (curing temperature) for 30 minutes at a ramp rate of 10ºC/ min and the ink showed stable behavior with only a 6.45% loss in weight.

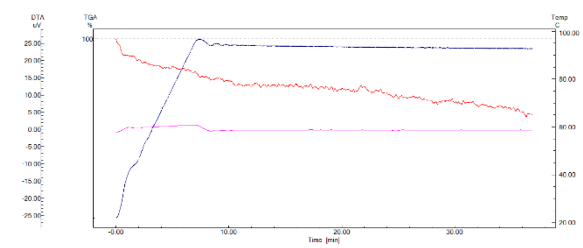

Fig.2. Themogravimetric analysis of RSI carried out at 90ºC for 30 mins at ambient conditions.

Electrical properties of RSI were measured using Hall effect measurements, for which the RSI film was deposited on a bare glass slide by dropping 0.4 mL of ink at 5000 rmp/30 sec. the resistivity of RSI was $4.569x10^{-3}$ Ω.cm at ambient conditions and the sheet resistivity was measured as 4.569 Ω/ □ , which is quite close to that for commercial silver paste [8].

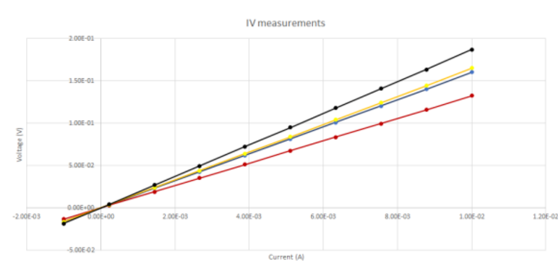

Fig.3. IV curve determined for drop-cast films of RSI using Hall measurements.

2.2 Fabrication of effectively transparent contacts (ETCs)

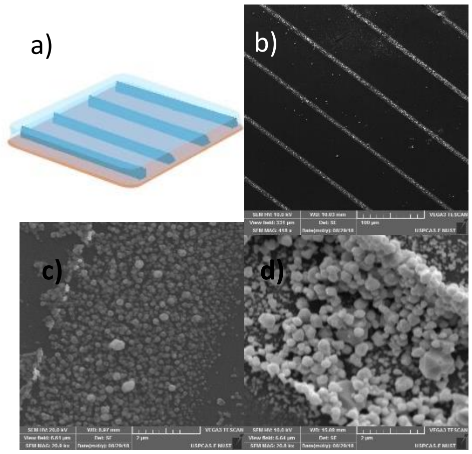

Fig.4. a) Schematic diagram of PDMS stamp with triangular micro-channel grooves, inverted on substrate. Ink is infilled through the sides and travels through the grooves via capillary action. SEM images of b) and c) ETC deposited on glass substrate with undiluted RSI and d) ETC using 1:1 EtOH: Ag ink mixture.

1x1 cm square pieces of the PDMS stamp were cut out and exposed to Medium power Ar/Air plasma (with flow rate 1:2) at ambient temperature. The Plasma treatment facilitates adhesion between the PDMS stamp and substrate [13]. Once removed from the plasma chamber, the stamp must be adhered immediately to a cleaned substrate because the effect of the plasma wears off quickly. After ensuring a tight seal between the PDMS and substrate, RSI (in various concentrations) was infilled from the sides via capillary action. Very minute quantities of ink are required to fill in the stamps, in the µL range. The substrate is heated for 15 minutes at 90ºC and then allowed to cool, before peeling off the stamp.

SEM of the deposited was carried out at 10 kV for the ETCs deposited using RSI in various ratios. The samples were sputtered with gold initially to form a conductive layer. Two samples were analyzed, ETCs formed using undiluted RSI (Fig.4. b and c) and the other using 1:1- EtOH:Ag ink (Fig.4.d). There was a clear difference between the particle size in both the samples. When cured at higher temperature (90 ºC -100 ºC), the ink forms highly porous structures that are discontinuous due to the formation of large pockets as the solvent evaporates since the reduction reaction is favored by higher thermal energy. The viscosity of the 1:1-EtOH:Ag ink is 3.8 mPa.s and weight percentage of Ag is 11.6% [14] as compared to 22% for the undiluted Ag ink [10]. A 10:1-EtOH:Ag ink was also tested but showed lower wettability and failed to flow into the grooves via capillary action. The boiling point of ethanol is 78.4 ºC, which means that curing the diluted ink at 90 ºC gives only a fraction of milliseconds for the solvent to evaporate, resulting in higher porosity at higher temperatures [14].

UV-VIS spectroscopy was carried out for transmittance measurements of the deposited contacts and a grid finger transparency > 80% was obtained.

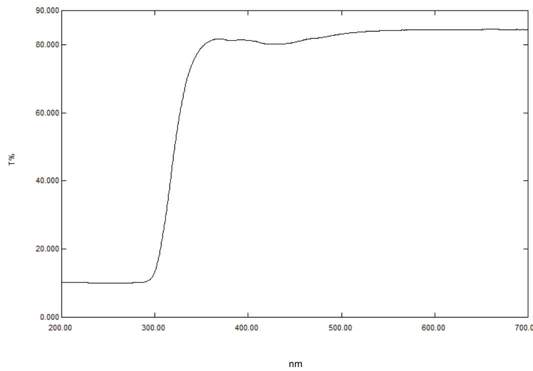

Fig.5. Transmittance measurements for RSI deposited effectively transparent contacts.

3. RESULTS

Reactive silver ink was used for the deposition of effectively transparent contacts (ETCs) on a glass substrate. These structures exhibited a resistivity equivalent to 4.569x10-3 Ω.cm and sheet resistance of 4.569 Ω/ ☐ which is impressively similar to that of commercially used screen printed silver paste. Thermogravimetric analysis of the ink shows that it is stable at 90 ºC with only a 6.45% loss in the total weight on the dried ink.

ETCs were deposited on bare glass slide and the structure was analyzed using SEM. ETCs formed using the 1:1 ethanol: Ag ink mixture showed better particle size and continuity, however, both compositions were not able to form the 3-D triangular finger structures as expected, due to poor control over evaporation rates of the solvent.

UV-VIS analysis of the ETCs showed great performance in terms of transmittance, which must be considerably high to allow sufficient light harvesting by the absorber layer.

4. CONCLUSIONS

We have demonstrated that effectively transparent contacts (ETCs) formed using low temperature reactive silver ink (RSI) have the potential to reduce losses incurred due to front grid metallization in solar cells, by minimizing shadowing, reflective and resistive losses. These high aspect ratio Ag fingers placed close enough can TCOs completely. The angle of incidence of these triangular microstructures is such that it maximizes light harvesting. Even though their use is not limited to any particular photovoltaic or optoelectronic device, the use of a low temperature curing ink makes them the ideal candidates for use in thermally sensitive solar cells like perovskites and Si heterojunction cells. The challenge is to optimize the process and find the best suited reactive silver ink composition that can be deposited at lower temperature to suppress formation of large pores during rapid evaporation of solvent upon curing. Once optimized, these low temperature curing ETCs formed using the reactive silver ink have great potential for replacing the conventional screen-printed silver grid fingers in many PV applications.

NOMENCLATURE

Abbreviations

PDMS	Polydimethylsiloxane
RSI	Reactive silver ink
ETC	Effectively transparent contacts
TCO	Transparent conductive oxides
rpm	rotations per minute

Greek capital symbols

Ω	Ohm
□	square

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