Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 93 (2015) 156–163
Acta MATERIALIA
www.elsevier.com/locate/actamat

Nickel–copper hybrid electrodes self-adhered onto a silicon wafer by supersonic cold-spray

Jong-Gun Lee,[a] Do-Yeon Kim,[a] Byungjun Kang,[b] Donghwan Kim,[b] Hee-eun Song,[c] Jooyoung Kim,[d] Woonsuk Jung,[d] Dukhaeng Lee,[d] Salem S. Al-Deyab,[e] Scott C. James[f] and Sam S. Yoon[a,*]

[a]*School of Mech. Eng., Korea University, Seoul 136-713, Republic of Korea*
[b]*School of Materials Science and Engineering, Korea University, Seoul 136-713, Republic of Korea*
[c]*Photovoltaic Research Center, Korea Institute of Energy Research (KIER), Daejeon, Republic of Korea*
[d]*Hojin Platech Inc., Ansansi, Kyeonggido, Republic of Korea*
[e]*Petrochem. Research Chair, Dept. of Chem., King Saud University, Riyadh 11451, Saudi Arabia*
[f]*Dept. of Geology and Mech. Eng., Baylor University, Waco, TX 76798, USA*

Received 27 February 2015; revised 6 April 2015; accepted 9 April 2015

Abstract—High-performance electrodes are fabricated through supersonic spraying of nickel and copper particles. These electrodes yield low specific resistivities, comparable to electrodes produced by screen-printed silver paste and light-induced plating. The appeal of this fabrication method is the low cost of copper and large area scalability of supersonic spray-coating techniques. The copper and nickel electrode was fabricated in the open air without any pre- or post-treatment. The spray-coated copper–nickel electrode was characterized by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction, and energy dispersive spectroscopy. Although both SEM and TEM images confirmed voids trapped between flattened particles in the fabricated electrode, this electrode's resistivity was order $10^{-6}\ \Omega$ cm, which is comparable to the bulk value for pure copper.

Keywords: Silicon solar cell; Nickel–copper electrode; Supersonic cold spraying; Contact resistivity; Specific resistivity

1. Introduction

Because of growing economic pressure, a less expensive substitute for silver is sought for the electrode material in traditional silicon solar cells. At only 1% of the cost, copper has been suggested as an alternative electrode material [1–6]. Copper is an appropriate conducting metal because its bulk resistivity ($\rho_{Cu} = 1.68 \times 10^{-6}\ \Omega$ cm) is only slightly higher than silver's ($\rho_{Ag} = 1.59 \times 10^{-6}\ \Omega$ cm). The International Technology Roadmap for Photovoltaic [7] predicts that silver consumption per cell will drop by 2/3 from 2010 to 2015 with increased use of copper.

However, direct deposition of copper onto silicon results in copper diffusion into the upper silicon layer, which deteriorates over time and eventually reduces the lifespan of a solar cell. This can be prevented by pre-applying a diffusion-inhibiting intermediate layer of nickel [7–12]. This nickel forms nickel silicide ($NiSi_x$) at various annealing temperatures after rapid thermal treatment. Not only does nickel silicide prevent copper diffusion, it also promotes adhesion between nickel and the silicon substrate due to the chemical bonds formed during thermal annealing [1,2,9,12–15]. Furthermore, nickel silicide lowers the contact resistance between silicon and nickel thereby increasing potential efficiency [1,2,12].

There are several techniques for depositing nickel–copper layers. Sputtering can be used to deposit the nickel layer, followed by laser annealing and vacuum deposition of copper [7]. More often, light induced plating (LIP) has been used to install nickel and copper layers [9,15]. In an LIP electroplating bath, once a solar cell is irradiated, electron–hole pairs are generated. Because the emitter is negatively charged, it attracts positive metal ions, forming a nickel or copper electrode. Although LIP has been widely used, drawbacks include the costly copper precursor, unsatisfactory adhesion, slow process, and scalability to commercial applications [13–17].

Considering the shortcomings of Ni–Cu LIP and Ag-paste screen printing, an alternative coating scheme is sought. Cold-spraying, where a supersonic gas stream deposits dry particles onto the substrate, yields a strong bond/adhesion between impacting particles and the substrate. Particles "self-adhere" as they sinter upon impact and convert their kinetic energy into thermal, bond, and

---

* Corresponding author; e-mail: skyoon@korea.ac.kr

http://dx.doi.org/10.1016/j.actamat.2015.04.012
1359-6462/

adhesion energy. Cold-spraying is rapid, scalable, and well suited for cost effective large-scale commercialization.

There is a wealth of literature on cold-spraying copper [18–20] and nickel particles [21,22]. These studies used fairly large particles ($D_p = 5 - 22$ μm) and thus are not suitable for high-resolution fine printing of electrodes for solar cells, which require line widths of less than 100 μm. Kim et al. [23] performed the only study that successfully fabricated 150-μm-wide copper electrodes. However, they did not use a diffusion-inhibiting nickel layer below the copper layer. Furthermore, the contact resistance and the specific resistivity were never reported or compared to results from conventional methods like screen-printing and LIP.

Herein, we fabricate nickel and copper electrodes for silicon solar cells using cold-spraying. The effects on contact resistivity from an added nickel layer below the copper are investigated. Furthermore, the specific resistivity of these fabricated electrodes is compared to those from conventional methods. Our cold-sprayed electrodes perform well in terms of specific resistivity and should be implemented in solar cell manufacture.

2. Experimental details

Fig. 1 is a schematic of the cold-spray coating system used in this study. The system consists of the powder feeder (Praxair 1264*i*, USA), which feeds the metal particles into the supersonic nozzle. Highly compressed gas is fed into a heater and then the hot gas expands through the converging–diverging nozzle to yield a supersonic flow. Sprayed particles impact against the substrate, which is attached to an x–y stage. The operating pressure and temperature are 4 bar and 350 °C, respectively. The volumetric flowrate of the carrier gas taking the particles to the nozzle is 10 L/min. The mass flowrate of particles leaving the powder feeder is less than 0.01 g/s. Table 1 summarizes the operating conditions for nickel and copper application. Because nickel is used as the seed layer and must remain thin (1–2 μm), only two nozzle passes are used and the traverse speed is twice that for copper. Furthermore, the nozzle-to-substrate distance was slightly farther than the one used for copper.

Table 1. Operating conditions for the cold-spray system for nickel and copper particles.

	Nickel coating	Copper coating
Pressure [bar]	4	4
Preheating temperature [°C]	350	350
Traverse speed [mm/s]	10	5
Spray distance [mm]	50	30
Number of layers (N)	2	10

Both glass and silicon wafer are used as substrates with roughness of $R_a = 0.1$ nm and 5 μm, respectively, based on atomic force microscopy (AFM) measurements. All substrates were cleaned in an ultrasonic acetone bath for 10 min to remove residues. The silicon wafer was submerged in a Buffered Oxide Etch solution for 1 min and then rinsed with DI water 5 times before use. A stainless steel mask with width between 200 and 1500 μm was used to limit the cold-spray to line printing.

Microstructures of sprayed metal particles were characterized with a high-resolution SEM (HRSEM, XL30SFEG Phillips Co., Holland at 10 kV) and TEM (HRTEM, JEM 2100F, JAPAN). EDS measured the elemental composition as a function of layer depth. Current–voltage data were acquired with a resistivity probe (Keithley Instruments, Cleveland) to measure resistance (R_T), which was converted into a specific resistivity (ρ_c).

3. Results and discussion

The effect of electrode-line aspect ratio of copper (width to thickness) on resistivity is known [23]. In this work, a nickel base layer is installed prior to copper deposition to prevent copper diffusion and possibly form nickel silicide if post annealing, which improves contact adhesion and reduces contact resistivity was applied.

Successful cold-spraying strongly depends upon the particle size at a given operating pressure and temperature [24,25]. Based on previous experience, the mean particle sizes for nickel and copper were maintained at about one micron to fabricate fine electrodes. Under operating conditions of 4 bar and 350 °C, 1-μm particles allow rapid particle acceleration and sufficient momentum to yield a functional coating. Fig. 2 shows SEM images of nickel and copper particles (Alfa Aesar, 99.9%) with average sizes of 1.64 and 0.8 μm, respectively, and distribution ranges of ±40% from the mean. The mean nickel particle size (1.64 μm) was suitable for a target electrode thickness of 1–2 μm and particles flatten upon impact [25,26].

Fig. 3 shows fabricated electrodes of various widths ranging from 200 to 1500 μm. A stainless steel mask with specified aperture covered the soda-lime glass substrate to print these fine electrodes. The fabricated electrode was

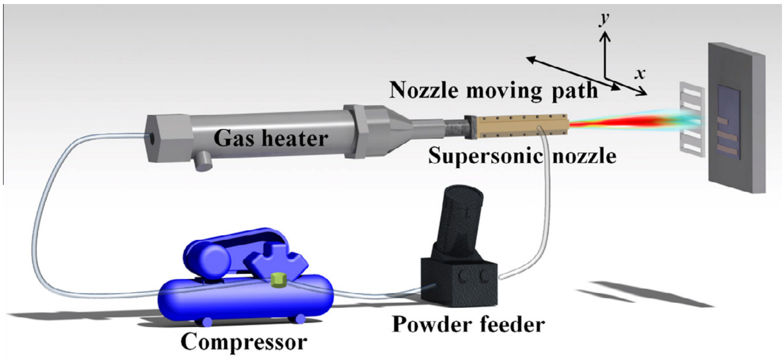

Fig. 1. A schematic of the cold-spray system for depositing nickel and copper particles.