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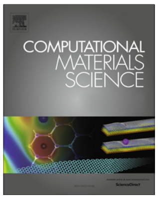

Thin film metallization by supersonic spraying of copper and nickel nanoparticles on a silicon substrate

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ABSTRACT

Copper and nickel nanoparticles are supersonically sprayed onto a silicon wafer to install a low-resistance, high-performance, and cost-competitive front electrode onto a crystalline silicon solar cell. Impact phenomena and the deposition processes of both single and multiple particles were simulated and the computational results were compared against experimental data. Jet formation and local sintering at the particle-to-substrate interface were observed due to adiabatic shear instabilities. Local temperatures increased with impact velocity and estimates of these temperatures were made with a simple energy balance. Multi-particle simulations reveals the processes of thin-film growth; particles are bonded through interfacial sintering that locks the particles into a film. Film plastic strains were highest at the interface and increase risks for delamination.

1. Introduction

Screen printing silver paste is one of the more common methods of fabricating top electrodes for silicon-based solar cells. Its low resistivity and accessibility have popularized its use in the industry [1–3]. However, use of copper has been considered as an alternative electrode material because of its low cost and comparable resistivity ($\rho_{Cu} = 1.68 \times 10^{-6}\,\Omega\,\text{cm}$ and $\rho_{Ag} = 1.59 \times 10^{-6}\,\Omega\,\text{cm}$) [4,5]. Addition of nickel minimizes copper diffusion into a silicon (Si) substrate, which lowers the contact resistance while maintaining comparable resistivity to silver paste [6–10].

Vacuum-based sputtering or light induced plating (LIP) have been used to deposit nickel and copper layers [11,9,12]. However, they are expensive processes because of costly vacuum requirements, slow fabrication, poor scalability, and most of all, unsatisfactory adhesion [7,9]. Because of these shortcomings, cold spraying has been used to deposit nickel–copper layers for use in silicon solar cells [13,14]. Cold spray supersonically sprays particles that flatten upon impact to form a thin film. These sprayed particles adhere to the substrate without any post-annealing treatment. The cold spraying method is also impurity-free, rapid, scalable, highly interlocking, and well suited for cost-effective large-scale commercialization.

To aid in understanding the mechanisms of film adhesion, numerical simulations are useful because they resolve time scales down to a few nanosecond, which are not observable experimentally. Experimental studies of copper and nickel particle deposition [15–19] can be used to validate corresponding computational studies [20–30]. These authors studied particle sizes of $D_p = 5–50\,\mu\text{m}$, but submicron-scale nanoparticles must be used to fabricate electrodes with widths on the order of tens of microns or less. Furthermore, most computational studies are limited to single-particle impact, although Yin et al. [31] used a few 20-μm copper particles. To observe thin-film growth, deposition of only a few particles is sufficient. At least tens of particle impacts must be simulated to observe a thin film growth.

Herein, we simulate 90 copper particles, their sequential impact, flattening, and thin-film growth while varying the impact scenario (i.e, different substrate materials and impact velocities). The computational results are validated against both experimental data and an analytic solution. We also propose a simple analytic approach that estimates the temperature of a particle during impact. By simulating multiple particle impacts, the interlocking thin-film growth phenomena of nickel–copper layers are elucidated.

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2. Modeling and experimental

2.1. Modeling

Table 1 summarizes our Ansys Autodyn (Canonsburg, PA, USA) simulations. Case 1 reflects the impact phenomena of an aluminum particle on a lead zirconate titanate (PZT) substrate. Case 2 reflects the impact phenomena of a copper particle on a Si wafer. Numerical simulations for Cases 1 and 2 were compared to experiments by King et al. [32] and to our own experimental data, respectively.

Once the model was verified against previous numerical and experimental results, our simulations were extended to nickel- and copper-particle impacts. The effect of impact speed was investigated for copper and nickel particle impact on a silicon wafer in Cases 3 and 4. As illustrated in Fig. 1 for a solar cell application, a nickel layer is first deposited onto a silicon wafer as a diffusion barrier and then copper is deposited. This scenario is simulated in Case 5. Case 6 is for multiple-particle impacts ($N = 90$) to observe thin-film growth of a copper layer on a silicon wafer.

In Autodyn, smoothed particle hydrodynamics (SPH) using a stress-failure model simulated flattening of the nickel and copper particles. Meshless Lagrangian nodes were interpolated with a kernel function to accurately track their behaviors. The substrates (silicon and nickel) were also modeled using Lagrangian nodes so that local fracture or materials erosion could be dynamically tracked as a function of impact speed. Equations of state (EOS) calculated the thermodynamic properties (pressure, temperature, specific volume, and internal energy density) during the particle flattening process. Various strength models are used to represent the equivalent plastic strain, the equivalent plastic-strain rate, and temperature dependencies [33]. Table 2 lists the individual models used for the materials (i.e, aluminum, nickel, copper, and silicon) in this study.

2.2. Experimental

Fig. 1 depicts 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 issuing as a supersonic flow. The sprayed particles impacte against the substrate, which was attached to an x–y stage. The operating pressure and temperature are 4 bar and 350 °C. The volumetric flowrate of particles is 10 L/min. Microstructures of sprayed metal particles were characterized with a high-resolution TEM (HRTEM, JEM 2100F, JAPAN). More details of our experimental setup are available in Refs. [34–39].

3. Results and discussion

3.1. Validation

Fig. 1 illustrates the cold-spray supersonic coating system used to deposit copper and nickel particles. First, the nickel layer was deposited onto a silicon wafer to prevent copper diffusion and to reduce contact resistance. Then the copper layer was deposited over the nickel layer to complete the nickel–copper bilayer electrode. The widths of these layers ranged from 50 to 200 μm, which was controlled by the mask attached to the substrate during coating. The top right inset shows results from a multiple copper particle simulation. The bottom left inset is also taken from a simulation describing particle-impact evolution with color representing local pressure.

Table 1
Summary of the case studies: Material type, number, substrate type, and particle size and speed.

ID	Particle		Substrate	D_p (μm)	V_p (m/s)
	Material	Number (N)			
Case 1	Al	1	PZT	20	600
Case 2	Cu	1	Si	0.8	400
Case 3	Cu	1	Si	0.8	100–500
Case 4	Ni	1	Si	1.6	100–500
Case 5	Cu	1	Ni	0.8	100–500
Case 6	Cu	90	Si	0.8	400

Case 1 is the benchmark case from King et al. [40] against which we verified our computational results. Smoothed particle hydrodynamics (SPH) form the basis of the interpolation scheme to model the flattening of an aluminum particle which King et al. used as the depositing material [40]. Gridless Lagrangian computational nodes ($N_s = 2512$) represented this single-particle impact Case 1. To maintain a reasonable computational expense, a two-dimensional axisymmetric model was used. The dimensions of the PZT substrate were 5 × 25 μm comprising 9600 nodes. The initial temperature of the system was set to 300 K. The particle-impact speed was assumed to be about 68% of the one-dimensional isentropic gas speed of $V_g = 883$ m/s (where $\gamma = 1.4$, $c_p = 1.041$ kJ/kg K, $T_0 = 350$ °C = 623 K, and $P_0 = 25$ bar), which is approximately $V_p = 600$ m/s.

$$V^2_{e,gas} = 2c_pT_o\left[1-\left(\frac{P_{amb}}{P_o}\right)^{\left(\frac{\gamma-1}{\gamma}\right)}\right]. \quad (1)$$

Under real operating conditions, the flow is not isentropic (flow decelerates due to viscosity), there are three-dimensional effects and formation of bow shock in front of the substrate [40–43].

The simulation result in Fig. 2a shows the “jet” moving outward paralled to the substrate surface because of adiabatic shear instability [20,40,44], which are responsible for successful bonding during cold spray coating. Numerous simulations and experiments have demonstrated jet formation as a result of adiabatic shear instability upon impact. When kinetic energy is converted into thermal energy upon impact, local sintering occurs, which melts of the particle such that it behaves like a molten drop with jet ejection droplet. Because the substrate is a hard material (PZT), it will not melt. We have characterized aluminum particle impact onto an unyielding PZT substrate, which is validated against the experimental image of Fig. 2b. The qualitative agreement between the numerical and experimental results in Fig. 2a and b, respectively, helps verify and build confidence in the model.

Fig. 3 is a further validation of the model through comparison of (a) TEM experimental results to (b) our simulation. The cross-sectional TEM image of a deposited copper particle was prepared by focused ion beam milling. The milled cross-sectional surface appears smooth and without pores. The diameter of the copper particle prior to impact was about 0.8 μm. Although the precise diameter of this copper particle prior to impact was not reported, the radius of the deposited particle was 1.2 μm indicating that the original particle size was between 0.8–1.2 μm. In the corresponding simulation shown in Fig. 3b, the copper particle diameter was 0.8 μm [14]. In the experiment, the stagnation pressure and temperature were $P_0 = 5$ bar and $T_0 = 720$ K, which yielded an isentropic gas velocity of $V_g = 730$ m/s according to Eq. (1). The corresponding simulated particle velocity was $V_p = 400$ m/s, and the resulting particle size and shape are comparable to the experimental TEM image in Fig. 3a. Because of this agreement, particle speed in subsequent simulations was set to $V_p = 400$ m/s.

3.2. Effects of impact material

Fig. 4 shows temperature and pressure distributions and their corresponding time series during impact for the various Cases;