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Particulate Contacts to Si and CdTe: Al, Ag, Hg-Cu-Te, and Sb-Te

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Abstract. Our team has been investigating the use of particle-based contacts in both Si and CdTe solar cell technologies. First, in the area of contacts to Si, powders of Al and Ag prepared by an electroexplosion process have been characterized by transmission electron microscopy (TEM), TEM elemental determination X-ray spectroscopy (TEM-EDS), and TEM electron diffraction (TEM-ED). These Al and Ag particles were slurried and tested as contacts to p- and n-type silicon wafers, respectively. Linear current-voltage (I-V) was observed for Ag on n-type Si, indicative of an ohmic contact, whereas the Al on p-type Si sample was non-ideal. A wet-chemical surface treatment was performed on one Al sample and TEM-EDS indicated a substantial decrease in the O contaminant level. The treated Al on p-type Si films exhibited linear I-V after annealing. Second, in the area of contacts to CdTe, particles of Hg-Cu-Te and Sb-Te have been applied as contacts to CdTe/CdS/SnO₂ heterostructures prepared by the standard NREL protocol. First, Hg-Cu-Te and Sb-Te were prepared by a metathesis reaction. After CdCl₂ treatment and NP etch of the CdTe layer, particle contacts were applied. The Hg-Cu-Te contacted cells exhibited good electrical characteristics, with $V_{oc} > 810$ mV and efficiencies > 11.5 % for most cells. Although $V_{oc} > 800$ mV were observed for the Sb-Te contacted cells, efficiencies in these devices were limited to 9.1%, presumably by a large series resistance ($>20 \Omega$) observed in all samples.

INTRODUCTION

In this paper, we discuss the use of particulate-based contacts for solar cells. The use of particulate systems is attractive for a number of reasons. First, given the existence of proper synthetic routes, particles with variable compositions (e.g., Hg_{1-x}Cu_xTe) can be synthesized with controlled stoichiometries. Also, particulate-based inks are amenable to low-cost deposition approaches such as spray deposition, as well as screen and ink-jet printing. The use of small-sized particles could lead to narrower line widths and patterns not easily attainable by conventional approaches.

We present results on the application of metallic Al and Ag nanoparticles to Si and the application of Hg-Cu-Te and Sb-Te particles to CdTe.

Al AND Ag CONTACTS TO p- AND n-TYPE SILICON

Aluminum-to-silicon contact metallizations via evaporation of Al or Al-glass screen-printed pastes are well established. In certain configurations, these metallizations lead to shading losses that degrade efficiency. Toward this end, a reduction in the present lithographic limitations of screen-printed conductors (i.e., linewidth $> 100 \mu\text{m}$) [1] could serve to enhance overall solar-cell performance. The use of metallic inks that comprise nanosized particles could lead to smaller linewidths. This could be realized by tailoring the ink properties for screen printing with appropriate optimization of the lithography process. Given suitable characteristics of the nanoparticles, both physical (i.e., particles $< 0.5 \mu\text{m}$ in diameter) and chemical (i.e., appropriate reactivity), this approach also may be amenable to ink-jet printing. We report in this paper our preliminary results of research aimed at developing such metallic particle-based inks.

Experimental

Powders of Al and Ag were obtained from Argonide Corp. after preparation by Russian scientists via the electroexplosion (i.e., exploding wire) process. The Al sample was shipped under kerosene, whereas Ag was received as a dry powder. Samples were prepared for TEM by sonication of isopropanol slurries of the dried powders. P-type Si (Wacker, $3.3 \Omega \cdot \text{cm}$) and n-type Si (Wacker, $2.9 \Omega \cdot \text{cm}$) were etched with 5% HF and rinsed with deionized water. The samples for annealing studies were prepared by dropping toluene slurries of the metallic nanoparticles onto the Si substrates using a modified disposable pipette in a He-filled glovebox. The Al on p-type Si samples were annealed at $645\text{--}650^\circ\text{C}$ for 1 h under Ar, whereas the Ag on n-type Si samples were annealed at 882°C for 1 h under Ar. After annealing, the deposits were crumbly and did not provide electrical contact. The residues were removed using an isopropanol-wetted cotton swab, and Ag paint was applied to the alloyed areas and also to non-reacted areas on the Si to provide a control. Electrical testing of the areas showed evidence of contact formation in the areas where the particles had reacted, but none in the control spots. I-V measurements were performed using an Optical Radiation Corporation Solar Simulator 1000 and computer-controlled I-V instrumentation.

Results

The Al powder was characterized by TEM, with representative results shown in Figure 1. Two separate fractions were isolated by mixing the Al in methanol and decanting the top fraction (fines) from the bottom fraction (coarse). The fines fraction (Fig. 1a) is characterized by a bimodal distribution, with $\sim 50\%$ spheres $50\text{--}100 \text{ nm}$ in diameter and $\sim 50\%$ non-spherical Al $< 10 \text{ nm}$ in diameter. The coarse fraction (Fig. 1b) is composed of $\sim 90\%$ spheres and $\sim 10\%$ non-spherical Al, $50\text{--}300 \text{ nm}$ in diameter. TEM-ED indicated these particles are crystalline, whereas TEM-EDS shows Al and a major O contaminant, as is expected in a large-surface-area sample exposed to air.

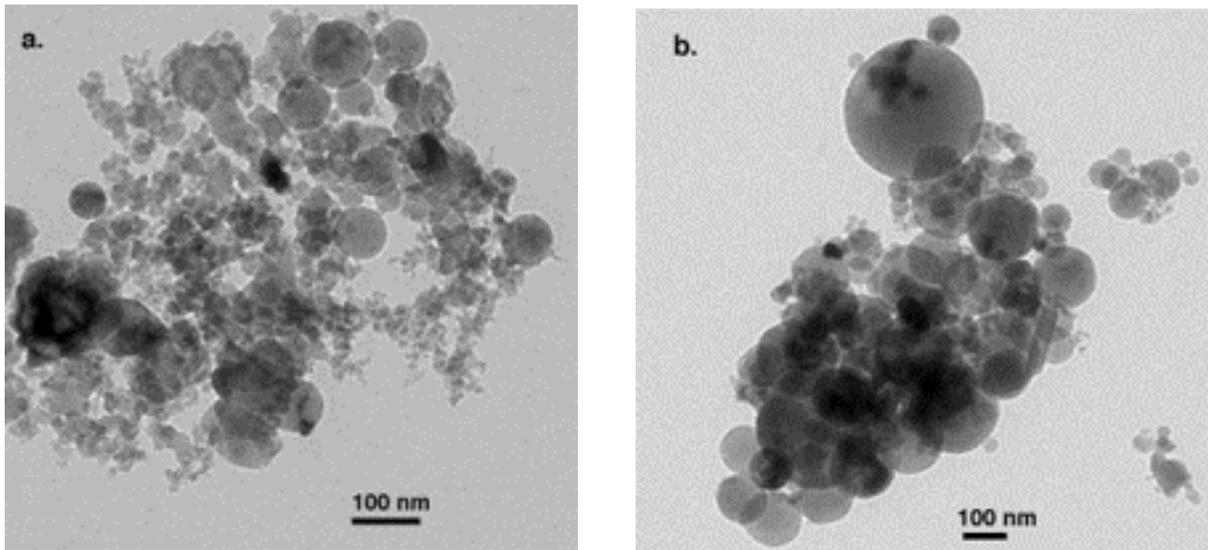


FIGURE 1. TEM micrographs of Al prepared by electroexplosion method.

The Ag sample characterized by TEM consists of agglomerates mostly 100-300 nm in diameter, with some particles > 500 nm (Fig 2a). Necking of the particles is observed (Fig. 2b), and the sample is crystalline by TEM-ED and contains no O impurities by TEM-EDS. The Al and Ag were applied onto p- and n-type Si, respectively, and subjected to annealing (see above). Figure 3 shows I-V characterization of these films after annealing. The Al to p-Si sample (Fig. 3a) shows

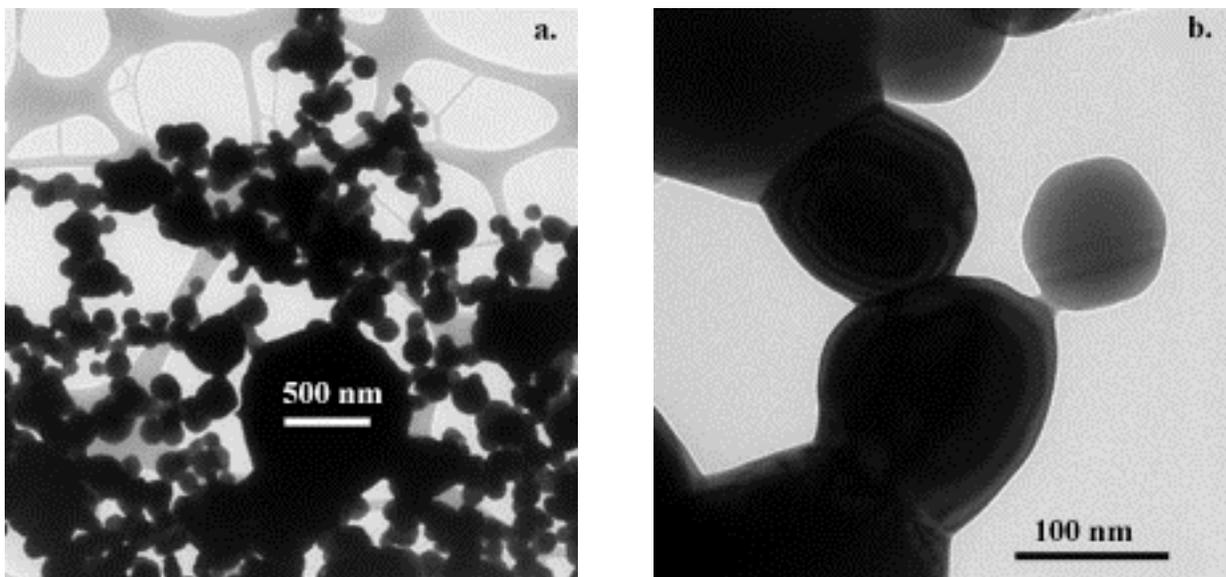


FIGURE 2. TEM micrographs of Ag prepared by electroexplosion method.

a slight deviation from linearity in its I-V, whereas the Ag to n-Si sample (Fig. 3b) exhibits a linear I-V indicative of an ohmic contact. Quantitative contact-resistance measurements are planned for the future.

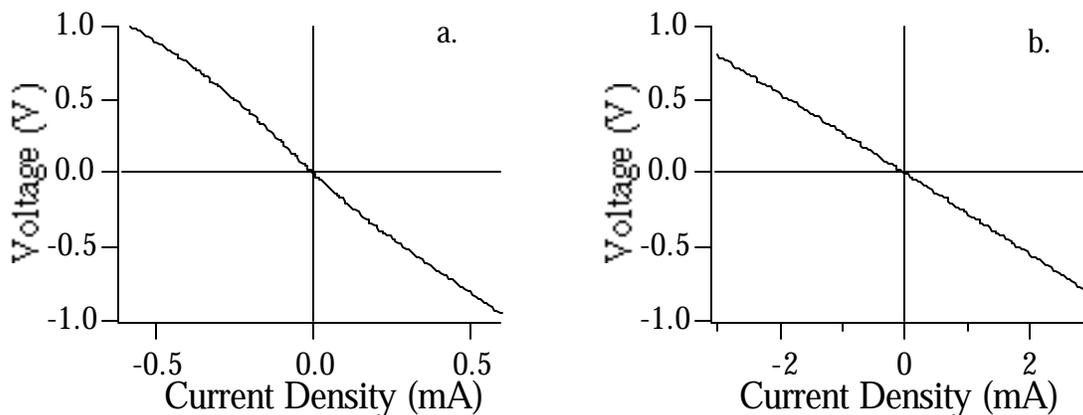


FIGURE 3. I-V characterization of (a) Al to p-type Si and (b) Ag to n-type Si.

In an effort to produce an ohmic contact to p-type Si using Al, we performed experiments to remove the surface oxide. After an NREL-developed wet-chemical treatment, the Al was observed to contain a much lower amount of O impurity by TEM-EDS. This treated Al was next applied as a contact to p-type Si and annealed as above. I-V characterization of this sample shows a marked improvement in the ohmic character of the treated Al (Fig. 4) versus untreated Al (Fig. 3a).

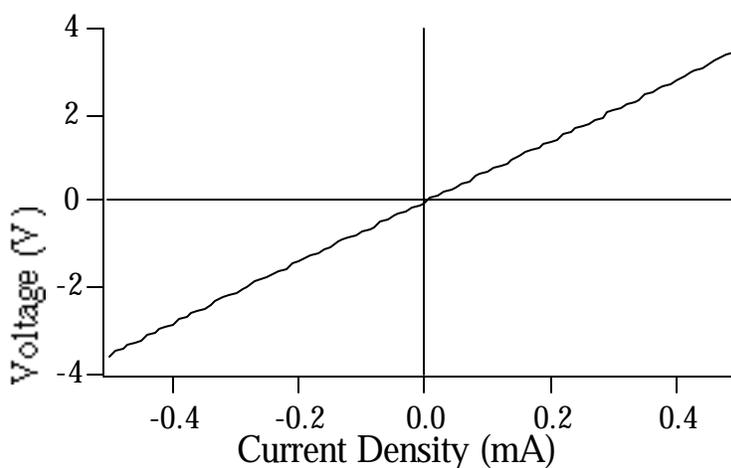


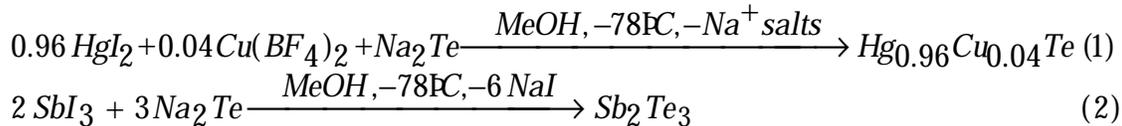
FIGURE 4. I-V characterization of chemically treated Al to p-type Si contact.

Hg-Cu-Te AND Sb-Te CONTACTS TO CdTe

Our team has been developing new approaches to form back contacts to CdTe solar cells using nanoparticles. The standard NREL back-contact is a graphite-based Cu-doped HgTe material similar to that described by Britt and Ferekides [2]. The use of solution-synthesized Hg-Cu-Te nanoparticles in graphite-paste contacts was evaluated to determine feasibility versus the micron-sized particles that are normally used. Sb-Te particles were employed in preliminary studies as a contacting material based on the recent report of a Cu-free contact by the Parma group [3].

Experimental

Hg-Cu-Te and Sb-Te materials were prepared by metathesis reactions of metal salts with sodium telluride in methanol at reduced temperature according to Eqs. 1 and 2, respectively. TEM, TEM-EDS, and X-ray diffraction (XRD) characterization of as-synthesized Hg-Cu-Te particles showed the samples are micron-sized agglomerates composed of smaller particles ($d \sim 10\text{nm}$), with the HgTe (Coloradoite) phase (PDF #32-665) and Hg, Cu, and Te present, but no C or O. Characterization of the Sb-Te materials is presently under way. After CdCl_2 treatment and NP etch of the CdTe layer, particle contacts were applied. In the case of Hg-Cu-Te, a graphite-based paste was formulated and painted onto the CdTe layer, with subsequent thermal treatment under Ar. Sb-Te particles were applied to CdTe by spray deposition of a methanol ink at 150°C , followed by a thermal treatment under N_2 . In both cases, Ag paint was added as the final layer, with devices finished according to standard NREL protocol. CdTe solar cells were characterized by standard light and dark I-V.



Results

The amount of Hg-Cu-Te in graphite dag was varied from 18-55 wt.%, and the contact anneal temperature/time was varied from 220°C - 320°C /20-40 min. Preliminary experiments consisted of two data sets: (1) comparison of 18 vs. 55 wt.% Hg-Cu-Te in graphite dag at three annealing conditions (i.e., 220°C for 20 min, 220°C for 40 min, and 320°C for 20 min); and (2) comparison of 18 vs. 37 wt.% at three annealing conditions (i.e., 220°C for 20 min, 220°C for 40 min, and 270°C for 20 min). In the former, CdTe solar cells contacted with 18 wt.% exhibited better performance in all I-V categories, with optimal performance (i.e., $V_{oc} = 834 \text{ mV}$ and $\text{Eff.} = 10.9\%$) observed for the film annealed at 220°C for 40 min. In the latter, CdTe devices contacted with 37 wt.% exhibited better performance for 220°C

anneals, whereas the 18 wt.% seemed better at 270°C (see Table I). The statistical significance of these results is yet to be determined.

Table I. I-V Data for CdTe Solar Cells Contacted with Nano-Hg-Cu-Te Dag.

	220°C / 20 min		220°C / 40 min		270°C / 20 min	
	18 wt.%	37 wt.%	18 wt.%	37 wt.%	18 wt.%	37 wt.%
V _{oc}	793	811	813	820	812	799
J _{sc}	20.7	22.5	19.9	23.0	21.7	22.5
FF	57.5	63.8	60.8	66.9	67.4	64.2
Eff.	9.4	11.7	9.8	12.6	11.9	11.5

A preliminary study of sprayed Sb-Te contacts on CdTe was also performed. Although V_{oc} > 800 mV was observed for Sb-Te contacted cells annealed at 300°C, efficiencies in these devices were limited to 9.1%, presumably by a large series resistance (>20 Ω) observed in all samples.

CONCLUSIONS

Nanosized Al and Ag prepared by electroexplosion have been successfully applied as contacts to silicon. The degree of ohmicity of the contact appears to be related to the amount of surface oxide on the particles. Results from preliminary experiments of particulate Hg-Cu-Te and Sb-Te to CdTe contacts are reasonable in the former graphite-based material, whereas the latter spray-deposited material may be limited by a large series resistance.

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REFERENCES

- 1 "Light-Trapped, Interconnected, Silicon-Film Modules," *Final Technical Status Report*, DOE Subcontract #ZAF-5-14142-02, AstroPower Inc., Newark DE.
2. Britt, J.S., and Ferekides, C.S. U.S. Patent 5 557 146, 1996.
3. Romeo, N., Bosio, A., Tedeschi, R., and Canevari, V., "High Efficiency and Stable CdTe/CdS Thin Film Solar Cells on Soda Lime Glass," presented at the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, July 6-10, 1998.