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Nanoparticle Derived Contacts for Photovoltaic Cells

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NANOPARTICLE DERIVED CONTACTS FOR PHOTOVOLTAIC CELLS

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ABSTRACT

Contacts are becoming increasingly important as PV devices move to higher efficiency and lower cost. We present an approach to developing contacts using nanoparticle-based precursors. Both elemental, alloy and compound nanoparticles can be employed for contacts. Ink based approaches can be utilized at low temperatures and utilize direct write techniques such as ink jet and screen printing. The ability to control the composition of the nanoparticle allows improved control of the contact metallurgy and the potential for thermodynamically stable interfaces. Key is the ability to control the interface between particles and between particles and the substrate. We illustrate some of these principals with recent results on Al, Cu and (Hg,Cu)Te. We show for the elemental materials control of the surface can prevent oxide formation and act as glue to control the reactivity of the nanoparticles.
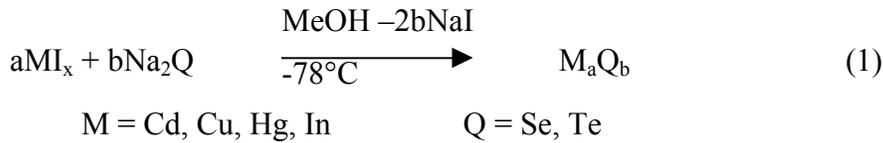
INTRODUCTION

In the areas of both photovoltaics and microelectronics there is an increasing need for improved contacts. At the 1999 Spring Meeting of the Materials Research Society there was an entire symposium on the development of Cu contacts for ICs. Key is that as line width decreases Al, the current standard, is no longer sufficient. Though line widths for photovoltaic cells are not as small as for VLSI, the ability to go to smaller lines increases the active area and thereby increases efficiency. Other concerns in both areas are the stability of the contact and the cost of deposition. In the case of photovoltaics both of these latter concerns are paramount. Because of the environment under which PV devices operate and their expected active life, the stability of all interfaces is especially important. Cost is an increasingly critical issue for increased market penetration of photovoltaics. Meeting the demanding requirements of electrical contact, stability and low cost is not easy for any current technology.

Ink based technologies that can be deposited by low cost ink jet or screen printing approaches have the potential for low cost with adequate resolution for PV applications. By using nanoparticullate precursors as the base for the ink may allow a degree of compositional control needed to meet the electrical and stability requirements. Recent results on Pt have shown that even with a 200 dollar, 300 dpi ink jet it is possible to obtain 80 micron dots [1]. Current ink jet technology can offer at least a factor increase in resolution.

It is important that there are existing approaches that make feasible the production of nanoparticles of elements, alloys, and compounds. For elemental particles there are a number of chemical approaches to their deposition using essentially a redox approach. This approach does not work particularly well for alloy formation especially where metals with significantly different electron affinities are involved. In an alternative approach, we have been exploring an exploding wire technology first pioneered by the Russians [2-5]. In this approach a very high current pulse is put through a small section of wire. In addition, the wire explodes producing small particles. Some of the advantages of the approach are that particles can be created for almost any alloy that can be fabricated into a wire. The surface chemistry can be controlled to some extent by altering the atmosphere during the synthesis or by capturing the particles in a reactive solvent. Some of the disadvantages are that reactive metals can have oxide layers and there can be a wide dispersion in particle size distribution. This synthesis approach is under continuing investigation.

For compound nanoparticles such as CdTe, Cu(In,Ga)Se$_2$, and (Hg,Cu)Te, our group's primary synthetic approach is to react sodium chalcogenide with metal iodides (Eq. 1) or metal tetrafluoroborate (Eq. 2) in distilled, degassed methanol at low temperature [6-8].

$$aMI_x + bNa_2Q \xrightarrow[-78°C]{MeOH -2bNaI} M_aQ_b \qquad (1)$$

$$M = Cd, Cu, Hg, In \qquad Q = Se, Te$$

$$Cu(BF_4)_2 + Na_2Se \xrightarrow{MeOH, 2NaBF_4} CuSe \qquad (2)$$

If there is a suitable pair of salts then the synthesis can produce the desired nanoparticles with a ready separation of the salt as in the NaI in equation one. One great strength of this approach is the ability to produce very complex multi-element stoichiometries very reproducibly.

The nanoparticle approach allows tremendous flexibility in the composition of the particles that is hard to duplicate by other techniques. But the critical issue is how to get the nanoparticles onto the substrate and to form into a continuous contact. Some of the key concerns are:

- Particle Size – the particles need to be as small possible to achieve the highest line resolution (some applications are large area and this may not be as important), to best cover the surface topology and to produce the densest precursors. It is important to minimize the surface contamination on the particle (i.e. oxide or adsorbates) to facilitate further reactions. This may require an active capping of the particles with organic or inorganic protectants. This will also potentially aid with the control of the resultant ink solution properties.
- Ink Formulation – the particles must be integrated into an ink with a rheology appropriate to the delivery system. The particles need to be adequately suspended in the ink and the ink constituents should not impede further processing.
- Ink Deposition – Whether delivered by screen printing or ink jet techniques etc. it is important that the deposition approach is appropriate to the application (i.e. large area or fine line, thick or thin film, etc.).
- Annealing – ideally the ink chemistry would be such as to directly deposit a viable contact at the deposition temperature (typically room temperature to 200 °C). If this is not possible it is important to have the annealing temperature compatible with the materials and construction of the device. To some extent, this can be controlled by the particle size and surface chemistry of the particle. Smaller size particles have higher surface energies that result in lower sintering temperatures and higher reactivities [9]. This can be combined with modifications to the particle surface, which enhances reactivity. We have recently demonstrated and will discuss in this paper the use of a surface with a metalorganic compound that can react at low temperature to glue the nanoparticles together and to the substrate. Incorporation of a component in the ink to activate the surface (by etching for example) may also be useful.

In the remainder of this paper will present data from some recent results on the development of nanoparticle precursors for elemental and compound contacts. The principal examples will be Al for contact to Si, (Hg,Cu)Te for contact to p-type CdTe, and the deposition of nano-Cu films at 200 °C.

EXPERIMENTAL

Nanopowders of Al were obtained from Argonide Corp. after preparation by Russian scientists via the electroexplosion (i.e., exploding wire) process [2-5]. The Al sample was shipped under kerosene. Samples were prepared for TEM by sonication of isopropanol slurries of dried powders. P-type Si (Wacker, 3.3 Ω•cm) was etched with 5% HF and rinsed with deionized water. The samples for annealing studies were prepared by dropping toluene slurries of Al nanoparticles onto the Si substrates using a modified disposable pipette in a He-filled glovebox. The nano-Al on p-type Si samples were annealed at 645-650 °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 activity in the areas where the nanoparticles had reacted but none in the control spots. IV characterization was performed using an Optical Radiation Corporation Solar Simulator 1000 and computer-controlled I-V instrumentation [10].

Hg-Cu-Te materials were prepared by metathesis reactions of metal salts with sodium telluride in methanol (Eq. 1). 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≤10nm), with the HgTe (Coloradoite) phase (PDF #32-665) and Hg, Cu, and Te present, but no C or O [2]. After $CdCl_2$ treatment and NP etch of the CdTe layer, particle contacts were applied to finish the CdTe/CdS/SnO_2/glass solar cells. In this instance, Hg-Cu-Te was mixed with graphite-based and painted onto the CdTe layer, with subsequent thermal treatment under Ar. 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 [6].

RESULTS AND DISCUSSION

1) Elemental Contact Particles and Films

Contacts are ubiquitous in the fields of photovoltaics and microelectronics. Nanoparticle precursors to contacts could have the potential advantages of easy deposition, densification and ready ink formulation for spatially resolved contacts [10]. In addition, nanoparticles offer the opportunity of formulating compound contacts improving both the ohmic nature of the contact and the thermodynamic stability. To explore this we have investigated metallic contacts to Si.

Nanoparticle inks were fabricated from particles produced in Russia by the electroexplosion of Al and Ag wires [10-11]. Typical morphologies are shown in Figure 1. The particles appear to have a bimodal distribution with smaller and a larger component.
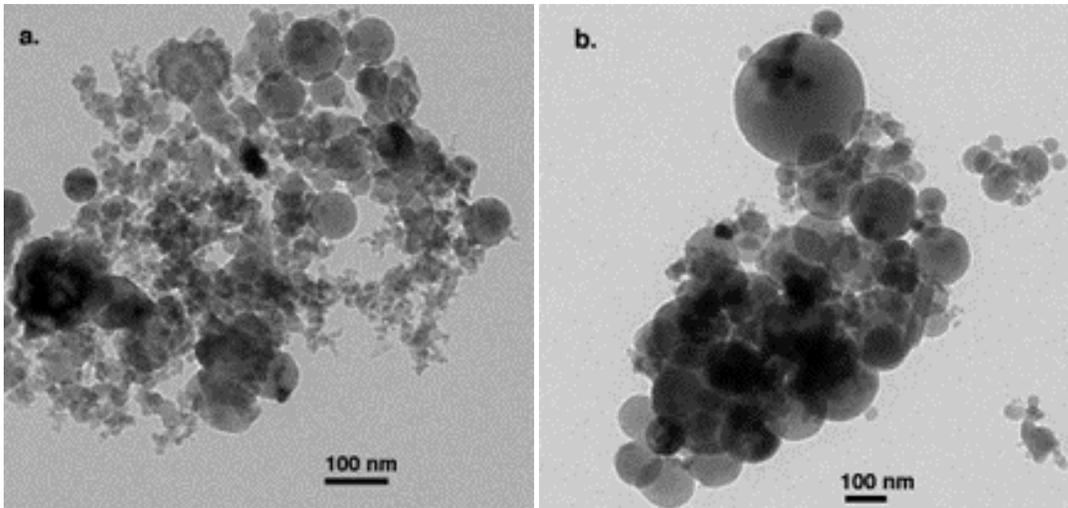
Figure 1: Typical fractions from electroexplosion generated Al particles illustrating a small particle fraction and a large particle fraction.

Contacts were made directly to HF cleaned p-type silicon wafers with Al slurries. Initial results showed non-linear IV indicative on non-ohmic contacts as shown in Figure 2a. This was found subsequently to be due to the presence of oxide layers on the as-synthesized Al nanoparticles as determined by TEM-EDS [10]. Two different approaches were employed to alleviate the problem of this surface oxide.

After either the NREL-developed wet-chemical treatment or the improved Al starting material, 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. 2b) versus untreated Al (Fig. 2a).

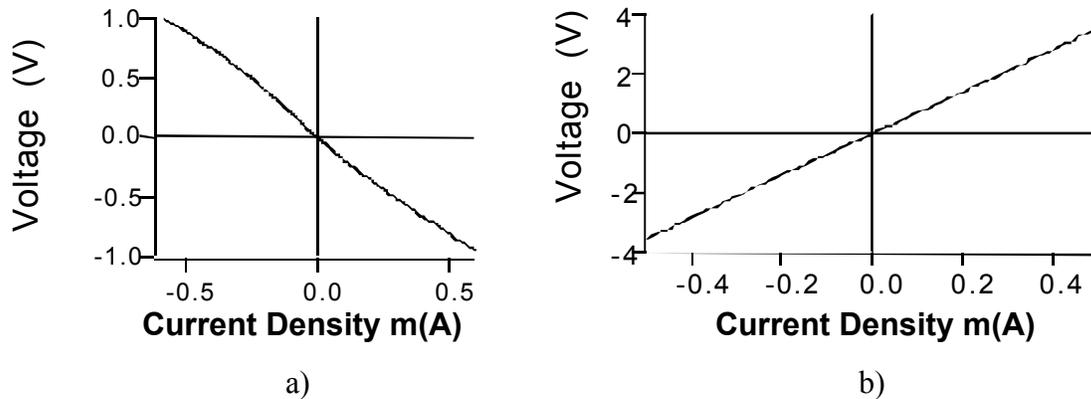a)   b)

Figure 2. I-V characterization of nanoparticle contacts to p-type Si using (a) as-received and (b) chemically-treated nano-Al.

2) Compound Contact Particles and Films

The standard NREL back-contact is a graphite-based Cu-doped HgTe material similar to that described by Britt and Ferekides [12]. 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. 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˚-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 mV and 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. However, cells contacted with 37 wt% had efficiencies up to 12.6%.

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

	220˚C / 20 min 18 wt.%	220˚C / 20 min 37 wt.%	220˚C / 40 min 18 wt.%	220˚C / 40 min 37 wt.%	270˚C / 20 min 18 wt.%	270˚C / 20 min 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

3) Copper Thin Films Spray Deposited At 200˚C

We investigated the application of metals for contacts via the development of inks containing metal nanoparticles, an organometallic bonding agent and appropriate additives to control the rheology of the inks. Initial experiments have been extended from simple slurry deposition of metal nanoparticles (i.e., Al and Ag) to spray deposition of nanoparticle Cu. Accordingly, nano-Cu particles are mixed with a metal-organic Cu complex used in chemical vapor deposition (CVD). Given appropriate conditions, a

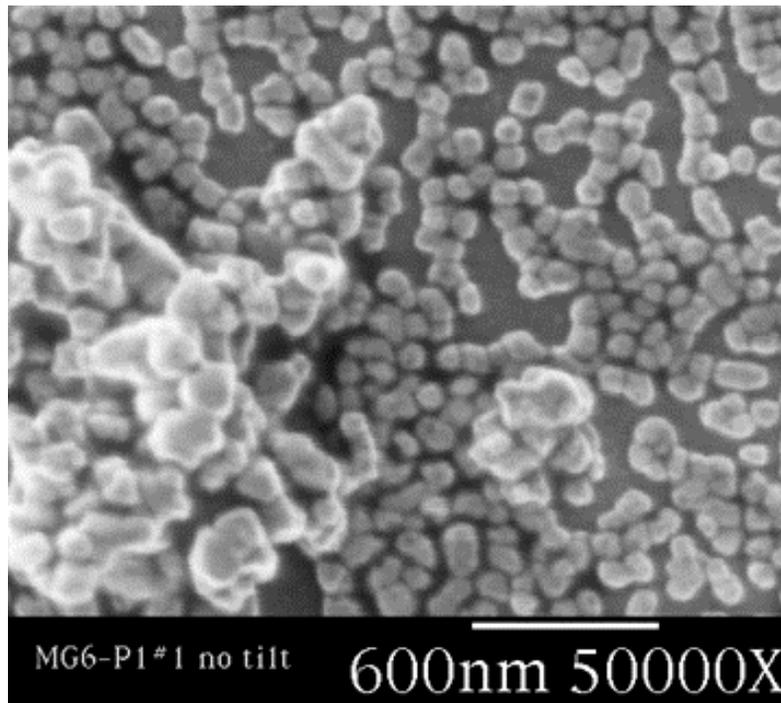MG6-P1#1 no tilt   600nm 50000X

Figure 3. SEM image of a film spray deposited using a nano-Cu/copper complex ink.

nanoparticle derived film is formed as the metal organic complex decomposes to yield a metal bond between neighboring particles (i.e. interparticle) and between particles and the substrate. Steps in this process would approximate those in standard soldering: (1) surface preparation; (2) proximate placing of the components to be joined and, (3) introduction of joining agent.

Several processes occur during the spray deposition of the ink. First, the ink is sprayed onto a wetable heated substrate. As the temperature of the ink droplets increase past the boiling point of the solvent, the solvent is evaporated leaving nanoparticles and the metal-organic complex. Finally, as the temperature increases, the MO complexes react with the FNPs evolving gaseous byproducts. The final reaction of the properly functionalized particle with the MO reaction products continues with neighboring particles joining to form an electrically conductive assemblage. This behavior has already been observed in our lab during initial studies using a deposition temperature of only 200 ˚C. Cu nanoparticles mixed with a copper metal-organic complex in toluene were spray deposited onto both inorganic (i.e. silicon single crystals and molybdenum coated glass) and polymeric (i.e. Kapton tape) substrates. An SEM image of a Cu film grown from an ink containing the both Cu nanoparticles and the copper metal is shown in Figure 3. The deposited film passes a tape test even on the Kapton. Given appropriate formulation, we envision this approach to be applicable to the deposition of small line-widths (<20 μm) using ink-jet technology as well as large area deposition using standard air-atomized spray deposition.

CONCLUSIONS

Current experimental work has demonstrated an ability to produce elemental, alloy and compound nanoparticles. There is an ability to control composition to a high degree and progress toward getting small (<10 nm) monodisperse populations. Particles have been incorporated into inks. These have been subsequently written onto semiconductor substrates and processed into ohmic contacts. It is clear that it will be necessary to actively control the interfacial chemistry to achieve good particle to particle and particle to substrate connections. This has been successfully demonstrated for Al and Cu. This approach should be generally applicable. If the rheology can be appropriately tailored then screen printing or ink jet printing should be able to produce lines with the feature sizes desirable for photovoltaic applications.

ACKNOWLEDGEMENTS

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