

**DEVELOPMENT OF MANUFACTURABLE PROCESS
TO DEPOSIT METAL MATRIX COMPOSITES ON
INVERTED METAMORPHIC MULTIJUNCTION
SOLAR CELLS**

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1 SUMMARY

Metal films imbedded with carbon nanotubes (CNTs), otherwise known as metal matrix composites (MMC), possess reinforced mechanical strength against stress-induced fracture. For the proposed effort, this reinforcement technique is applied to silver (Ag) metal contacts on inverted metamorphic multijunction (IMM) space solar cells. The IMM cells fracture during packaging or after prolonged cycles of temperature fluctuations encountered in low earth orbit operation. This cell fracture leads to cracks in metal contacts, electrically isolating fractured units and subsequently reducing power generation. However, the composite metal contacts are expected to maintain the electrical connection to the fractured units and overall power generation.

During the period of 9/26/2013 – 9/25/2014, we were able to (1) establish an electrodeposition procedure for Ag with bright finish, which is associated with better electrical and physical properties than non-bright finish, (2) increase Ag adhesion strength to gallium arsenide (GaAs) substrates using a titanium (Ti) adhesion layer, and (3) characterize hardness and electrical conductivity of plated Ag before and after rapid thermal annealing. This Ag film characterization provides the baseline to compare with the metal matrix composites (MMCs).

We have been exploring two microstructures for MMCs: Ag/CNT layer-by-layer structure and randomly distributed CNTs in Ag matrix. To electrodeposit CNTs in an alternating fashion with Ag or simultaneously with Ag in an electrolyte solution, we have successfully produced two groups of surface-functionalized CNTs: 1st group with COOH for negative surface charge and 2nd group with NH₂ for positive surface charge. The organic surface functionalization makes CNTs soluble in aqueous solutions and is expected to improve the adhesion strength of CNTs to metal. Nanodiamond conjugation to CNTs also improves CNT dispersion in the aqueous solution, but the transmission electron micrograph (TEM) images of deposited conjugates indicate a wide size distribution for nanodiamonds and nanodiamond agglomeration. Thus, we did not pursue nanodiamond conjugation further.

During the performance period, we have established a protocol to deposit Ag and CNTs in a layer-by-layer fashion as one of the microstructures to consider for improved electrical continuity upon substrate fracture. We observed that the layer-by-layer deposition with COO⁻-terminated CNTs leads to large void fraction in MMCs due to Ag erosion during CNT deposition. The anodic silver erosion occurs while the substrate is biased with positive polarity to attract negatively charged CNTs. Based on the porosity resulting from COO⁻-terminated CNTs, we have decided to focus on NH₃⁺-terminated CNTs in the near future. We plan to explore the two microstructures with different levels of CNT loading; characterize their electrical conductivity and mechanical strength with and without strain; and develop a composite material model based on a finite element method (FEM) that would predictably estimate these physical properties.

2 INTRODUCTION

Electrodeposition of metal, otherwise known as plating, has largely remained an art. While the importance of charge transport in the plating solution is recognized, maintaining or adjusting the solution composition to consistently produce the film of sufficient quality and finish has been challenging in manufacturing. During 2013-2014 performance period, we have primarily focused on silver (Ag) plating on gallium arsenide (GaAs) substrates as the basis of comparison. The electrical and mechanical properties of electrodeposited Ag films constitute the baseline to be compared to those of metal matrix composites (MMCs). Our expectation is that the microstructure of MMC (e.g., layer-by-layer Ag-CNT stack and CNTs randomly distributed in Ag matrix) would strongly govern the mechanical and electrical properties of Ag in such a way to maintain the electrical continuity in metal contacts despite the substrate fracture.

3 METHODS, ASSUMPTIONS, AND PROCEDURES

In this section, we describe the electrodeposition procedure of Ag and surface functionalized CNTs that form the basis of creating MMCs.

3.1 Electrodeposition of Silver

The electrodeposition of Ag is first optimized using a commercially available plating solution. We use E-Brite 50/50 RTP (ready to plate) from Electrochemical Products, Inc. This commercial solution is cyanide-free, whereas traditional Ag plating solutions are cyanide-based typically with a trace amount of sulfur-based brightener (e.g., sodium thiosulfate). While the cyanide-based solutions may provide a superior metal finish, we chose the cyanide-free commercial solution to avoid the toxic properties of cyanide.

Table 1. Manufacturer's suggested optimum plating parameters for E-Brite 50/50 RTP

Category	Optimum	Range
Silver Metal Concentration (M)	0.14	0.10 – 0.17
pH	9.2	9.0 – 9.6
Temperature (°C)	20	16 – 24
J_c (mA/cm ²)	3.2 – 10.8	2.2 – 22.0
J_a (mA/cm ²)		2.2 – 10.8

Many operating parameters (e.g., pH, ionic strength, temperature, and agitation) affect the outcome of plating. For E-Brite 50/50 RTP, the manufacturer's suggested *optimum* plating specifications are given in Table 1. While the tabulated parameters provide guidance, these parameters need to be further tuned for a specific plating bath. In our case, we vary the current density (J_c) on the cathode as the main parameter, while keeping Ag metal ion concentration, pH, and bath temperature constant at 0.14 M, 9.2 and 20 °C, respectively. We use a magnetic stir bar to agitate the plating solution: Mono-Mold magnetic stir bar with a setting of 4 on a Corning Stirrer Hot Plate.

Figure 1 shows the cathode potential (V_c) vs. cathode current density (J_c) with corresponding images of Ag film electrodeposited on GaAs. The abscissa is marked with E, D, L, and H.¹ Point E is 0.6 mA/cm² in our case below which current stops flowing at the equilibrium potential. Point D demarcates the decomposition potential where the electrode reaction begins, and Ag starts to deposit. Point L defines the limiting current density, above which Ag deposition is transport-limited, V_c becomes very unstable, and the plated Ag becomes “spongy.” The region between Point D and Point L defines the ideal operating window where the plated Ag appears bright. *For our plating bath and geometry, J_c of 3 mA/cm² consistently results in a bright finish.* Point H is where hydrogen evolves rapidly, and the hydrogen overvoltage is exceeded.

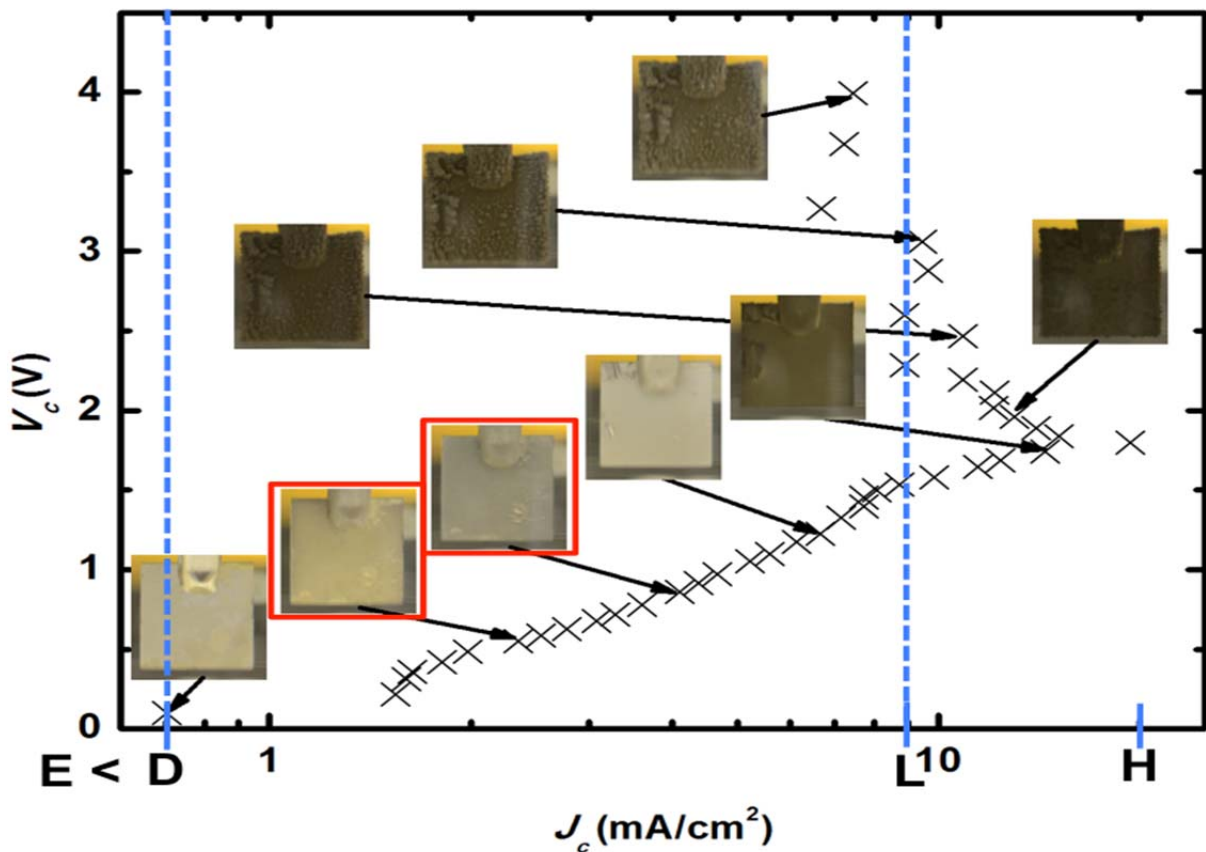


Figure 1. Cathode potential (V_c) vs. cathode current density (J_c).

3.2 Electrodeposition of Multiwalled Carbon Nanotubes

Similar to Ag plating, Figure 2 shows V_c vs. J_c characteristics for COOH-terminated CNTs. In contrast to Ag plating, both V_c and J_c are stable beyond 10 mA/cm^2 . The checkered area is expected to be the optimum operating range. We have been depositing COOH-terminated CNTs at 1 to 2 mA/cm^2 . Above the marked range, V_c rapidly rises with increasing J_c . While the operating current density is comparable to that of Ag, however, the deposited mass of CNTs is much less than that of Ag due to multi-valency of CNTs. Typically, the CNT deposition time ranges from 30 min to an hour, and the resulting thickness is only on the order of $\sim 10 \text{ nm}$. This disparity between Ag and CNT leads to void formation when negatively charged CNTs are being deposited on top of Ag to form a layer-by-layer structure. That is, when the substrate is positively biased, the Ag erosion occurs at a much faster rate than CNT deposition. This void formation will be further discussed in the next section.

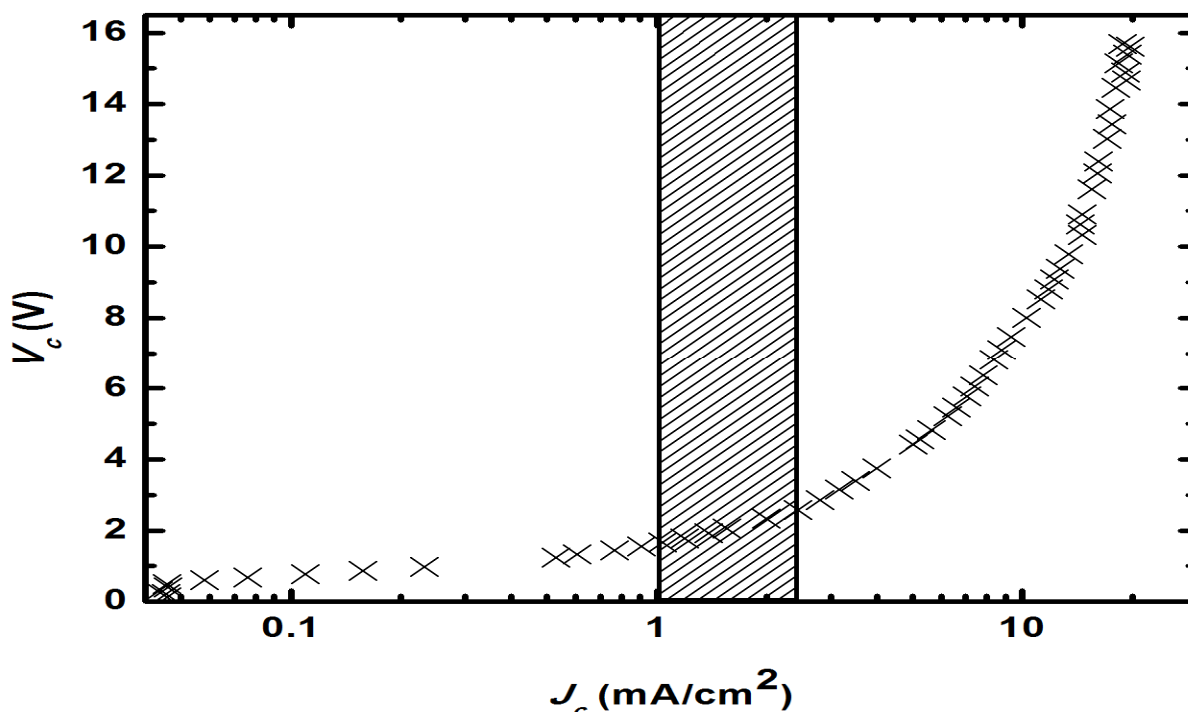


Figure 2. V_c vs. J_c for COOH-terminated MW-CNTs.

4 RESULTS AND DISCUSSION

This section describes the electrical and structural characterization of electrodeposited Ag before and after rapid thermal annealing (RTA). The results from Ag provide the basis of comparison with MMCs. For MMCs, we have first explored a layer-by-layer microstructure, where COOH-terminated CNTs are electrodeposited in an alternating fashion with Ag. We present the structural characterization of MMCs using SEM as well as their mechanical strength characterization under tensile strain by measuring electrical resistivity along MMC lines during mechanical failure.

4.1 Materials Characterization of Electrodeposited Silver

The electrodeposited Ag film is polycrystalline, and its grain size is often small (~ 10 nm)², rendering the film hard but brittle with relatively low electrical conductivity. To increase the grain size, improve the electrical conductivity, and increase the ductility,^{2,3} we anneal the plated Ag using rapid thermal annealing (RTA) under N₂ or 5% H₂ forming gas. We have conducted a series of annealing experiments with different recipes compatible with solar cell manufacturing. The annealing time is kept constant at 5 min, while 4- μ m-thick electrodeposited Ag films are annealed at different annealing temperatures.

Figure 3 shows the results where resistivity decreases, and therefore conductivity increases when the annealing temperature is approximately 380 °C, but any excess temperature reverses this trend (rapid thermal annealing conducted under N₂ or 5 % H₂ forming gas). We also observe that the forming gas annealing improves the conductivity better than N₂ annealing. The resistivity from as-deposited control samples is shown in Figure 3 for comparison. The corresponding scanning electron micrograph (SEM) cross-sectional images in Figure 3 show that

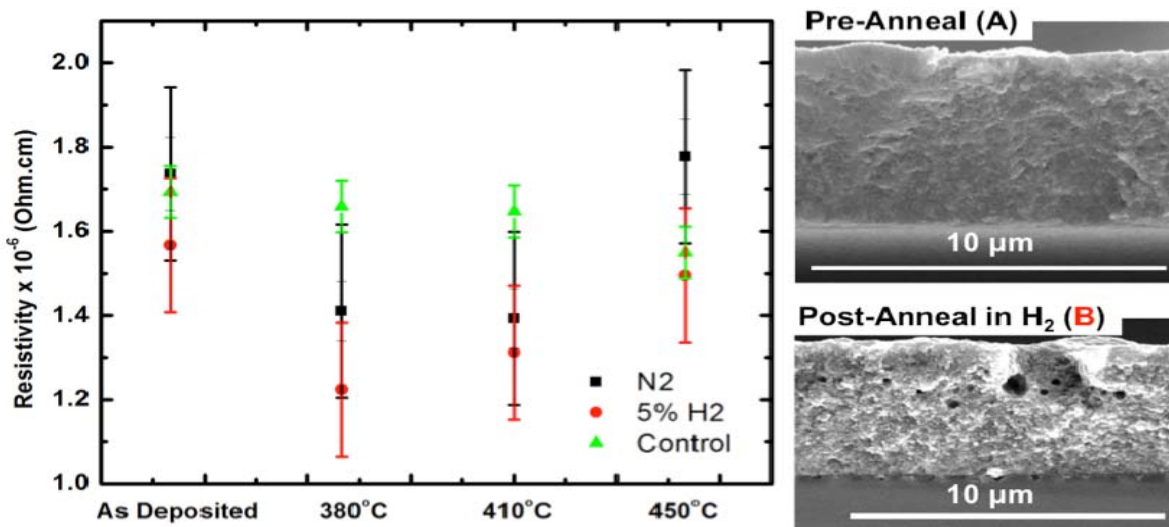


Figure 3. Resistivity of as-deposited and annealed Ag films.

Ag films become porous after annealing, especially in the forming gas (5% H₂) ambient. The voids that form upon annealing in the H₂-based reducing ambient partly explain why the conductivity would eventually suffer with excess temperature or excess annealing time.

In addition to the electrical conductivity, we are currently in the process of measuring hardness (h) and elastic modulus (e) of Ag films before and after annealing, using nanoindentation. These measurements will also be made on MMCs for comparison. We will examine how proper ratios of h and e (e.g., h/e and h^3/e^2) correlate to elastic/ductile failure as well as plastic failure. These mechanical properties will also be compared to the computational modeling in the future.

4.2 Layer-by-Layer Electrodeposition of Silver-CNT Composites

Before exploring NH₂-terminated CNTs, we made use of COOH-terminated CNTs to create the layer-by-layer microstructure. First, we electrodeposit a 1- μ m-thick Ag film on a thin (\sim 10 nm) sputter-coated Ag on GaAs and then electrodeposit a layer of CNTs. The Ag and CNT electrodepositions are repeated three more times to create multi-stack Ag-CNT MMC films ($>$ 4 μ m). The reason that COOH termination is suitable for the layer-by-layer microstructure is that the typical pKa value of COOH groups is approximately 2.3. Therefore, COOH-terminated CNTs are negatively charged in solution pH greater than 2.3. However, this negative surface charge entails that the working electrode must be positively biased (i.e., anode) to deposit CNTs; therefore, the plated Ag dissolves back into the solution during CNT deposition. Depending on the level of Ag dissolution, the CNTs can infiltrate the Ag layer, and conversely Ag can backfill the open void in the CNT-on-Ag stack during subsequent Ag plating. Figure 4 is a scanning electron microscope (SEM) image of CNTs deposited on a 10-nm-thick, sputter-coated Ag on GaAs, in which the Ag dissolution is clearly observed during negatively charged CNT deposition on positively biased working electrode. The thin sputter-coated Ag is used in this case to clearly show the Ag dissolution that reveals the underlying GaAs.

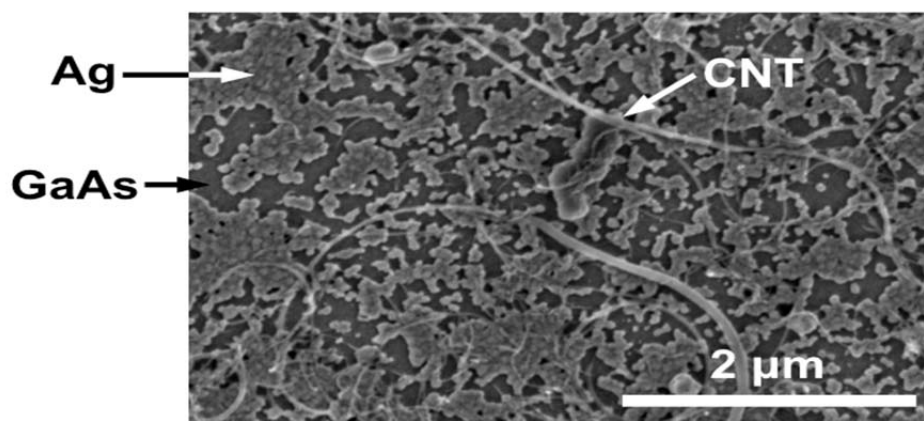


Figure 4. SEM image of COOH-terminated CNT deposited on 10-nm-thick sputter coated Ag.

Counter to our expectation that Ag would backfill the regions that had dissolved into the solution during CNT deposition, the SEM images of layer-by-layer microstructures ($> 4 \mu\text{m}$) in Figure 5 show that some of the voids remain within the MMC. The anode current density (I_c) and CNT deposition time (t), when compared to the SEM images, suggest that increasing current density and/or CNT deposition time leads to increasing porosity within MMC. We attribute the increasing porosity to Ag erosion during negatively charged CNT deposition. Among the three samples we characterized, the porosity increases from MMC3 to MMC2 to MMC1. To characterize the mechanical strength of these samples, the electrical resistance of MMC lines ($2 \text{ cm } l \times 1.5 \text{ mm } w \times 4 \mu\text{m } h$) is measured under tensile strain (i.e., displacement) until the MMC lines plastically fail (Figure 5). Figure 5 also shows the electrical conductivity of Ag lines of equal dimensions during failure for comparison. The results indicate that the intermediate porosity of MMC2 Sample may provide the mechanical strength greater than that of Ag. This result is yet to be repeated and confirmed. While the porous MMCs may provide increased mechanical strength, the porosity may compromise the electrical conductivity of MMCs over a long-term. Therefore, we have decided to pursue NH_2 -terminated CNTs that are positively charged. By maintaining the same polarity as the Ag^+ cations, we expect that the Ag erosion would be eliminated during CNT deposition.

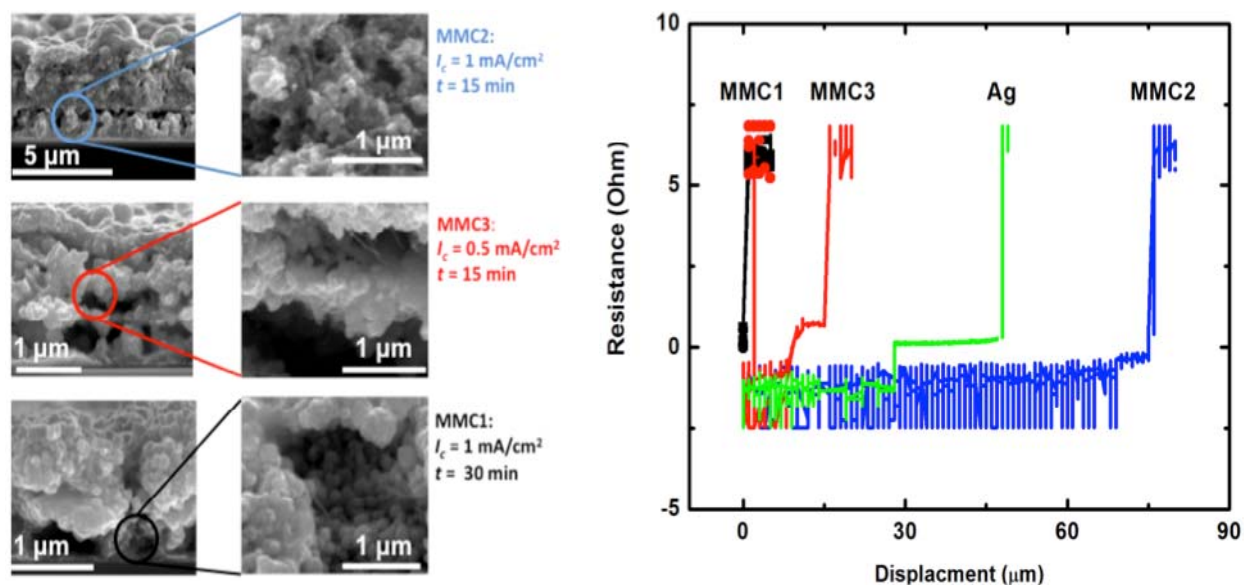


Figure 5. SEM images showing different levels of porosity and the associated resistance as a function of displacement for each case.

We will continue our study of the two microstructures with NH_2 -terminated CNTs: (1) Ag/CNT layer-by-layer structure and (2) CNTs randomly distributed within the Ag matrix. For the random distribution, we will make use of NH_2 -terminated, positively charged CNTs to co-deposit Ag and CNTs simultaneously. Since the optimum pH operating window of E-Brite AgNO_3 -based solution is approximately 9.2, and the typical pK_a of NH_2 is near 9.3, we may have to lower the pH of E-Brite solution by adding an acid or select a different plating solution that operate at a pH much lower than 9.2 to fully protonate the NH_2 groups and maximize the positive charge on CNTs.

5 CONCLUSIONS

During 2013-2014 period, we were able to establish the optimum parameters for Ag electrodeposition, the baseline materials characterization of plated Ag, the synthesis protocol to surface-functionalize CNTs either with COOH or NH₂, and the deposition procedure for Ag-CNT layer-by-layer microstructure. We measured that the conductivity of Ag improves with thermal annealing; however, excess temperature and duration may reverse this improvement. For the layer-by-layer MMC microstructure, we observed that the use of COOH-terminated CNTs leads to pronounced porosity in MMCs due to Ag erosion during CNT deposition. In the near future, we plan to complete the rapid thermal annealing experiments on electrodeposited Ag to understand the ideal temperature and duration to increase the grain size, electrical conductivity, and ductility that are compatible with solar cell manufacturing process. We will also characterize the electrical and mechanical properties of layer-by-layer and randomly distributed Ag-CNT MMCs, using NH₂-terminated CNTs, and compare them with the baseline electrodeposited Ag as well as to the values estimated by a computational approach based on a finite element method.

ENDNOTES

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- ² F. Ren, L. Yin, S. Wang, A. A. Volinsky, and B. Tian, "Cyanide-free silver electroplating process in thiosulfate bath and microstructure analysis of Ag coatings," *Trans. Nonferrous Met. Soc. China*, **23**, 3822-3828 (2013).
- ³ C. Sha and C. C. Lee, "Solid State Bonding of Silicon Chip to Silver Buffer on Copper Substrates," *IEEE T. Compon. Pack.*, **2**, 194-198 (2012).

LIST OF ACRONYMS

Ag – Silver

CNT – Carbon Nanotube

FEM – Finite Element Method

GaAs – gallium arsenide

IMM – Inverted Metatmorphic Multijunction

MMC – Metal Matrix Composite

pKa – Acid Disassociation Constant

RTA – Rapid Thermal Annealing

RTP – Ready to Plate

SEM – Secondary Electron Microscope

TEM – Transmission Electron Microscope

Ti – Titanium

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