

Synthesis and Characterization of One-dimensional Cu-Sn Nanowire Diffusion Couples for Nanowire Assembly and Interconnection

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Abstract—In this work, we show that Cu-Sn based nanowires can be used as a one-dimensional (1-D) diffusion couple to study the atomic diffusion. In order to control the nanosoldering process and form reliable nano-joints (nanoscale interconnects between nanowires), fundamental study of wetting and intermetallic diffusion at the small dimension is necessary. An electrodeposition method is used to synthesize multisegmented nanowires in nanoporous templates in the diameter range of 15-200 nm and length up to 20 μm . By choosing two-segment Sn-Cu nanowires and symmetric three-segment Sn-Cu-Sn nanowires as the model systems in which Sn acts as the solder element and Cu serves as a functional element, we aim to understand the nanoscale soldering reaction along the one-dimension. The morphological evolutions of Sn and Cu segments and Kirkendall void formation in the Cu segment during the oven based soldering process have been observed. The fundamental principles of diffusion kinetics, primarily at a phenomenological level, are discussed. These studies and results provide important understanding in the design, assembly and integration of functional nanowires into nanoelectronics and nanodevices.

Keywords—Nanowires; Soldering; Nanoelectronics; Interconnects; Lead-free; Intermetallic Compounds (IMC)

I. INTRODUCTION

Even though nanotechnology has experienced dramatic development in the past two decades and a wide range of nanomaterials and nanostructures have been synthesized and fabricated, many challenges still remain before reaching the stage of widespread manufacturing and adoption of nanoelectronics and nano-products. Particularly, for the field of nanoelectronic devices, one key challenge is the lack of efficient and effective strategies for the joining and integration of nano-components into functional and complex nanodevices. Nanowires, one-dimensional (1-D) nanostructures that can be composed of metallic, oxide, polymeric, or hybrid structures, face the same challenge as well.[1-3]

The diffusion couple of Cu-Sn (or solder) has been extensively investigated in bulk materials due to its technological importance for electronics packaging applications.[4-9] However, relatively little has been reported on Cu-solder diffusion in nanostructured materials, which exhibit physical and chemical properties distinctively different from bulk materials. Metal diffusion in

nanomaterials is of great interest, yet the detailed dynamic and kinetic behavior of such diffusion remains elusive.

Nowadays, many nanoscale discovery and nanotechnology-driven processes can benefit from the *in situ* transmission electron microscopy (TEM) technique. For example, *in situ* TEM is widely used to investigate the individual nanoparticle behavior, such as nanocrystal aggregates, nanoparticle growth, and electron beam induced nanoparticle morphology change, etc.[10-12] The TEM equipped with *in situ* heating can be used to study the thermal stability, phase transformation, and diffusion at the atomic level.[13, 14] This technique helps people to understand fundamental physical phenomena associated with nanowire or nanotube materials, revealed by following transformations in real time and high resolution.[15]

In this work, we show that Cu-Sn based nanowires can be used as a 1-D diffusion couple to study the diffusion phenomena, in which Sn acts as the solder element and Cu serves as a functional element. Both the Cu-Sn and Sn-Cu-Sn couples are synthesized for thermal treatment in a tube oven or with the *in situ* heating TEM. The morphology and composition change of the nanowire couples were examined by SEM and TEM, which allowed for understanding the differences of diffusion in bulk material and nanomaterials.

II. EXPERIMENTAL METHOD

A. Synthesis of Cu-Sn and Sn-Cu-Sn Nanowire Diffusion Couples

The two-segment Cu-Sn and three-segment Sn-Cu-Sn nanowire diffusion couples were synthesized through a template assisted electroplating method. The detailed synthesis procedure was illustrated in Figure 1. As shown in Figure 1 (a), a piece of polycarbonate porous membrane with nanosized pores was used as a template. The average pore size is around 50-80 nm. One side of the membrane was thermally evaporated and coated with a 200 nm thick Ag film in order to seal the pores and form an electrical conductive thin layer (Figure 1(b)). The nanopores were filled up by either Sn or Cu electrolyte and nanowires grew along the template (Figure 1(c)). For two or multi-segment nanowires, the electrolyte was changed in sequence to obtain the Cu-Sn or Sn-Cu-Sn couples, as shown in Figure 1 (d-e). During the nanowire growth, the electrodeposition density was controlled at 18 mA/cm² and 2 mA/cm² for Sn and Cu,

respectively. The length of each segment was controlled by the electrodeposition time, varied between 30 seconds to 4 min. After the electroplating, the template was dissolved in dichloromethane and nanowires were released in the solution, such as Figure 1 (f). After three cycles cleaning by dichloromethane and ethanol, respectively, the nanowires were stored in the ethanol at room temperature.

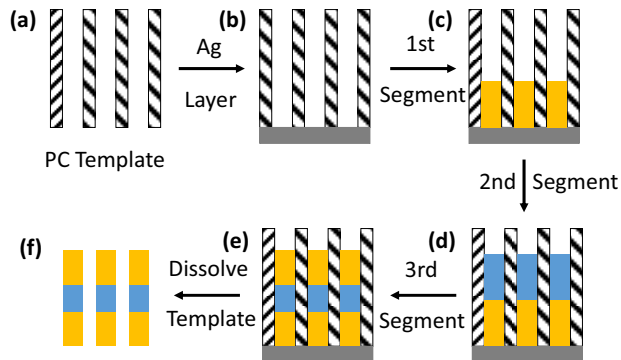


Figure 1. Schematic of Cu-Sn multi-segment nanowire diffusion couple synthesis through a template assisted electroplating method.

B. Thermal Treatment for Diffusion

The thermal diffusion study of the Cu-Sn nanowires was either conducted in a tube oven with nitrogen environment or observed directly by *in situ* heating TEM under vacuum. For the thermal treatment in the tube oven, the nanowire suspension was first drop casted on a piece of Si wafer and dried in the air, then the whole piece of sample was placed in the center of the oven. The temperature was elevated from room temperature to 200 °C in 10 min, and then held at this temperature for another 5 min. After that, the oven was cooled down to the room temperature and the sample was examined by SEM imaging. For the *in situ* TEM observation, the nanowire suspension was dropped on a Mo TEM grid (purchased from Ted Pella) and dried in the ambient environment, which was then mounted onto a Gatan heating holder with rapid heating capability using a Gatan hot-stage temperature controller. All the in-situ TEM experiments were carried out with low dose electron condition (~ 5 pA/cm²) to minimize the beam effect. The temperature was elevated at the rate of 20 °C/min and held at 200 °C for several minutes, and the morphology and structure evolution of the nanowires can be monitored in real time.

C. Materials and Reagents

The polycarbonate membrane with the nominal pore size of 50 nm and thickness of 6 μ m was purchased from Whatman. The electrolytes of Sn (Sn Concentrate with Makeup Solutions) and Cu (Cu U-bath RTU) were purchased from Technic Inc. The dichloromethane (99.9%, Extra Dry, anhydrous) which was used as template dissolving solvent, was purchased from Acros Organics.

D. Instrumentation

The electrodeposition of nanowire growth was carried out by a VersaSTAT 3 electrochemical research system. The Ag layer was thermally deposited using a CHA 6 Pocket Electron Beam Evaporator with the deposition rate between 1 Å ~ 5 Å/s. A JEOL 7401 Scanning Electron Microscope (SEM) was used to characterize the morphology of nanowires. The backscattered mode images were taken to identify the Sn and Cu segment through different contrast in each segment. *In situ* TEM observations of the Cu-Sn nanowire diffusion and intermetallic growth were performed using a JEOL JEM2100F TEM operated at 200 kV. The Energy-dispersive X-ray spectroscopy (EDS) mapping was used to evaluate the element distribution of Cu and Sn along the nanowire.

III. RESULTS AND DISCUSSION

A. Cu-Sn based Nanowire and Diffusion Couple

The multi-segment nanowires were designed as diffusion couples to study the 1-D diffusion. Since the diameter of nanowires was controlled between 100-150 nm (based on the template selection), and the naturally formed surface oxide serves as a good confinement layer of the inner metallic materials, the diffusion can be well controlled only along the axial direction. Figure 2 shows SEM images of Cu-Sn nanowire diffusion couples before and after the thermal treatment. The electroplating method provides a clear interface between the Cu and Sn segments in the diffusion couple, maximally eliminating impurities which would affect the atomic interdiffusion and intermetallic formation. Since the atomic number of Sn is larger than Cu, the Sn segment usually shows brighter in the SEM backscattered mode images due to the heavier atom of Sn than Cu, as shown in Figure 2(a). The first growing segment, such as Cu, shows a thinner diameter than the Sn segment. One possible reason is that: during the Ag layer thermal deposition process (Figure 1 (a-b)), some of the Ag was deposited into the channel and thinned channels occurred for the nanowire growth. And the non-uniform wire shape would slightly affect the diffusion, especially in the symmetrical Sn-Cu-Sn nanowires.

The melting temperature of bulk Sn is 231.9 °C, and it was reported that the melting temperature of Sn nanowire was 231.2 °C.[16] Therefore, the thermal treatment at 200 °C would not result in the melting of Sn. Hence, the entire reaction in the Cu-Sn nanowire was controlled by a solid-state interdiffusion process. After the thermal treatment at 200 °C for 5 min, the Cu-Sn nanowire exhibited some change in morphology, and the diameter of nanowires became more uneven. From Figure 2(b), the contrast difference between the Cu and Sn segments cannot be distinguished, which indicated that the interdiffusion between Cu and Sn was significant during the thermal treatment. However, the 1D morphology of the nanowires was still maintained because of the effective confinement by the surface oxide covered on the metallic Cu and Sn, for which we can model the system as a 1-D diffusion couple.

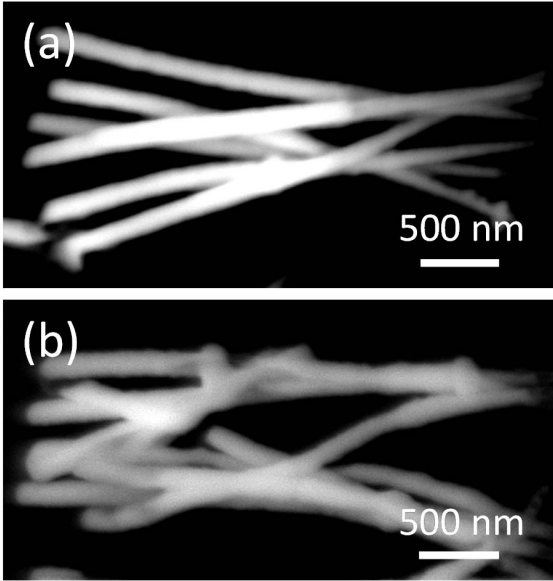


Figure 2. SEM images of Cu-Sn nanowire diffusion couple (a) before and (b) after the thermal treatment at 200 °C for 5 min.

B. *In situ* TEM Observation of Intermetallic Layer Formation and Growth

The detailed diffusion induced growth of the intermetallic layer in the Cu-Sn nanowire was observed under *in situ* TEM at 200 °C, as shown in the Figure 3. Due to the low dose electron condition (5 pA/cm²), the electron beam effect on nanoparticle motion is a few orders of magnitude smaller than the thermal effects, hence, the effect of electron beam on the Cu-Sn nanowire, including local heating, direct momentum transfer from the e-beam and charging, is negligible. [17]

At the ambient temperature (t=0 min), the Cu and Sn segment interface can be distinguished through the contrast in the bright field TEM image, as marked in the red arrows. When the Cu-Sn nanowire was heated and held at 200 °C, the surface oxide perfectly confined the migration of metallic atoms inside the nanowire. Because it took 10 minutes for the heating holder to ramp to 200 °C, an intermetallic layer was formed between the Cu and Sn segment before the temperature reached 200 °C. The structure of the intermetallic layer was confirmed from the previous study that the initial intermetallic layer is η-phase (Cu₆Sn₅) induced by the interdiffusion of Cu and Sn.[18] Hence, there are two interfaces exist along the nanowire, which are Cu-Cu₆Sn₅, and Cu₆Sn₅-Sn interfaces, respectively. After 1 min of heating at 200 °C, it is obviously noticed that the Cu-Cu₆Sn₅ interface shifted to the Cu side. The observed interface shifting to the Cu side indicated that Cu was the more rapidly diffusing species at the beginning. The η-phase intermetallic Cu₆Sn₅ was very easily formed at relatively low temperature. And once it was formed, the Cu₆Sn₅ serves as diffusion barrier between the Cu and Sn segments. In order to continue the metallurgical reaction and form more Cu₆Sn₅, both the Cu and Sn would overcome the barrier layer and migrate

towards the Cu₆Sn₅. Therefore, it is observed that the Cu/Cu₆Sn₅ interface shifts towards the Cu segment and Cu₆Sn₅/Sn interface shifts towards the Sn segment with time. After heating for 6 min, the intermetallic layer has grown to nearly one third of nanowire in length. It can be assumed that the continued growth of η-phase intermetallic was largely controlled by diffusion of both Cu and Sn through the Cu₆Sn₅ layer.

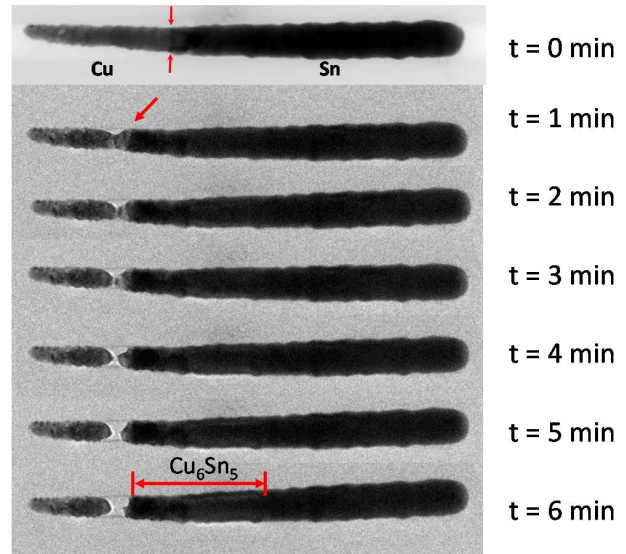


Figure 3. *In situ* HRTEM observation of the morphological evolution of a single Cu-Sn nanowire diffusion couple at 200 °C. The original interface and void formation in the Sn and Cu segments is denoted by red arrows. The η-phase intermetallic was labeled in red at t=6 min.

After the IMC formation, it is observed that the Kirkendall void formed. Since the Cu concentration gradient is considered as the driving force of dissolution of Cu atoms, the relative short Cu segment would result in the low concentration of Cu and the void would grow larger with longer time (t = 1 ~ 6 min), as shown in the Figure 3. The void would shut off the supply of Cu atoms from the left end of the nanowire.

C. Elemental Analysis of 1-D diffusion Couple

In order to study the nanowire joining and interconnect possibility, the symmetrical structure of Sn-Cu-Sn nanowire couple was synthesized. The elemental analysis of a single Sn-Cu-Sn nanowire diffusion couple was performed by the EDS mapping under TEM. Figure 4 shows the dark field TEM image of Sn-Cu-Sn nanowire corresponding with the elemental distribution of Cu (red) and Sn (green) in the as prepared Sn-Cu-Sn nanowire. It is observed that there is a slightly overlap area at the two Cu/Sn interfaces, indicating the interdiffusion of Cu and Sn occurred at room temperature. There are two possible reasons for the diffusion occurring at room temperature: (1) the electrical transport during the electroplating would result in the atomic migration between the interfaces of the two segments;[19] (2) the interstitial diffusion mechanism of Cu in Sn.[20] Previous study found

that this initial atomic level diffusion at room temperature does not form any intermetallic compound. [18]

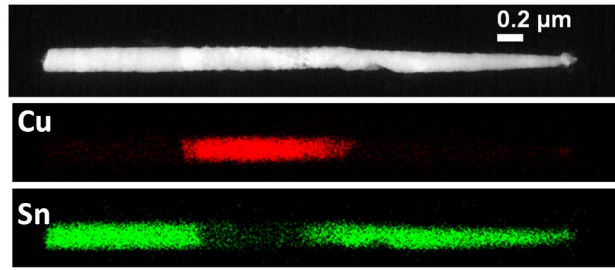


Figure 4. EDS mapping analysis of Sn-Cu-Sn nanowire diffusion couple at room temperature.

According to the Boltzmanm-Matano method, the concentration dependent interdiffusion coefficients can be theoretically estimated if the position of the Matano plane is known (e.g., the Matano plane can be the origin of the x-axis at the interface of the diffusion couple, or the x coordinates can be determined by the experimental measurement).[21] For this Cu-Sn binary nanowire diffusion couple, the interdiffusion coefficients will be experimentally obtained by using the EDS line mapping method. By scanning and measuring the profile of the diffusion elements of Cu and Sn through the EDS line mapping, the concentrations of C_{Cu} and C_{Sn} along the diffusion couple, can be measured by the in-situ TEM experiments, thus the diffusion coefficient can be further determined.

D. Investigation of Diffusion models for 1-D diffusion

In order to better understand the 1-D diffusion along the nanowires, mathematic model development is necessary to evaluate the diffusion properties, such as diffusion coefficient and intermetallic growth rate. Many studies have been carried out to investigate the interfacial reaction and diffusion in downsizing solder joint with the Cu substrate in the bulk material, which are mainly limited to the micron size scale. Figure 5 (a) shows the schematic diagrams of a typical Cu_6Sn_5 grains formed in a Cu-Sn diffusion couple in bulk material (top-view). The Cu_6Sn_5 intermetallic is a primary feature in the microstructure of solder joints such as SAC 305 alloy. The grain structure of the intermetallic layer has an important effect on diffusion. In the bulk material study, the η -phase layer shows scallop geometry and the average grain size ranges from few micron to hundreds of micron.

It is believed that the interfacial reaction in solder joints is a dynamic response to a combination of effects of intermetallic compound growth, consumption of Cu substrate and composition variation at the interface.[5] Most of the mathematic models were established from the analysis of flux of Cu atoms during the diffusion. Figure 5 (b) illustrates the interfacial Cu fluxes between the scallop-shaped intermetallic grains and solders. In Figure 5 (b), J_1 represents the Cu flux diffusing along the grain boundaries from the Cu substrate into the Cu_6Sn_5 /solder interface zone; J_2 represents the Cu flux diffusing from the Cu substrate to the

Cu_6Sn_5 /solder interface zone via bulk diffusion, which is also called volume diffusion; J_3 represents the Sn fluxes diffusion along the grain boundaries into the Cu_6Sn_5 /solder interface, and J_4 represents the volume Sn/solder into the Cu_6Sn_5 /solder interface, respectively. In the bulk materials, J_1 is considered to be dominant because the consumption of the Cu substrate is a grain boundary controlled process. The total flux through the η -phase is the sum of grain boundary and volume diffusion of Cu and Sn, and then typically, the Fick's law would be used to derive the diffusion coefficient. Based on the different assumptions, the Fick's law and its derived equations would be accordingly modified, hence, the calculated diffusion coefficient and growth rate would be more or less different.

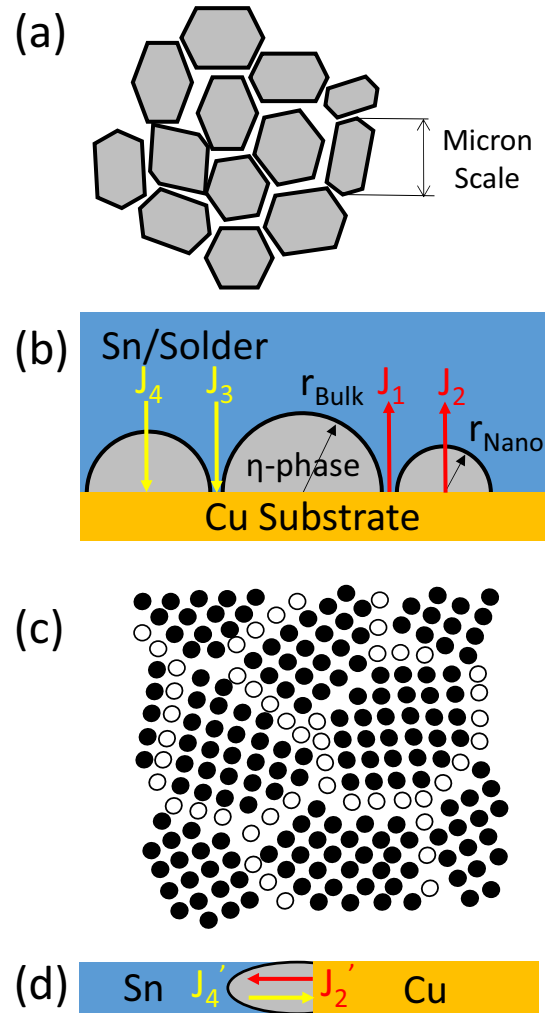


Figure 5. Schematic diagrams of Cu-Sn diffusion couple in traditional 2-D view and nanocrystal diffusion. (a) Top-view of the Cu_6Sn_5 intermetallic grain formed in the bulk Cu-Sn diffusion couple; (b) Cross-section of scallop shape Cu_6Sn_5 intermetallic grains and interfacial Cu and Sn fluxes; (c) Schematic view of a nanocrystalline material; (d) Proposed 1-D diffusion model along a single Cu-Sn nanowire.

Most of the nanomaterials were synthesized through bottom-up method and the grain size (also can be described as nanocrystal for nanomaterials) ranges between few nanometers to hundreds of nanometers, which is nearly 3 orders smaller than that of bulk materials. Figure 5 (c) shows the schematic structure of a two-dimensional nanocrystalline material. The nanocrystals are illustrated by full circles in different crystallographic orientations and open circles around the crystal boundaries. Due to the crystal misorientations and boundary inclinations, the atomic structure of each core region of the boundaries between the crystallites is different. The reduced atomic density and interatomic spacing deviating from those crystallites result in the boundaries. In nanomaterials a large amount of atoms is located in grain boundaries or interfaces, hence, the grain boundaries and interfaces are high-diffusivity paths. Although there is some assumption that grain-boundary diffusion plays no significant role at ambient temperature in bulk materials, this may not be true for nanostructured materials.

Jiang *et al* had derived a grain size-dependent diffusion model based on the well-known Arrhenius dependence for intrinsic diffusion coefficient of interdiffusion $D(r, T)$. It is found that as the size of the nanocrystals decreases, the diffusion activation energy of atoms decreases and the corresponding diffusion coefficient strongly increases due to the Arrhenius relationship between them, which leads to evident diffusion at room temperature.[22] This can also explain the Cu-Sn nanowire diffusion occurring at ambient temperature, which has been discussed in the EDS mapping analysis.

The nanowire growth through the electroplating method typically shows the polycrystalline structure and the grain size is current density dependent, ranging from several nanometers to tens of nanometers.[23] Since the diameter of each nanowire is usually less than a hundred nanometers, when the grain grows at high temperature and diffusion takes place, the intermetallic segment formed between the diffusion couple can be seemed as one grain, so the diffusion along radical direction and the grain boundary diffusion can be neglected. Hence, the dominant Cu and Sn fluxes are simplified as the diffusing fluxes of Cu and Sn into the η -phase, labeled as J_2' and J_4' , respectively in Figure 5 (d).

Furthermore, there are several challenges in the investigation of 1-D diffusion models:

1. Understand the precise mechanism of diffusion in the nanomaterials is still very difficult. Due to the extremely small size of nanomaterials, the observation of diffusion phenomenon at the atomic level is very difficult. The atomic level diffusion could occur during the material synthesis, storage and react at ambient temperature, which are hardly observed. Although *in situ* techniques has been increasingly utilized, changes in the nanometer scale can be hardly noticed and captured in a very short period of time, especially at elevated temperatures. On the other hand, TEM is only focused in a single nanoparticle or nanowire, which sometimes cannot represent the behavior of the entire sample. In addition, due to the features of nanomaterial synthesis, the uniformity of nanoparticle or nanowire is

difficult to control, which brings more difficulty to analyze the mechanism of diffusion precisely.

2. The experimental data can be difficult to correlate to the computational data. The computational data, such as models were usually established based on many assumptions and neglected many realistic problems. However, the experiment has to face the issues. For example, the 1-D nanowires were synthesized through template, so the geometry of the template affected the uniformity of the nanowires. Specifically, the Cu-Sn diffusion couple in this study always shows shaper on one end, while the model would assume that the geometry of the nanowire is a perfect cylinder; the nanowire would naturally form an oxide layer which confined the metallic atoms inside, while the computational simulation typically would not consider the oxidation layer effect. Hence, the computational data would not perfectly represent the real situation in the experiments.

Further detailed study of the correlation between experimental and computational data will be conducted to better understand the Cu-Sn nanowire diffusion system.

IV. CONCLUSION

Multi-segment Cu-Sn based nanowire diffusion couples were successfully synthesized via a template assisted electrodeposition method. These 1-D nanowires showed the atomic diffusion and behaved similar to the bulk material. It is found that the Cu-Sn interdiffusion occurred at room temperature and the high temperature would result in the η -phase intermetallic growth and Kirkendall void formation. The simplified diffusion model based on the volume diffusion of Sn and Cu can be used to represent the 1-D nanowire diffusion, without considering the grain boundary diffusions.

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