Low-Temperature Copper Bonding Strategy with Graphene Interlayer

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Supporting Information

ABSTRACT: The reliability of lead-free Cu bonding technology is often limited by high bonding temperature and perpetual growth of intermetallic compounds between Sn solder and Cu substrate. Here, we report a low-bonding-temperature and highly reliable Cu bonding strategy with the use of graphene as an interlayer. By integrating a nanoscale graphene/Cu composite on the Cu substrate prior to thermocompression bonding, we observe a macroscale phenomenon where reliable Sn–Cu joints can be fabricated at a bonding temperature as low as 150 °C. During the bonding process, nanoscale features are replicated in the Sn solder by the Cu nanocone array morphology. Compared to microscale Sn, nanoscale Sn is mechanically weaker and thus can distribute on the Cu substrate at a much lower temperature. Furthermore, insertion of a graphene interlayer, which is one atom thick, can successfully retard the intermetallic compounds’ growth and preserve a high bonding yield, following 96 h of aging, as confirmed through SEM and shear strength analyses. Our graphene-based Cu bonding strategy demonstrated in this work is highly reliable, cost-effective, and environmentally friendly, representing a much closer step toward industrial applications.

KEYWORDS: integrated circuit packaging, copper interconnects, tin solder, copper nanocone array, graphene

Bondering technology is indispensable in electronic packaging, as it provides mechanical support and electrical interconnections between semiconductor chips. Reliability of bonding joints greatly influences the power consumption and performance of electronic systems, and thus it is essential to have a reliable bonding technology, especially when packaging density dramatically increases with device scaling. Copper (Cu) is the mainstream interconnect material, owing to its superior conductivity, in the existing complementary metal oxide semiconductor (CMOS) technology. Lead–tin (Pb–Sn) eutectic was once a popular solder material in Cu bonding technology, the most widely used bonding technique, with a bonding temperature as low as 183 °C. Nevertheless, Pb is very hazardous and its usage in electronic products has been restricted by the European Union in 2003, spearheading the exploration of lead-free solders such as Sn–Ag–Cu and Sn–Cu eutectics. To date, after more than a decade of research efforts, lead-free Cu bonding technology has been entangled in two critical issues limiting its reliability: high bonding temperature (∼260 °C) and aging degradation. The prior issue increases not only the thermal budget of chip fabrication but also the failure rate for temperature-sensitive chips. The latter issue, induced by excessive growth of brittle intermetallic compounds (IMC) between the Sn solder and Cu substrate, significantly reduces the lifetime of bonding joints. To overcome these issues, a number of approaches have been attempted including ultrasonic bonding, electrochemical deposition of metal nanostructures, and metal sacrificial layer (Au or Ni). Despite the effectiveness of these approaches in addressing either one of the issues, a solution that concurrently solves both issues remains elusive.

Here, we report a simple Sn–graphene–Cu-based bonding technology that is of low bonding temperature and high reliability. We electrochemically deposit a layer of Cu nanocone array on the Cu substrate and cover it with a graphene sheet,
prior to thermocompression bonding. When subjected to heat, microscale Sn solder deforms and replicates the Cu nanocone array morphology, hence introducing nanoscale features in Sn. It is worth noting that the mechanical strengths of nanoscale Cu and Sn have opposite dependence on their sizes. "Smaller is stronger" for nanoscale Cu and "smaller is weaker" for nanoscale Sn, due to the much lower melting point of Sn and facile surface diffusion. Since nanoscale Sn is weaker than its microscale form, lower energy is required for it to deform and uniformly distribute on the Cu substrate, forming Sn–Cu metallurgical bonds. In contrast, the Cu nanocone array does not deform at the same temperature due to its higher melting point and ultrahigh strength. This phenomenon effectively contributes to a lower bonding temperature in our bonding technology. On the other hand, by inserting graphene, a one-atom-thick carbon sheet that is highly conductive and mechanically robust, as an interlayer between Sn solder and Cu substrate to retard the growth of IMCs, effectively impedes the aging issue. Notably, a monolayer graphene sheet is capable of protecting the underlying Cu substrate from oxidation and diffusion. In addition, a graphene–Cu-layered composite has a superior mechanical strength, thermal conductivity, and resistance to fatigue damage compared to Cu of the same dimension, as the graphene interlayer blocks dislocations in Cu. Through shear strength analyses, we demonstrate that, for the same aging duration, the shear strength of Sn–Cu joints degrades by 2-fold, while insertion of a graphene interlayer successfully preserves the shear strength of Sn–Cu joints, with no observable degradation, confirming that our bonding technology is highly reliable. Importantly, our lead-free Cu bonding technology creates reliable bonding joints at 150 °C, which is lower than that in harmful lead-based Cu bonding technology (183 °C).

RESULTS AND DISCUSSION

In our low-temperature Cu bonding technology, the fabrication of a nanoscale graphene/Cu composite involves only three steps: deposition of the Cu nanocone array (NCA) and synthesis and transfer of graphene. Figure 1 illustrates how the fabrication processes of the nanoscale graphene/Cu composite can be integrated into the Cu bonding technology (see Methods for details). Large-area monolayer graphene was first synthesized on a Cu foil using low-pressure chemical vapor deposition (LPCVD) (Figure 1a). A layer of polymer was spin-coated on the synthesized graphene as a support layer followed by etching of the Cu foil (Figure 1b). Subsequently, an annealed Cu nanocone array (Cu NCA) substrate is used to fish out the polymer-supported graphene film. The polymer is then removed in a solvent, resulting in a graphene-coated Cu NCA substrate. (c–f) Photographs of a commercial C194 Cu substrate (2 cm × 1 cm), an as-fabricated Cu NCA substrate, an annealed Cu NCA substrate, and a graphene-coated Cu NCA substrate. (g) A commercial bonding tester is then used to solder the Sn–Ag–Cu eutectic to the graphene-coated Cu NCA substrate. (h) Illustrated zoomed-in view of a good Sn–graphene–Cu bond. Schematics shown in (g) and (h) are only for illustration purposes, and the features are out of scale.
supported graphene film. The sample was initially blow-dried with N₂, followed by 80 °C oven-baking. After that, the polymer support layer was removed in the solvent, leaving behind a graphene-coated Cu NCA substrate (Figure 1f).

Finally, a commercial bonding tester was used to solder a Sn–Ag–Cu eutectic (760 μm diameter) to the graphene-coated Cu NCA substrate, by applying a constant force of 1500 gf (~14.7 N) to the substrate for 5 min at 150 °C (Figure 1g). In this study, a Sn–Ag–Cu eutectic was chosen, as it is the most promising substitute for Sn–Pb solder among hundreds of lead-free candidates.22–24 Figure 1h shows an illustration of a good Sn–graphene–Cu soldering joint. It is worth noting that direct synthesis of monolayer graphene on the Cu NCA substrate is currently challenging, as the nanocone structures would have collapsed at the present graphene growth temperatures (Figure S1b).

We have been able to observe a 100% bonding yield in our Sn–graphene–Cu joints fabricated at low bonding temperatures (150–160 °C) and that is maintained even after 96 h of aging. For this study, we define bonding yield as the ratio of solder joints with shear strength greater than 20 MPa to the number of solder joints tested. Specifically, from previous studies, 20 MPa has been considered as the minimum shear strength for an effective bonding between the Cu NCA and the Sn–Ag–Cu solder.25 In this research, bonding yield remains 100% if we slightly increase the shear strength criterion to 25 MPa, as shown in Figure S2a. To extract the shear strength of each bond, we conducted a shear strength test using a Rhesca PTR-1101 commercial bonding tester. As illustrated in Figure 2a,b, a bonding tip was first brought to the side of a bonded Sn solder and then set to move horizontally with increasing force. The tip stops moving once the Sn solder was levered, and the bonding tester records the shear force required. Shear strength of a bond can be extracted by taking the maximum shear force required to lever the Sn solder and dividing by the measured area size of the bond. (c) Bonding yield of the Sn–graphene–Cu bond as a function of bonding temperature. Each group of data was collected from 30 bonds. (d) Shear strength distribution of both the Sn–Cu and Sn–graphene–Cu bonds as a function of bonding duration. Each average value was collected from five bonds. (e) Shear strength distribution of the Sn–Cu bonds as a function of aging duration. The average shear strength degrades with aging duration up to 2-fold for only 96 h of aging. (f) Shear strength distribution of the Sn–graphene–Cu bonds as a function of aging duration. Our Sn–graphene–Cu bonds are very robust and show no degradation in terms of average shear strength, after the same 96 h of aging.

Figure 2. Shear strength test results of our Sn–graphene–Cu bonds. (a, b) Schematics showing how a shear strength test is performed. A bonding tip is first brought to the side of a bonded Sn solder (a) and then set to move horizontally with increasing force. The tip stops moving once the Sn solder was levered (b), and the bonding tester records the shear force required. Shear strength of a bond can be extracted by taking the maximum shear force required to lever the Sn solder and dividing by the measured area size of the bond. (c) Bonding yield of the Sn–graphene–Cu bond as a function of bonding temperature. Each group of data was collected from 30 bonds. (d) Shear strength distribution of both the Sn–Cu and Sn–graphene–Cu bonds as a function of bonding duration. Each average value was collected from five bonds. (e) Shear strength distribution of the Sn–Cu bonds as a function of aging duration. The average shear strength degrades with aging duration up to 2-fold for only 96 h of aging. (f) Shear strength distribution of the Sn–graphene–Cu bonds as a function of aging duration. Our Sn–graphene–Cu bonds are very robust and show no degradation in terms of average shear strength, after the same 96 h of aging.
required shear force. The shear strength of each solder joint was then calculated by taking the maximum shear force required to lever the Sn solder and dividing by the measured area size of the solder joint.

More than 210 Sn–graphene–Cu bonds were fabricated at seven different bonding temperatures (130, 140, 150, 160, 170, 200, and 230 °C). Each bonding yield was collected from at least 30 bonds. Figure 2c shows the bonding yield of our Sn–graphene–Cu bonds, when they were as-fabricated and aged, as a function of bonding temperature. For comparison, we have fabricated the same amount of bonds at each bonding temperature using the same approach, but without the graphene interlayer, namely, Sn–Cu bonds, and the bonding yield of Sn–Cu bonds is plotted in Figure S2b. As can be seen from Figures 2c and S2b, the bonding yield of both Sn–graphene–Cu and Sn–Cu bonds shows a consistent trend. Specifically, the bonding yield increases with temperature initially and achieves 100% when the bonding temperature rises from 150 °C. This observation is supported by an earlier study that proved that the creep rate of the Sn–Ag eutectic increases with temperature and shows an abrupt increase at 150 °C. In addition, Tian et al. found that nanoscale Sn deforms based on diffusional plasticity such as Nabarro-Herring or Coble creep. As discussed earlier, a solid Sn solder requires a certain amount of energy to deform and uniformly distribute on the Cu substrate. At 150 °C, the sudden increase in Sn creep rate allows it to distribute at a faster rate on the Cu substrate, forming Sn–Cu metallurgical bonds. Consequently, the Sn–Cu bond fabricated at 150 °C is strong with relatively high yield. Apart from that, in the absence of Cu NCA, Sn–Cu bonds between the Sn solder and flat Cu substrate are normally fabricated at temperatures higher than 220 °C because the Sn solder is hard and does not deform well below 220 °C. We note that the Sn solder deforms at a lower temperature in our bonding technology as the melting point of Sn systematically reduces with decreasing size. For example, the melting point of a Sn particle with 10 nm diameter is only ~160 °C. On the other hand, for bonding temperatures higher than 180 °C, the bonding yield of both Sn–graphene–Cu and Sn–Cu bonds drastically drops with increasing temperatures (Figures 2c and 2d). This phenomenon can be attributed to the partial collapse of Cu NCA as the tensile strength in Cu becomes weaker and weaker when temperature increases. All bonds were then subjected to a 96 h aging, and the bonding yield of aged bonds is also plotted in Figures 2c and S2b, for comparison purposes. Typically, the bonding yield of aged bonds is much lower compared to that of as-fabricated bonds. However, the bonding yield of aged Sn–graphene–Cu bonds fabricated at 150 and 160 °C remains at 100%, while that of all aged Sn–Cu bonds shows severe degradation, regardless of the bonding temperature. These results suggest that the insertion of a graphene interlayer at the Sn–Cu bonds plays a significant role in impeding the aging degradation issue.

We further note that the shear strength of each bond strongly relies on the bonding duration. In Figure 2d, we compare the as-fabricated shear strength of both Sn–graphene–Cu and Sn–Cu bonds made with different bonding duration, varying from 1 to 5 min. Each group of data was collected from five bonding joints. We observe that the as-fabricated shear strength of both types of bond increases with bonding duration. For 5 min of bonding duration, the average shear strength of Sn–Cu bonds (42 ± 4 MPa) is slightly larger than that of Sn–graphene–Cu (34 ± 6 MPa), when the bonds were freshly made. These results suggest the presence of graphene indeed hindered Sn and Cu from bonding with each other, but as the thickness of graphene is only one atomic layer, such effect is minor, and effective bonds can still form when the bonding duration is 4 min or longer. On the other hand, the average shear strength of Sn–Cu bonds degrades by 2-fold following 96 h of aging (Figure 2e). In contrast, our Sn–graphene–Cu bonds are very robust and show no observable degradation in terms of average shear strength, following the same 96 h of aging (Figure 2f). These observations show that, with the presence of a one-atom-thick graphene interlayer, the aging degradation is effectively avoided.

To understand how the insertion of a graphene interlayer at the Sn–Cu bonds helps in addressing the aging degradation issue, we performed a series of scanning electron microscopy...
SEM analyses on both Sn–Cu and Sn–graphene–Cu bonds when they were as-fabricated and aged for different duration (i.e., 24, 48, and 96 h), as shown in Figure 3. We observe excessive growth of a scallop-like IMC along the Sn–Cu interface following the 24 h of aging (Figure 3b), and the IMC gradually grows into a μm-thick continuous layer following the 96 h of aging (Figure 3d). These observations are consistent with previous reports, and the IMC formed has been identified as Cu₆Sn₅ through X-ray diffraction analysis, which is very brittle and induces severe aging degradation at the Sn–Cu bonds.2,3 In contrast, we do not observe significant growth of an IMC along the Sn–graphene–Cu interface, even for the 96 h aged sample (Figure 3h). These results indicate that the insertion of a graphene interlayer impedes the aging degradation at the Sn–Cu bonds by effectively retarding the growth of a Cu₆Sn₅ IMC.

As mentioned earlier, the surface of the Cu NCA substrate is very rough and contains numerous valleys, as shown in Figure S1a. Achieving a conformal graphene coating on rough Cu NCA is not easy, and the conventional poly(methyl methacrylate) (PMMA)-assisted graphene transfer technique cannot serve the purpose, as illustrated in Figure 4a–c. In the PMMA-assisted graphene transfer technique, the PMMA/graphene stack is first brought into proximity of Cu NCA in deionized (DI) water (Figure 4a). The sample is then dried in an oven. Due to the mechanical rigidity of PMMA, the PMMA/graphene stack does not conform to the rough features of Cu NCA well, leaving behind voids, as illustrated in Figure 4b. Consequently, tearing of graphene is often observed on the Cu NCA substrate once the PMMA layer is removed, presumably due to the large surface tension or an aggressive nitrogen stream, during the sample drying processes (Figure 4c,d). To overcome this problem, we utilized an ethylene-vinyl acetate (EVA)-assisted graphene transfer technique.29 Specifically, EVA has a 20 times larger elastic modulus and higher elongation capability compared to PMMA. In the
EVA-assisted graphene transfer technique, the EVA/graphene stack is first brought into proximity of the Cu NCA substrate in DI water (Figure 4e). As the EVA/graphene is much more elastic than the PMMA/graphene case, conformal coating on the Cu NCA can be obtained (Figure 4f), and after EVA removal, a much better graphene coverage can be achieved (Figure 4g.h). Details of both graphene transfer techniques are available in the Methods section.

It is worth noting that the Cu NCA surface is super-hydrophilic as-fabricated, but is easily oxidized once exposed to air and becomes hydrophobic, as confirmed by the water contact angle measurement (Figure 5a,b). To ensure a conformal graphene coating on the rough Cu NCA, it is essential to have a hydrophilic Cu NCA substrate prior to using it to fish out the EVA/graphene stack in DI water; otherwise the EVA/graphene stack will loosely lie on the hydrophobic Cu NCA surface (Figure 5c). Such loose attachment of the EVA/graphene stack to the underlying Cu NCA substrate may induce the formation of interfacial voids that seriously deteriorate the bonding quality and should be avoided (Figure 5d). To make the Cu NCA surface hydrophilic again, we annealed the Cu NCA substrate at 250 °C in a forming gas environment for 1 h, prior to using it to fish out the EVA/graphene stack in DI water. Figure 5e shows a typical SEM image of an annealed Cu NCA surface. As can be seen, some sharp NCA tips collapse but the cone-like morphology remains, similar to that in Figure 5a. Importantly, the annealed Cu NCA surface is hydrophilic, with a water contact angle of 119° (Figure 5f). Figure 5g shows a typical SEM image demonstrating the EVA-supported graphene stack adheres well to the annealed Cu NCA surface, along the edge of the transferred EVA/graphene stack. SEM images of other similar samples are shown in Figure S3. As can be seen in Figure S3c,d, the EVA/graphene stack nicely conforms to the Cu NCA morphology in the sample’s central region. This minimizes the formation of interfacial voids at the Sn–Cu interface, as confirmed by cross-sectional SEM analysis (Figure 5h). Overall, the results suggest that both EVA-assisted polymer transfer and a hydrophilic Cu NCA surface are critical to ensure conformal adhesion of graphene on the Cu NCA substrate, optimizing the bonding quality.

In our bonding technology, graphene at the Sn–Cu interface effectively retards the growth of the IMC layer, thus impeding the aging degradation. The results further indicate that the one-atom-thick monolayer graphene preserves the advantages of the nanocone array in lowering the bonding temperature. Despite its one-atom thickness, the large-area graphene used must be able to restrict Sn from diffusing into Cu, forming an IMC layer, and hence it must be of good quality. Through systematic material characterizations, we show that both EVA-assisted polymer transfer and a hydrophilic Cu NCA surface are critical to ensure conformal adhesion of graphene on the Cu NCA substrate, optimizing the bonding quality.

In summary, we have devised a graphene-based Cu bonding technology with high reliability. Instead of a flat Cu substrate, we demonstrated that the insertion of the graphene/Cu NCA composite on the flat Cu substrate concurrently addresses the high-bonding-temperature and aging degradation issues, which have long been limiting the reliability of the lead-free Cu bonding technology. Specifically, nanoscale metal reduces the thermal budget by lowering the energy required to establish Sn–Cu metallurgical bonds. Graphene, on the other hand, retards the IMC growth and thus impedes the aging degradation, as confirmed through shear strength and SEM analyses. Importantly, our bonding technology creates reliable soldering joints with bonding temperature as low as 150 °C, lower than that of hazardous lead-based technology (183 °C). With the advancement in graphene synthesis and transfer technology, we show that the Sn–graphene–Cu bonding technology presented in this work can be integrated into the existing commercial Cu bonding technology for industrial applications in the foreseeable near future.

METHODS

Fabrication of a Copper Nanocone Array Substrate. The Cu NCA was fabricated on a commercial C194 Cu substrate (2 cm × 1 cm, shown in Figure 1c) using a one-step electroless plating approach. Prior to the electroless plating, the C194 Cu substrate was dipped in a degreasing solution for 120 s, followed by acid cleaning (20% H2SO4) for 30 s and PdCl2 activation for 30 s. Subsequently, the Cu nanocone array was electroless plated on the Cu substrate in an electrolyte composed of CuSO4·5H2O (0.03 mol/L), NiSO4·6H2O (0.0024 mol/L), Na2HPO4·2H2O (0.24 mol/L), Na2C2H3O2·2H2O (0.05 mol/L), and 6H2O (0.24 mol/L), Na2C2H3O2·2H2O (0.05 mol/L), and NaOH (0.5 mol/L).
pH regulator buffer H3BO3 (0.50 mol/L), and crystallization modifier (i.e., polyethylene glycol (5 ppm)). The electrolyte solution was maintained at a temperature of 65 °C and pH values of 7.5–9.5, adjusted using NaOH solution. After 20 min of electroless plating, the sample was rinsed with DI water and blown dry with N2. Figures 1d and S1a show the as-fabricated Cu NCA on a commercial C194 Cu substrate. We note that the Cu NCA surface is superhydrophilic as-fabricated, but easily oxidizes once exposed to air and becomes hydrophobic, as confirmed by the water contact angle measurement (Figure Sb). To make its surface hydrophilic again, we annealed the Cu NCA substrate at 250 °C in a forming gas environment (200 sccm of H2 and 200 sccm of Ar at atmospheric pressure) for 1 h.

**Graphene Synthesis.** For large-area monolayer graphene synthesis, 25 μm thick Cu foil purchased from Alfa Aesar (#13382), with 99.8% purity, was used as the growth substrate. Prior to the growth, the Cu foil was treated using commercial Ni etchant (nickel etchant TFB, Transense). Graphene was then synthesized on the treated Cu foil in a LPCVD system. The Cu foil was first annealed at 1030 °C for 30 min in a hydrogen environment (10 sccm of H2 at 320 mTorr). Subsequently, 3.5 scm of methane (CH4) was introduced to the LPCVD system for graphene synthesis, and the system was maintained at 1030 °C for another 30 min in a hydrogen environment. Finally, the furnace lid was flung open to let the sample cool quickly to room temperature.

**EVA-Supported Graphene Transfer.** EVA solution (Aldrich, vinyl acetate 40 wt %, 10 wt % dissolved in xylene) was first spun at 4000 rpm for 60 s, on the graphene synthesized on Cu foil. The sample was then baked in an oven at 80 °C for 60 min. Subsequently, the sample was floated on top of the Cu etchant (copper etchant TFB, Transense) for 20 min to remove the Cu foil. The sample (EVA/graphene stack) was then rinsed with deionized water several times. Next, the targeted substrate (annealed Cu NCA substrate) was used to scoop out the EVA/graphene stack and the sample was initially dried with a N2 stream, followed by oven baking at 80 °C for more than 8 h. Finally, the sample was soaked in xylene at 80 °C for 20–30 min to remove the EVA film, leaving behind a Cu NCA substrate with a conformal graphene coating on it (Figures 1f and S3).

**PMMA-Supported Graphene Transfer.** PMMA 950 A5 (Microchem Inc.) was first spun, at 2500 rpm for 60 s, on the graphene synthesized on Cu foil. The sample was then baked in an oven at 80 °C for 60 min. Subsequently, the sample was floated on top of the Cu etchant (copper etchant TFB, Transense) for 20 min to remove the Cu foil. The sample (PMMA/graphene stack) was then rinsed with deionized water several times. Next, the targeted substrate (Cu NCA or Si/SiO2 substrate) was used to scoop out the PMMA/graphene stack, and the sample was initially dried with a N2 stream, followed by oven baking at 80 °C for more than 8 h. Finally, the sample was soaked in acetone at room temperature for more than 1 h to remove the PMMA film.

**Bonding, Aging, and Shear Strength Tests.** A modified Rhesca PTR-1101 bonding tester was used to make all Cu bonding, and the solder ball used is Sn-3.0Ag-0.5Cu (in wt %) with 760 μm diameter by applying a constant force of 1500 gf (~14.7 N), throughout this work. The bonding duration and temperature used for each bond is 5 min and 150 °C, respectively, unless otherwise specified. For the aging test, the bonded samples were baked in an oven at 150 °C for a duration of 96 h, unless otherwise specified. For the shear strength test, a bonding tip installed on the Rhesca PTR-1101 bonding tester was first brought to the side of a bonded Sn solder and then set to move horizontally with increasing force (Figure 2a,b). The tip stops moving once the Sn solder was levered from the Cu NCA substrate, and the bonding tester records the shear force required. Shear strength of each bond was then calculated by taking the maximum shear force required tolever the Sn solder divided by the measured area size of the bond.

**Graphene Characterization.** The Raman measurement was carried out using a Horiba-Jobin Yvon system with a 532 nm Ar+ laser line. The laser power used was around 1 mW on the sample, and a 100× objective was used to focus the beam. The size of the laser beam on the sample was around 1 μm. An AFM topography image was obtained using a Veeco Digital Instrument Nanoscope III. Field-emission scanning electronic microscopy was conducted using a FEI-Sirion 200. For TEM studies, the graphene synthesized on Cu foil was transferred to a Quantifoil 1.2/1.3 Au grid (300 mesh) and then characterized using a FEI Tecnai G2. Aberration-corrected STEM was carried out using a Nion UltraSTEM100.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b07739.

SEM characterization of the Cu NCA surface prior to and following graphene synthesis, bonding yield for Sn–graphene—Cu and Sn–Cu bonds, SEM characterization of EVA/graphene stack transferred on an annealed Cu NCA substrate, characterization of our CVD-grown monolayer graphene, bonding mechanism in a graphene sheet with nanosized holes, and Figures S1–S5 (PDF).

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**Notes**

The authors declare no competing financial interest.

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