Investigation of Lead-free Nanosolder Reflow and Wettability Property for Electronics/Nanoelectronics Assembly and Packaging

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ABSTRACT

The approach of nanosoldering has shown promise in the construction of functional and interconnected nanostructures from nano-building blocks by utilizing nanosolder reflow processes. However, in such a reflow process, the surface oxidation and wettability of nanosolders are critical factors in the practical nanosoldering applications. In this study, the usage of a vapor phase-based flux process demonstrates the efficiency of cleaning nanosolder surface oxide and ensuring good nanosolder reflow. We show the interaction of nanosolders with metallic surfaces of copper nanowires and substrate. The effect of two industrially relevant fluxes has been studied on nanosolder reflow processes. These studies provided necessary first-hand knowledge in developing the nanosoldering techniques and their potential applications in nanomaterials assembly and nanodevice fabrication.

Keywords: nanosolder, nanowire, reflow, wetting, nanoelectronics assembly

1. INTRODUCTION

The demand for high-performance interconnects in advanced packaging pushes the dramatic scaling down of the electronics packaging feature size from microscale to nanoscale. Novel or enhanced interconnection and packaging techniques have to be developed to meet a variety of needs for device or system level integration. Nanosolder-based joining and interconnection techniques provide a wonderful opportunity to form robust joints between nanostructures and to integrate nanocomponents into a functional device or complex system [1].

We envision that nanosolder applications should be classified into at least two types of approaches. Fig. 1 is a schematic representing the possible nanosolder applications using both approaches. One approach is the development of nanosolder paste which is an extension to the conventional solder paste composing of micron-sized solder balls (Fig. 1a). The other approach is nanosolder joint formation between functional nanostructures. This includes the situation of joining nanowires with nanowires and/or joining nanowires with other structures such as contact pads (Fig. 1b). Recently different kinds of solder nanoparticles based on tin material such as Sn/Ag [2], Sn/Ag/Cu [3], and Sn/Cu/Bi [4] alloys have been synthesized and characterized which have been explored as an alternative to the micron-sized solder balls in order to obtain lower melting point of solder materials and avoid component damage [5]. During the reflow process, the nanoparticles will melt and merge together to form a larger solder bump on the substrate, as shown in Fig. 1(a). Although the size dependent effect of nanoparticles has been proven by most simulated studies when the radii of nanoparticles are less than 20 nm, experimental results did not bring significant decrease of melting temperature which may be due to many factors such as particle agglomeration, surface oxidation, etc [6].

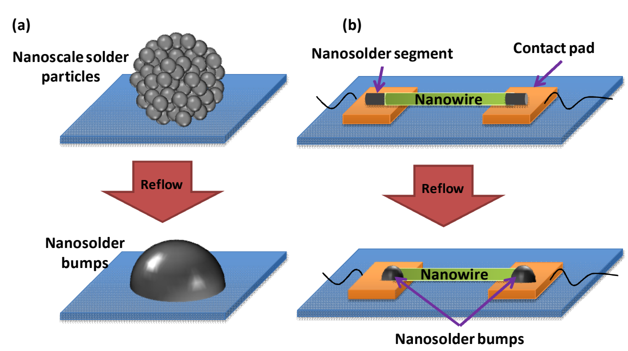

Figure 1. Schematic of nanosolder assembly and packaging techniques. (a) Conventional solder paste alternative. (b) Nanojoint formation between nanowire structures.

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The more significant need for nanojoint is the formation of nanojoints and/or nanoscale interconnections between nanostructures, which is a more promising approach because the solder segment on the nanowires can be precisely controlled and effectively joined by a reflow process without intensive extra processing [7-8]. The realized one-dimensional nanowire bridge has shown potential for many sensor applications through the formation of functionalized and ordered nanostructures on the bridge structure. Hence, the technique of nanosolder joints between nanowires and contacts stands out to lay the foundation of reliable functional device construction, as shown in Fig. 1(b). Nanowire, a model one-dimensional nanostructure, provides an almost perfect system to study the intermetallic diffusion and wetting properties of nanosolder systems in one direction.

Here, the melting and wetting behavior of nanosolders on nanowires and on substrate were studied. A Cu-Sn two-segment nanowire system was used to investigate the melting behavior confined in 1-dimensional wire structures. Nanosolder reflow was studied by pure Sn nanowires on a Cu substrate. Two commercial fluxes were used in this work, both of which showed strong ability of oxide cleaning and enhanced the reflow result.

2. EXPERIMENTAL METHOD

2.1 Nanowire Fabrication

Nanowires with different materials and compositions were fabricated by a template assisted electrodeposition method. A polycarbonate nanoporous template (50 nm in pore size, Whatman) was used for nanowire fabrication. The electrolytes of Sn and Cu were purchased from Technic Inc. After nanowire fabrication, the template was dissolved in Dichloromethane to release the nanowires. The fabricated nanowires were stored in ethanol. The detailed fabrication process can be found from our previous publication [9].

2.2 Nanosolder Reflow Process

Reflow soldering is a critical step in electronics assembly and manufacturing, in which the electrical components are assembled and connected onto contact pads or printed circuit board by using a solder paste in a reflow oven. Flux is an essential part of the solder paste and has been widely used to clean the solder surface oxide and enhance the wettability of solders in the reflow process. Conventionally, the micron sized solder balls are mixed with a flux at a certain ratio, and form a solder paste, as shown in Fig. 2(a). During the reflow, the flux is activated and reacts with the oxide on the solder surface, and thus enhances the wettability of the solder. However, for the nanosolders, flux usage and activation may be challenging. Especially for nanosolder joint formation, it is very difficult to mix the flux directly with a small amount of nanosolders; also, the flux residue is not easily cleaned away from the sample surfaces. Hence, using flux vapor to replace the semi-liquid flux will be a good option to be applied in the nanosolder reflow process. Fig. 2(b) illustrates the concept of nanosolder reflow using a vapor phase based flux process. Once the reflow temperature reaches the flux activation point, the vaporized flux molecular will surround the nanosolders and react with the surface oxide (normally a few nanometer thick) to insure a good reflow result, as well as to minimize the flux residue after the reflow.

2.2.1 Nanosolder reflow on nanowires

The Cu-Sn two-segment nanowire suspension was drop casted on a piece of Si/SiO_2 wafer. The sample was dried and then placed in a temperature controlled tube furnace with nitrogen gas purge. Wafer is a relatively inert substrate because it will not react with either the Cu or the Sn segment in the nanowires. The actual temperature inside the tube was monitored with a thermometer. The nanowires were reflowed at a peak temperature for about 3 minutes. Rosin based liquid flux RMA (rosin mildly activated, Indium Corporation) was used for the nanosolder reflow on nanowires. After cooling the samples, the flux residues were cleaned by isopropanol.

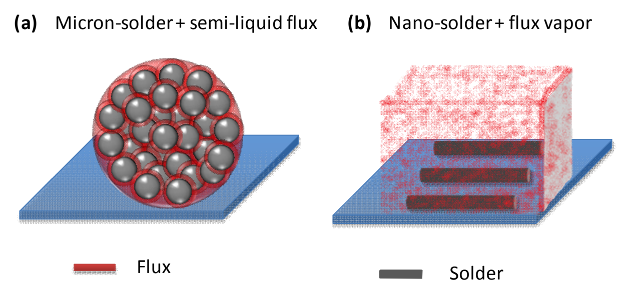

Figure 2. Schematic of traditional semi-liquid flux mixture and vapor phased flux applied for nanosolder reflow.

2.2.2 Nanosolder reflow on Cu substrate

The nanosolder reflow on a reactive substrate such as copper (Cu) was also studied. In this experiment, the reactive substrate Cu (20 nm thickness) was thermally evaporated on a Si/SiO_2 wafer. Single segment pure Sn nanowire suspension was placed on the substrate and then dried. The reflow process was carried out in a bench top reflow oven (Torch SMT Co. Model T200N) purged with nitrogen gas. To minimize the reaction between Sn solder and the Cu substrate, the reflow profile had a peak temperature of 180 °C and lasted for only 1 minute. Liquid flux #4OA (Indium Corporation) used in this experiment is a no-clean type flux, so no further cleaning step was taken.

2.3 Characterization

A JEOL JSM-7401F field emission scanning electron microscope (FE-SEM), equipped with an EDAX, was used to characterize the size, structure and composition of the nanosolders and nanowires.

3. RESULTS AND DISCUSSION

3.1 Lead-free Nanosolders and Multisegmented Nanowires

The nanowires in the form of pure solder materials or with multi segments were characterized by FE-SEM (Fig. 3). Fig. 3(a) shows the pure Sn nanowires with an average diameter of 80 nm and 5 μm in length which is a model nanosolder system since the single element would simplify the study system. In Fig. 3(b), the Cu-Sn two-segment nanowires were characterized by backscatter mode SEM imaging and the two segments can be clearly identified through the different contrast. The lighter segment is Sn and the darker segment is Cu. Most of the interfaces between Cu and Sn are smooth and strong, and no obvious break or crack can be seen. The length of each segment can be controlled by the electrodeposition current and duration. Assuming there is no diffusion in the radius direction, the intermetallic diffusion, if any, will only be confined in the axial direction. Thus, nanowire will be a perfect model to study the nanoscale 1-dimensional diffusion.

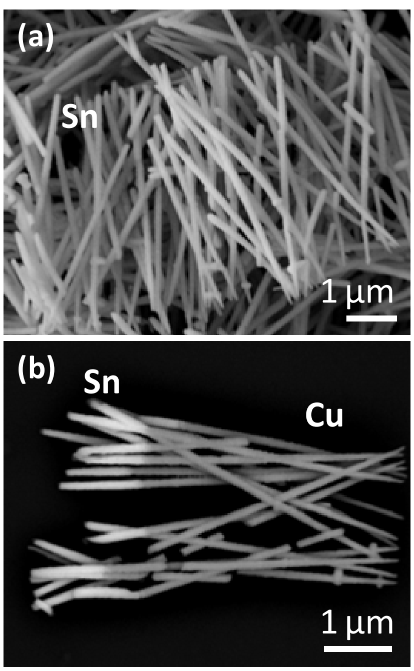

Figure 3. (a) One segment nanowire with pure Sn material as nanosolder. (b) Cu-Sn two-segment nanowires with tin nanosolders.

3.2 Solder Reflow on Cu-Sn Nanowires

The nanowire reflow in an inert environment has been reported [9], however, the nanowire surface oxide formed during the fabrication and washing stages could not be removed in the reflow process without a flux. The result was that the oxide shell of the nanowire confined the movement of solder inside upon melting and prevented the solder merging and joining with each other which will then lead to an unsuccessful reflow process.

In order to probe the melting and wetting properties of nanosolder on nanowire systems, the Cu-Sn two-segment nanowires were reflowed in the N_2 environment with a flux at different temperatures, as shown in Fig. 4. Since the melting point (M.P.) of bulk tin is 232 °C, the experiment was carried out at peak temperatures of 180 °C, 230 °C, 300 °C or 500 °C to study the melting and wetting behavior of Cu-Sn nanowire system. From Fig. 4(a), at the peak temperature of 180 °C, which is 52 °C lower than the bulk Sn M.P., the nanowires mostly retained their original shape and no obvious shape change was observed. Because the flux has not been activated at this temperature, the Sn segment did not melt. When the peak temperature increased to 230 °C, which is very close to the bulk tin M.P., the nanosolder segment has shown obvious shape change and partially diffused into the Cu segment, as shown in Fig. 4(b). Since the bulk Cu M.P. is 1084.6 °C, Cu should not melt at this temperature. Although the peak temperature is a few degrees lower than the bulk Sn M.P., the tin nanosolder almost melted completely which is probably due to the flux reacting with the SnO_x shell and leading the molten Sn to move freely.

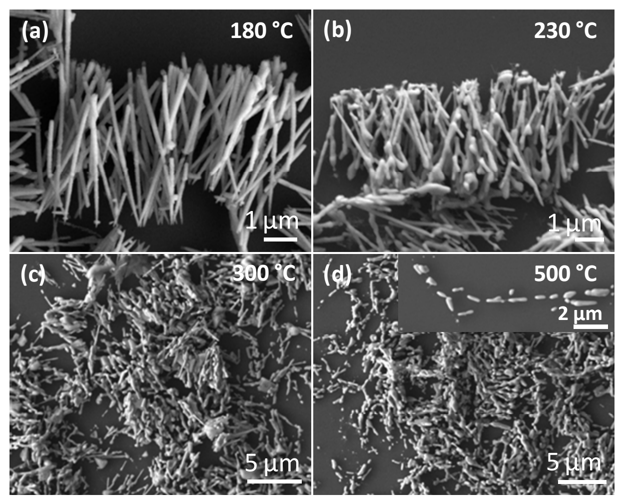

Figure 4. Reflow result of Cu-Sn nanowires at different reflow peak temperatures. (a) At 180 °C; (b) At 230 °C; (c) At 300 °C; (d) At 500 °C.

Fig. 4 (c) and (d) show the Cu-Sn nanowires reflowed at 300 °C and 500 °C, respectively. In both samples, the Sn segment cannot be identified from the Cu segment and the original smooth and continuous nanowire surface had broken. From Fig. 4(d), it is noticed that even the Cu segment was broken into smaller segments along the nanowire structure. Although the highest peak temperature is still 500 °C lower than the Cu M.P., the Cu segment could be affected significantly by the solder segment with the assistance of a flux.

3.3 Nanosolder Reflow on Cu Substrate

Different from the nanosolder reflow in nanowire system, the application of substrate assembly and packaging requires the study of solder reflow on certain reactive substrate, such as in ball grid array (BGA) applications. In this work the pure Sn solder nanowires were reflowed on a 20 nm thickness Cu that was evaporated on the Si/SiO_2 wafer. With a flux at a peak temperature even as low as 180 °C, the nanosolders changed their morphology significantly, as shown in Fig. 5 (a). It is clearly observed that the Sn nanosolders melted along the nanowire structure, and formed several separated solder bumps at the temperature much lower than the bulk material M.P.. This is similar to the reflow result of the Cu-Sn nanowires shown in Fig. 4 (c) and 4 (d). The circles around the nanowires were the bared wafer background. From the zoom in image of Fig. 5 (b), it is seen that the area of Cu substrate which did not react with Sn nanosolders formed many grains which indicates that the flux not only reacted with Sn surface oxide, but also affected the Cu substrate (there was a surface oxide layer on Cu too).

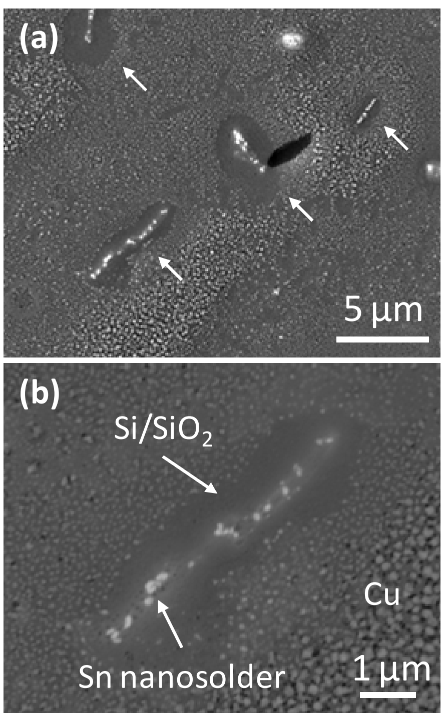

Figure 5. (a) Pure single Sn nanowires reflowed on a 20 nm thickness thermally evaporated Cu substrate at 180 °C. (b) Zoom in image of Fig. 5 (a).

Compared to the reflow result for Cu-Sn nanowires at the peak temperature of 180 °C, it is easy to find out that the two experiments at the same temperature led to different results: one did melt and the other one did not. This may be due to the different activity of the fluxes. The flux RMA could be activated around 200 °C, so the nanowire would not change lower than this temperature. However, the flux #4OA can be activated as low as 100 °C, and thus the nanosolders may have been melted (or pseudo-melted) even at a temperature as low as 180 °C. The lower activation temperature of the flux applied in the system, the easier the solder oxide will be removed. The reflow result is not only affected by the temperature, but also by the flux type. Systematical study of the effect of different fluxes on the nanosolder reflow at different temperatures is currently under investigation.

4. CONCLUSION

In summary, we have presented a bottom-up approach to fabricating one-dimensional nanowires in single and multi segments with solder materials. We have developed a flux vapor based reflow process for nanosolders. The flux assisted reflow was studied for nanosolders on both nanowires and on Cu substrate. It is found that the flux could effectively react with solder surface oxide. However, the flux selection for proper application should depend on different activation temperatures. Although the exact mechanism of diffusion, melting and wetting at nanoscale still needs to be further explored, nanosoldering technique, in combination with one or more assembling techniques, has the great potential not only in nanoscale assembly and nanoscale ball grid array (BGA) formation, but also in the integration of sophisticated sensor arrays and the enabling of nanoscale integrated circuits.

5. ACKNOWLEDGEMENTS

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