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In Situ Visualization of Metallurgical Reactions in Nanoscale Cu/Sn Diffusion Couples

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Pb-free nano solders offer exceptional opportunities for making nanoscale contacts as needed with the miniaturization of devices as well as the production of nanosized circuits. Pb-free solders have been extensively produced in bulk, powder and thin films. However, the knowledge of many properties of Pb-free nanosolders, including diffusion, intermetallic reaction mechanisms and phase evolution is still very limited. Using a two-segment copper-tin (Cu-Sn) nanowire as a model system, in which Sn acts as the solder element and Cu serves as a functional element, we perform an in-situ TEM study to elucidate the phase/structural transformation of various intermetallic compounds (IMCs) and its dependence on the relative length of the Sn and Cu segments as well as the formation and growth of Kirkendall voids by the reactive diffusion between Cu and Sn.

The Cu-Sn two-segment nanowires are fabricated by room-temperature sequential electrodeposition assisted with polycarbonate nanoporous membrane templates [1]. The as-prepared Cu-Sn nanowires are kept as a solution in ethanol, followed with ultrasonic dispersion and drop casting onto a lacey carbon film supported by TEM Mo grid, which is then mounted onto a Gatan heating holder controlled by a Gatan temperature ramping stage. In-situ TEM observations of the soldering reaction in the Cu-Sn nanowires are carried out on a JEOL JEM2100F TEM operated at 200 kV. STEM energy dispersive X-ray analysis and electron diffraction are performed to confirm the chemical composition and structure evolution of the IMCs during the soldering reaction.

A single nanowire is selected for in-situ heating TEM observations. Fig. 1(a) shows the morphological evolution of a nanowire while it is being heated from room temperature (RT) to 495.5 ℃ with the holding time of ~ 1 min for each temperature interval unless specified. The dashed line denotes the original interface region of the two segments with the Sn segment on the left and the long Cu segment on the right. The Sn/Cu length ratio of the two segments is about 1:3. The nanowire has no obvious changes in morphology until it is being heated to ~ 200 ℃, at which a bulge starts to become visible in the Cu segment near the Sn/Cu interface. Concurrent with the bulge formation, the diameter for the Sn segment near its end on the left is shrinking (see the corresponding TEM images at 200 ℃ and 205 ℃). This trend becomes more obvious as the temperature is raised to 207 ℃; the TEM image obtained at this temperature shows that a void is formed at the left end of the Sn segment, where the outer layer of the void is a native amorphous Sn oxide layer formed from the sample preparation. With further increase in temperature, the bulge grows larger with more Sn depleted from the end of the Sn segment, as seen from the void growth. Meanwhile, new voids are formed in the Cu segment near the bulge (see the image corresponding to the temperature of 215.5 ℃). The voids in the Cu segment migrate away from the bulge and merge, forming a larger void with the continued annealing at 217.5 ℃ for 5 min. Further increase in the annealing temperature to 364 ℃ and then to 495.5 ℃ results in the void growth that eventually leads to the breakage of the Cu segment. The above in-situ TEM observation reveals that the Cu-Sn metallurgical reaction occurs around 200 ℃ and the bulge formation around this temperature range can be attributed to the formation of the IMC η-phase Cu_6Sn_5, as identified by electron diffraction shown in Fig. 1(b). The η-Cu_6Sn_5 bulge is formed initially in the Cu segment, suggesting that Sn diffuses into the Cu segment to form the IMC. However, once the IMC is formed, the reaction is mainly limited to the Sn segment by Cu diffusion into Sn through the formed IMC. This is evidenced by the void formation in the Cu segment near the IMC/Cu interface due to the Kirkendall effect, i.e., the diffusion of Cu in the IMC is faster than that of Sn in the IMC. With the continued IMC growth, Sn is gradually consumed by reacting with incoming Cu atoms supplied by solid-state diffusion of Cu through the IMC layer, which results in the void growth at the end of the Sn segment. One can see that the void in the Sn segment has no noticeable change after the temperature is raised above 217.5 ℃ and thereafter, indicating that Sn has been completely consumed to form the IMC at this reaction stage. The continued growth of the Kirkendall void in the Cu segment at the temperature above 217.5 ℃ suggests that more Cu diffuses to the reacted region to form Cu-rich IMCs while the nanowire is being heated to the higher temperatures. The morphology and length of the Cu segment on the right of the Kirkendall void remains unchanged during the entire annealing process, demonstrating that there is little diffusion of Sn to the Cu segment due to the slower diffusion rate of Sn in the IMC than that of Cu in the IMC [2]. A full description and discussion of how the phase transformation pathway varies with the Sn/Cu length ratio will be presented and compared.

References:

[1] F. Gao *et al*, The Journal of Physical Chemistry *C* 113.22 (2009): 9546-9552.
[2] Q. Yin *et al*. Nanoscale (2015) in press.
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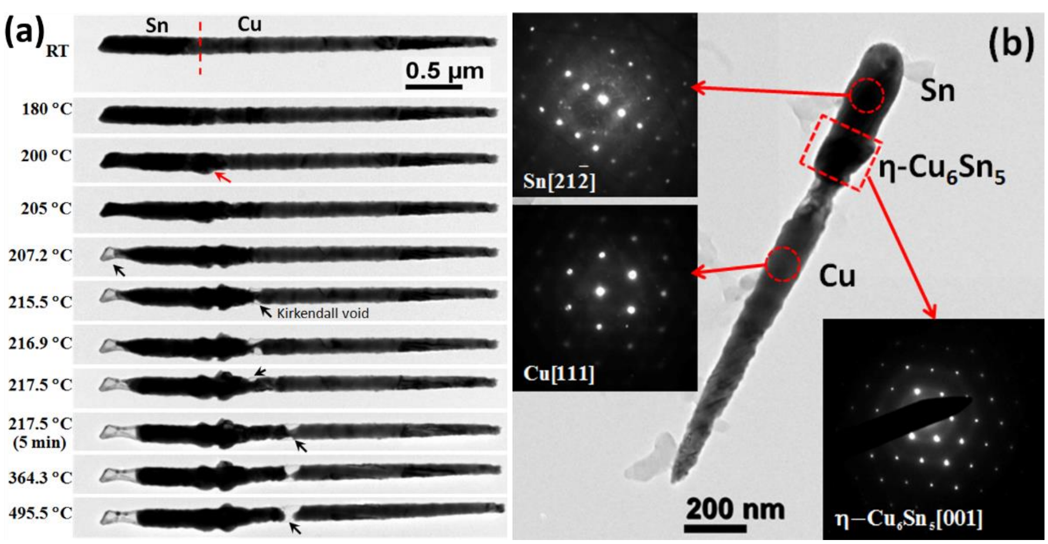

Figure 1. (a) In-situ TEM observation of the morphological evolution of a Cu-Sn two segmented nanowire upon heating from room temperaeture (RT) to 495.5 ℃. The red dashed line delineate the interface area between the Cu and Sn segment. The red arrow on the TEM image corresponding to the annealing temperature of 200 ℃ denotes the formation of a bulge in the Cu segment near the Sn/Cu interface. (b) TEM image with SAED pattern showing the η-phase Cu_6Sn_5.

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