Electronic Supporting Information

Bottom-up nanoarchitecture of semiconductor nano-building blocks by controllable in situ SEM-FIB thermal soldering method

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1. Synthesis of 97Sn3Cu nanowire solders

The electro-deposition was carried out in the three-electrode cell using a CHI630B electrochemical workstation at ambient temperature, in which the silver-evaporated PC membrane served as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a graphite plate as the counter electrode. The electrodeposition electrolyte was composed of 0.12 M $SnSO_4$, 2.50 mM $CuSO_4$•$2H_2O$, 0.25 M $C_6H_5Na_3O_7$•$2H_2O$, 0.5 g/dm^3

polyethylene glycol (PEG-2000) and 2 gL^{-1} hydroquinone. All chemicals used in this paper were of analytical grade. The solution pH was adjusted to 4.5-5.5 by adding 1 M sodium hydroxide or citric acid. Then, a constant -1.2 V potential was applied to obtain 1D 97Sn3Cu alloy nanosolders, and the typical electrodeposition time for each sample was 30 min with gentle stirring.

2. EDX spectra of the 97Sn3Cu and WO_3 nanowires in Figure 1.

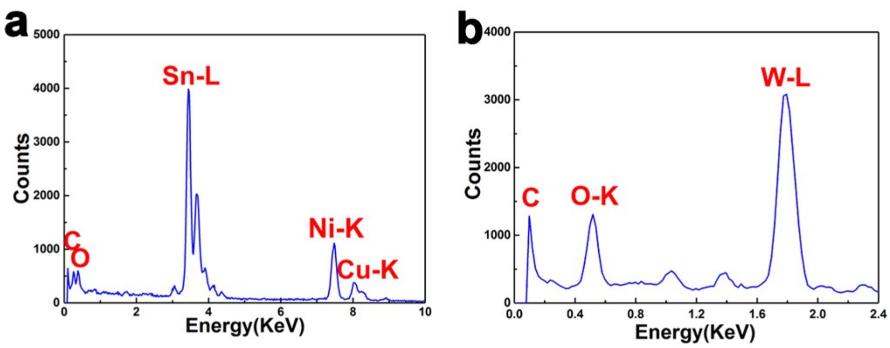

Figure S1. EDX spectra: (a) 97Sn3Cu nanosolders. (b) WO_3 nanowires.

Figure S1a shows a representative EDX spectrum of the 1D 97Sn3Cu nanosolders. The Sn and Cu peaks come from the 1D 97Sn3Cu nanosolders. The O peak originates from the 1D nanosolders, whose surfaces were partially oxidized due to the atmospheric exposure after released from the PC templates. The C and Ni peaks are confirmed to derive from the holy nickel-coated molybdenum grid. Figure S1b shows a representative EDX spectrum of the WO_3 nanowires.

3. Morphological and structural analysis of the WO_3 nanowires in Figure S2.

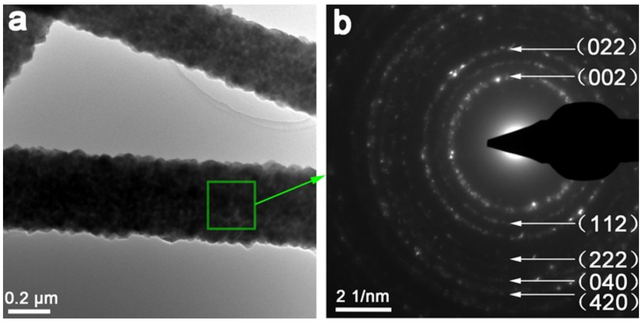

Figure S2. TEM structural analysis of WO_3 nanowires. (a) A representative TEM image of WO_3 nanowires. (b) A typical SAED pattern recorded from the area marked by the green square in (a).

4. XRD pattern of the 97Sn3Cu nanowire solders in Figure 3.

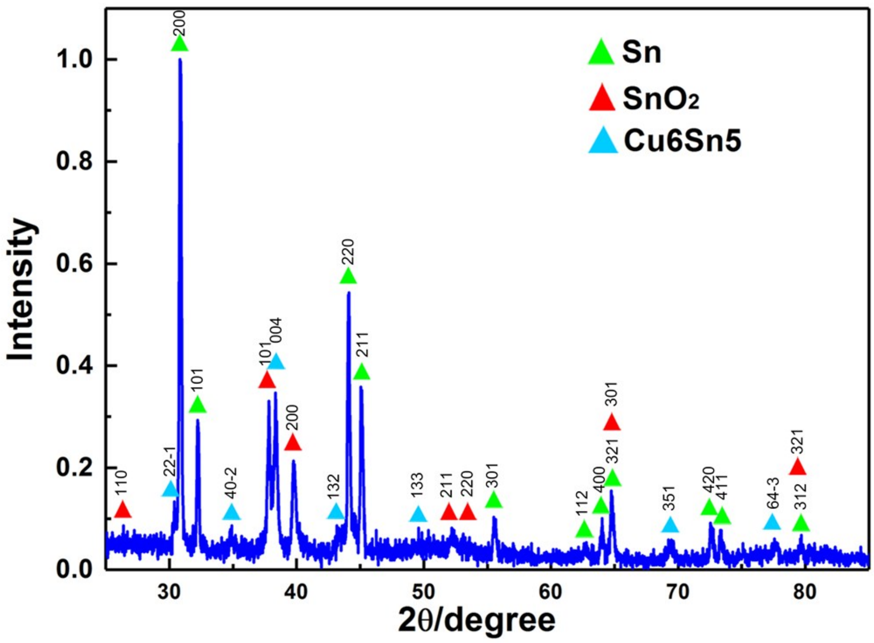

Figure S3. XRD pattern of the prepared 97Sn3Cu nanowires released from the PC template.

Figure S3 shows a representative XRD pattern of the 97Sn3Cu nanowires released from the PC template. The XRD peaks matched very well with those of β-Sn (I41/amd (141), 5.832*5.832*3.181<90*90*90>), η'-Cu6Sn5 (C2/c(15), 11.033*7.294*9.83<90*98.82*90>), and SnO_2 (P42/mnm (136), 4.72*4.72*3.17<90*90*90>). There are mainly three crystal structures including

Sn, Cu6Sn5 and SnO_2. This is further confirmed the existence of SnO_2 surrounding the 97Sn3Cu nanowire solders to form compact barrier layers, which has seriously hindered their completely reflow at the temperature near the melting-point.

5. **Thermogravimetric analysis curve of the 97Sn3Cu nanosolder in Figure S4.**

The thermogravimetric analysis (TGA) of 97Sn3Cu nanosolder (2 mg weight) was carried out from 50 ^{0}C to 700 ^{0}C at 10 ^{0}C min^{-1} heating rate under argon flow.

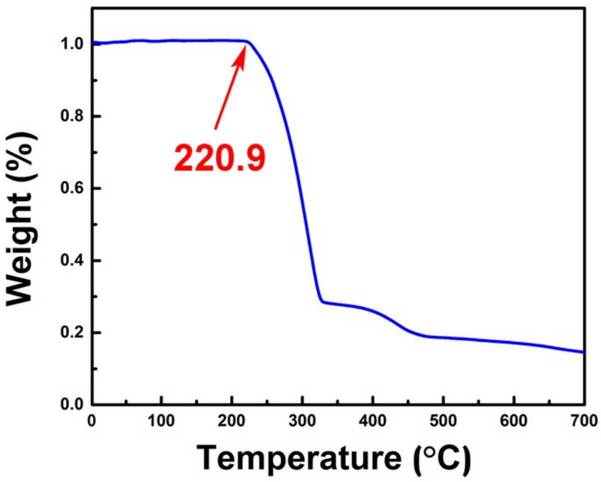

Figure S4. Thermogravimetric analysis curve of 97Sn3Cu nanosolder.

6. **XPS wide spectrum after Ar ion sputtering 97Sn3Cu nanosolder for 110s in Figure S5.**

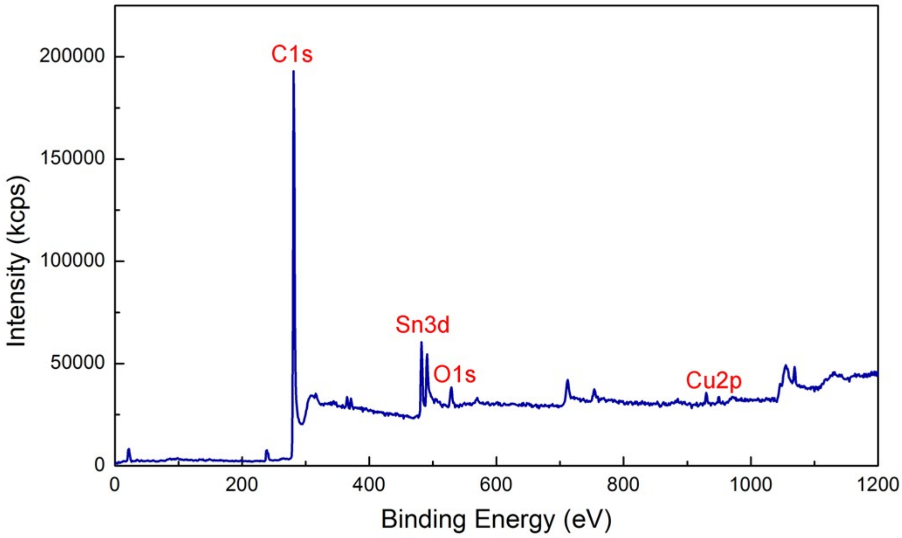

Figure S5. XPS wide spectrum after Ar ion sputtering 97Sn3Cu nanosolder for 110s

7. **Wettability experiments of the 97Sn3Cu nanosolder on WO_3 and SiO_2 substrates respectively in Figure S6.**

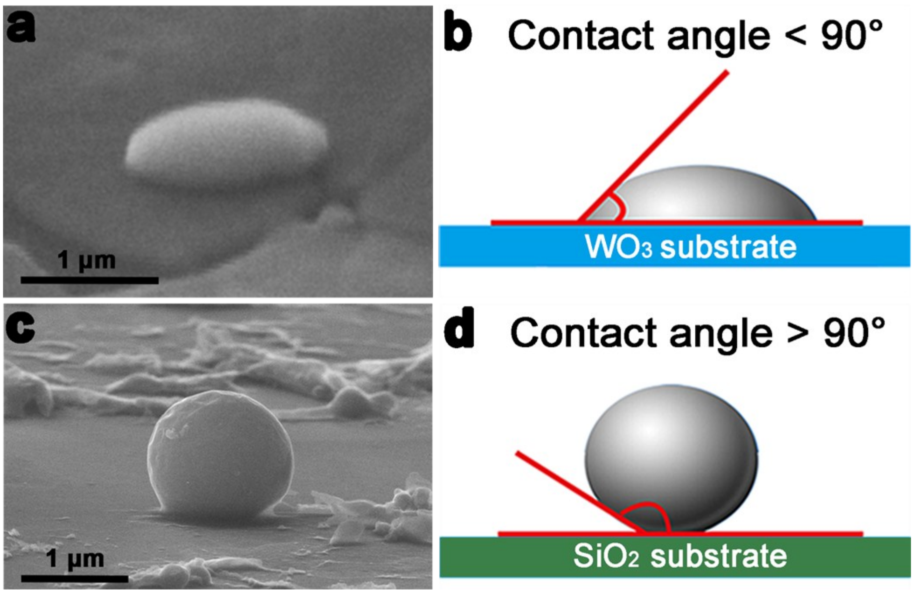

Figure S6. (a) The lateral profile SEM images of melted 97Sn3Cu nanosolder sphere on WO_3 substrate. (b) The schematic diagram corresponding to (a). (c) The lateral profile SEM images of melted 97Sn3Cu nanosolder sphere on SiO_2 substrates. (d) The schematic diagram corresponding to (c).

The wettability experiments were carried out by directly heating using *in-situ* heating apparatus in FIB-SEM. The nanowires of 97Sn3Cu in ethanol were dropped on the WO_3 substrate and SiO_2 substrate respectively, and then transferred into FIB-SEM. The reflow experiments were carried out according to the following order: preheating, reflow and cooling steps in FIB-SEM. The temperature of 180 ^oC was firstly set to preheat the nanosolders, then 2 minutes later the temperature was raised to 250 ^oC, at which temperature was dwelt for 3 minutes to ensure a complete reflow. Following the cooling process was carried out. After cooling process, the SEM was used to observe the contact angel of the reflow spheres on the substrates by tilting the SEM stage.

Figure S6a shows a representative image of the reflowed 97Sn3Cu alloy sphere on WO_3 substrate by tilting the sample of SEM to nearly 90°. It is observed that the reflowed nanosolder well spreading on the WO_3 substrate displayed powerful adhesive force between them, and the contact angle measured is far smaller than 90°, which confirms that the 97Sn3Cu nanosolder has a good wettability on WO_3 material. Its corresponding schematic diagram is shown in Figure S6b. The reflow experiment of nanosolder on SiO_2 substrate as a comparison was carried out in the same condition. An opposite result is observed that the contact angle measured is larger than 90° (Figure S6c), indicating a very poor or no wetting on SiO_2 material. Figure S6d shows its corresponding schematic diagram.

8. Thermal soldering individual WO_3 nanowires together using a bundle of line-style 97Sn3Cu nanowire solders in Figure S7.

By applying *in-situ* heating-induced thermal soldering technique, a bundle of 97Sn3Cu nanowire solders were utilized to bond two individual WO_3 nanowires together. Before the soldering, Ga^+ beam in SEM-FIB was applied to break the barrier layers outside of the sacrificial nanosolders as shown in Figure S7a. After that, the reflow process was carried out to thermally solder the individual WO_3 nanowires together by preheating at the 180 ^oC for 2 min and then heating at 250 ^oC for 3 min, which is enough to make the nanosolders completely melt at the junction. It is obviously seen that the bundle of nanowires has a good morphological transformation from line-style to spheres, indicating an excellent reflow was achieved (Figure S7b). In the thermal soldering, the reflowed spherical nanosolder has bonded two individual WO_3 nanowires together but with a limited diffusion at the interface of junction, in that a tightly, strong and reliable adhesion could be formed.

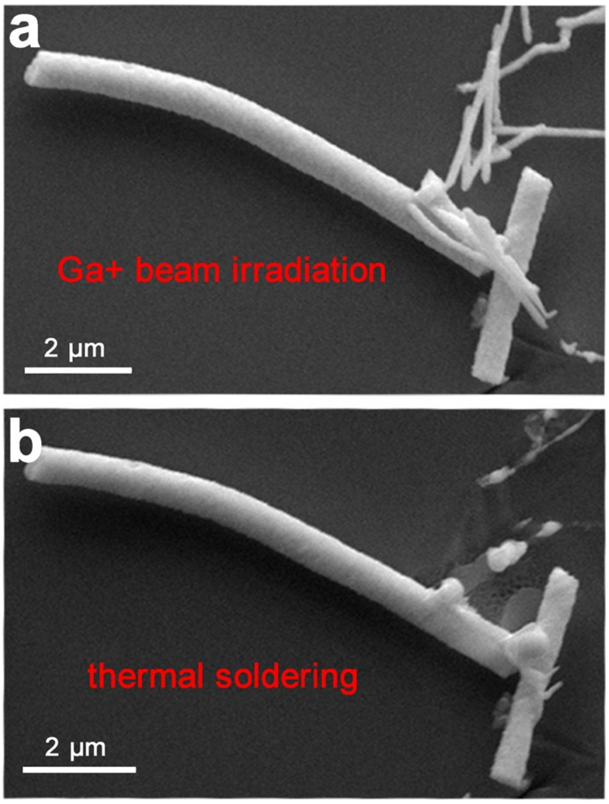

Figure S7. Thermal soldering two individual WO_3 nanowires using 97Sn3Cu nanowire solders. (a) Ga^+ beam irradiation of the bundle of 97Sn3Cu nanowires placed in the soldering point. (b) Thermal soldering the WO_3 nanowires together after preheating at 180 ^oC for 2 min and followed reflow heating at 250 ^oC for 3 min.