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COMMUNICATION

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

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Here we demonstrate that the building blocks of semiconductor WO\textsubscript{3} nanowires can be controllably soldered together by a novel nano-soldering technique of in situ SEM-FIB thermal soldering, in which the soldering temperature can precisely remain in an optimal range to avoid a strong thermal diffusion.

A number of research studies have recently focused on the transformation of nanoscale building blocks into functional nano-architectures with the continued development of nanotechnology, such as nano-devices\textsuperscript{5}, nano-sensors\textsuperscript{5} and nano-electronics.\textsuperscript{2} Nanoscale semiconductor nano-objects, made from materials like WO\textsubscript{3}, InP, Cu\textsubscript{2}O, ZnO, GaAs, SnO\textsubscript{2} etc., are essential building blocks for optoelectronic devices,\textsuperscript{4} photovoltaic diodes,\textsuperscript{4} nanowires lasers,\textsuperscript{6} photon- and gas-sensing nano-devices,\textsuperscript{7} owing to their unique optical, chemical, electrical and biological properties. Among them, WO\textsubscript{3} nanomaterials with outstanding electrochromic, optochromic, and gaschromic properties, have been widely utilized to manufacture various nano-structures such as high-performance flexible electrochromic device,\textsuperscript{9} optical switching devices,\textsuperscript{10} ultrasensitive NO\textsubscript{2} gas sensors,\textsuperscript{11} ultraviolet (UV) photodetector with high sensitivity and precise selectivity,\textsuperscript{12} nonvolatile memory devices,\textsuperscript{13} WO\textsubscript{3}\textsubscript{x}-based nanoionics device\textsuperscript{14} and so forth. The ability to bond individual semiconductor nano-objects together to form secure, intimate, functional, and long-lasting bonds is a necessity for integrated nano-devices.

Nanoo-soldering techniques, are crucial and have been used to assemble nano-structures composed of nanowires, nanotubes, nanobelts or other functional nanomaterials. To date, several feasible nanosoldering techniques have been proposed, including laser heating,\textsuperscript{15} soldering technique,\textsuperscript{16,17} Joule heating,\textsuperscript{18} high-energy electron beam irradiation,\textsuperscript{19} ion beam deposition,\textsuperscript{20} ultrasonic soldering,\textsuperscript{21} thermal heating\textsuperscript{22} and electron-beam-induced deposition.\textsuperscript{23} Among these, the soldering technique with a sacrificial nanosolder has the greatest potential because of its controllability, flexibility and the crucial advantage of avoiding detrimental effects on the nano-objects to be joined.\textsuperscript{16,17} One technique is to locally deposit nanoscale volumes of solder at the soldering site by electricity-induced Joule heating.\textsuperscript{16} Another approach is laser-induced heating nanosolder at the soldering site.\textsuperscript{17} The soldering technique can be divided into three steps: solder melting, element diffusion and cooling process. Diffusion as an important factor in soldering will play a crucial role in determining the tightly bonding of semiconductors, because doping of atoms into semiconductor through diffusion largely determines their corresponding semiconductor properties, and these properties can thus be destroyed. During soldering, metal atoms of solder have thermal diffused into base materials by a grain boundary diffusion at low temperature.\textsuperscript{24,25} At high temperature, the diffusion mechanism will become more complex, leading to much more severe diffusion at the interface. It is known that the chemical diffusion coefficient expressed by an Arrhenius-like equation \( D = D_0 \exp(-Q/RT) \), in which \( D_0 \), \( Q \), \( R \) and \( T \) denote diffusion constant, activation energy, gas constant and absolute temperature respectively. One can see that the diffusion coefficient will be exponentially increasing with higher temperature to finally induce a mild diffusion. To achieve an efficient and limited diffusion in soldering, the temperature should be precisely controlled. One can see that the factors induced heating at nanosolder are indirect electricity and laser, which have the opportunity to produce a localized uncertain high temperature. A higher temperature may cause more active
Herein we have developed a novel nanosoldering method of in situ Focused Ion Beam Scanning Electron Microscopes (SEM-FIB) thermal soldering, and have applied it into welding a nano-architecture of WO$_3$ nanowires together by using novel SnCu nanosolder as a demonstration. The temperature of the heating apparatus can be precisely controlled to cause only the nanosolder to melt completely, while the nano-building blocks with a higher melting point than the nanosolder retain their original structures and properties. This method is appropriate for nanomaterials whose melting points are higher than those of the nanosolders. During the soldering process, the temperature and holding time can be accurately controlled to ensure an efficient but limited diffusion between the solder and welded material, so that not only a strong, metallurgical and conductive bonding could be formed, but also the semiconductors will retain their original properties to achieve a proper function of semiconductor devices. The direct heating-induced nanosoldering shows several prominent advantages: solving the nanosoldering of high-temperature semiconductor materials with a limited diffusion; not strictly requiring the specific and perfect morphology of nanosolder; reducing the difficulty of the nanoscale manipulation; pretty suitable for large-scale soldering works. Our work is believed to open a promising way to construct nanoarchitectures of semiconductor nanomaterials.

The heating apparatus of this in situ SEM-FIB thermal soldering was designed and produced by our group, which is mainly composed of heating groove, temperature control system and measurement system. Its maximum temperature can reach 500 °C with a 0.5 °C precision. The schematic of the heating groove is shown in Figure 1a. The groove part provides a constant temperature area, and the silicon wafer with sample is placed there. The magnified schematic of soldering site in the groove is demonstrated in Figure 1b. In a typical soldering process, the SEM is to monitor the whole process. The heating-induced thermal soldering involves three steps: the nanomanipulation of nanosolder in the soldering junction of the nano-pattern to be welded (Figures 1b-c), the clean of soldering site by removing the impurities outside the surface of nanopattern such as oxide, carbide or organics (Fig. 1d), and the set-up of optimal temperature and holding time to melt the nanosolder for thermally soldering nano-pattern (Fig. 1e).

In this method, a high-quality nanosolder with low melting point and excellent wetting property is one of crucial factors for the success of forming reliable nano-bonding. A large number of studies have revealed that the copper has a good ability to thermally diffuse into WO$_3$ films beyond the temperature of 135 °C. Among Cu-based nanosolders, SnCu solder is considered as the most promising candidate alloy to replace the traditional SnPb solder for soldering because of their low-cost, distinguished mechanical, electrical and chemical properties. It is also known that 97Sn3Cu (weight ratio) alloy nanosolder has a moderate melting point (310 °C), prominent isothermal creep resistance and high mechanical reliability. Hence, there is credible to utilize 97Sn3Cu alloy nanosolders to solder semiconductor WO$_3$ nanowires together, in that a reliable metallic bonding instead of a simple mechanical combination could be formed. The nanowires of 97Sn3Cu alloy solders were fabricated by DC electro-deposition into polycarbonate porous membranes (Whatman) with pore size of 80 nm in diameter (PC), and the detailed fabrication process has been introduced in the ESI†. The semiconductor material of WO$_3$ nanowires were prepared by electrospinning method, which is similar with other’s report. The obtained WO$_3$ nanowires were calcined at 500 °C for 2 h at the heating and cooling speed of 1 °C min$^{-1}$.

![Figure 1. Schematic diagram of the heating-induced thermal nanosoldering technique in SEM-FIB. (a) Schematic of the heating groove inside the SEM-FIB. (b) The magnified schematic of the soldering site on wafer inside the groove in (a). (c) Placement of a sacrificial nanowire solder in soldering junction of the nano-pattern to be welded using W nanotips. (d) Cleaning the soldering site by Ga$^+$ beam irradiation. (e) Thermal soldering the nano-objects together by directly heating.](image)
Figure 2. Characterization of 1D 97Sn3Cu nanowires solder and WO$_3$ nanowires. (a) A representative SEM image of a bundle of 1D 97Sn3Cu nanowires dissolved from PC templates. (b) HAADF-STEM image of individual 97Sn3Cu nanowires. (c) A SEM image of the WO$_3$ nanowires fabricated by electrospinning. (d) HAADF-STEM image of individual WO$_3$ nanowires. (e, f) The EDX elemental mappings of Sn-L and Cu-K from the areas marked by the red square in (b). (g, h) The EDX elemental mappings of W-L and O-K from the areas marked by the red square in (d). (i) A representative TEM image of a bundle of 1D 97Sn3Cu nanowires dissolved from PC templates. (m) Magnified view of the blue square in (i). (j-l) Lattice-resolution images of the areas marked by the red square ‘J’, ‘K’ and ‘L’ in (m), respectively. (n-p) CBED patterns of the area marked by the red square ‘J’, ‘K’ and ‘L’ in (m), respectively. The insets show the relevant crystal models of the CBCD patterns obtained.

The morphological, chemical and structural analysis of the 1D SnCu alloy nanowire solder and WO$_3$ nanowires were characterized by transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDX), scanning transmission electron microscope (STEM), X-ray diffraction analysis (XRD), high-angle annular dark-field and scanning transmission electron microscopy (HAADF-STEM). A representative SEM image of a bundle of SnCu alloy nanowires solder is shown in Figure 2a, indicating a 5 µm average length. Figure 2b shows a representative HAADF-STEM image, revealing that the bottom diameter of the 1D SnCu alloy nanowires is approximately 80 nm and their middle diameter is approximately 135 nm. It is also observed that the SnCu alloy nanowires with an even contrast show a continuous structure, relevant uniform size and even chemical composition along the nanowire length. The representative EDX spectrum of the 1D SnCu alloy nanosolders was shown in ESI† (Figure S1a). A quantitative analysis of this spectrum reveals that the chemical composition of individual 1D nanosolders is approximate a 97.0:3.0 weight ratio of Sn-Cu (molar ratio is close to 17.3:1 of Sn to Cu), inferring a 97Sn3Cu chemical composition. Figures 2e-f further show the EDX elemental mappings of Sn-L and Cu-K. The elements of Sn and Cu are nearly evenly distributed throughout the whole nanosolder, indicating a uniform 97Sn3Cu chemical phase. Figure 2c shows a representative SEM image of WO$_3$ nanowires fabricated by electrospinning with a diameter of approximately 300 nm. A representative EDX spectrum of the WO$_3$ nanowires was showed in Figure S1b. A quantitative analysis of this spectrum indicates the molar ratio of W to O is close to 1:3, inferring a WO$_3$ composition. Figure 2d shows a HAADF-STEM image of WO$_3$ nanowires, which have a continuous structure and uniform diameter. Figure 2g-h further show the EDX elemental mappings of W-L and O-K from the area marked by red square in Figure 2d, indicating a uniform WO$_3$ chemical phase. A representative TEM image of WO$_3$ nanowires is shown in Figure S2a, of which relevant selected-area electron diffraction (SAED) pattern (ESI†, Fig. S2b) can be well indexed to the crystal planes of monoclinic WO$_3$.$^{12}$ The crystal structures of individual 1D 97Sn3Cu nanosolders were characterized in detail by using high-resolution TEM (HRTEM) and convergent beam electron diffraction (CBED). A representative TEM image of a bundle of 97Sn3Cu nanowires were showed in Fig. 2i. Figure 2m shows a magnified TEM image of the area marked by a blue square in figure 2i. Figure 2j-l show lattice-resolution images of the areas marked by the red squares ‘J’, ‘K’ and ‘L’ in Figure 2m, respectively. The interplanar distances are measured to be 2.79 Å and 2.91 Å for area J, which matches the (101) and (200) planes of body-centered tetragonal (BCT) β-Sn; 1.90 Å and 4.05 Å for area K matching the (1-33) and (20-2) planes of monoclinic Cu$_6$Sn$_5$; and 2.64 Å for area L matching the (101) plane of tetragonal SnO$_2$. The SnO$_2$ phase could be observed because the surfaces of nanosolders were oxidized after released from the PC template. The corresponding CBED patterns of the ‘J’, ‘K’ and ‘L’ areas are shown in figure 2n-p. The corresponding crystal structures models of the three crystal phases were also simulated, as shown in the insets of Figure 2n-p. In addition, the XRD spectrum of the 97Sn3Cu solders again shows the existence of the three crystal phases (ESI†, Figure S3). It is then concluded that the 1D 97Sn3Cu nanosolder is composed of matrix β-Sn and intermetallic compound Cu$_6$Sn$_5$, which is the same as the crystal phases of bulk 97Sn3Cu.$^{37}$

In situ SEM-FIB heating-induced nanosolder reflow is firstly demonstrated, which strongly determines the success of nanosoldering. To get the suitable reflow temperature (or the soldering temperature), TA Instruments Q100 differential scanning calorimeter (DSC) was used to measure the melting point of nanowire solders, which was carried out from 50 °C to 550 °C at 5 °C min$^{-1}$ under argon flow. Figure 3a shows a representative DSC curve of 1D 97Sn3Cu nanowires solder (2 mg). Only one peak in this curve can be seen, which corresponds to the 220.4 °C melting point of the nanosolder. This value is lower than that of bulk 97Sn3Cu solder (310 °C).$^{38}$ which should be due to the small size effect of the nanoscale solder. The thermogravimetric analysis (TGA) curve of 97Sn3Cu nanosolder is shown in Figure 4. The measured melting point of 97Sn3Cu is close to that of bulk Sn3.5Ag (221 °C),$^{39}$ so the representative reflow temperature of 250 °C could be utilized for the reflow of
97Sn3Cu nanosolder. According to our previous work, the reflow experiment of 97Sn3Cu nanosolder should be composed of preheating at 150-180 °C (A), thermal soak at 180-220 °C (B), reflow at 220-250 °C (C) and cooling process (D), which are composed in Figure 3b. Then the dynamic reflow experiment of 97Sn3Cu nanowires solder in Ni-grid was carried out in SEM-FIB precisely controlled by in situ heating apparatus. All the process was dynamical monitored by SEM showed in Figure 3c-j. After preheating at 150-180 °C, one can see that the nanowires nearly have retained their original morphology but the softening of nanowires marked by yellow dotted square has been appeared, which was shown in Figure 3d and e. Then the temperature raised to 220 °C, at which the different dwelling time were demonstrated in Figure 3f-i. It is seen that the melted nanowire marked by green dotted square in Figure 3f has flowed along the nanowire, in which an obvious nanotube was observed. This nanotube is deduced to originate from the surface oxide layer or contaminations like carbon and organics. It is confirmed that the nanotube has largely hindered the reflow progress of nanosolder. With the rising temperature of reflow at 250 °C, one can see that the melted nanosolder will keep flowing along the nanotube, then a protuberance finally formed in the area marked by green dotted square showed in Figure 3j. From a series of SEM images (Figure 3e-j), it is obviously seen that the bundle of nanowires solder marked by red dotted square were gradually melted, and then formed into a sphere, due to be that the nanowires have less oxide layer or contamination.

To verify the barrier layer which has hindered the reflow melting of nanosolder, TEM technique was employed to check the surfaces of the 97Sn3Cu nanosolders. Figure 4a shows a typical TEM image of individual 97Sn3Cu nanowire solder. Figure 4b further shows the EDX elemental mappings of O-K. It is seen that the element of O is nearly evenly distributed throughout the whole nanosolders, revealing a thin layer oxide covered on the surface of 97Sn3Cu solder. This oxide was proved to come from oxidation after they are released from the PC templates, which is SnO2. The previous crystal structural analysis and XRD spectrum of the 97Sn3Cu solders all show an existence of SnO2 (ESI†, Fig. S3). Figure 4c shows the reflowed nanosolders after high energy electron beam irradiation in TEM, in which the temperature is much high than their melting point. It is seen that the most reflowed nanosolders have changed into spherical morphology, which is because the high energy electron beam irradiation has broken the surface barrier layers. The residual oxide surface layers remain the original place. However, there are some obvious positions not to completely melt as marked by
yellow dotted circle. It is deduced to be that the melted nanosolders were restricted by the tube-like surface layers, in which the energy was not high enough to conquer the high-melting point of surface layers. The magnified TEM image of this position shown in Figure 4d further verifies the existence of barrier oxide layers. In order to accurately determine the chemical states, the as-grown 1D SnCu nanosolders were further examined by XPS (X-ray photoelectron spectroscopy) while they were still embedded in situ in the PC templates by Ar ion beam sputtering. The templates were cross-sectioned, parallel to the 1D SnCu nanosolder length axes, by sputtering away (layer by layer) the top surface of the PC template. The relevant XPS spectra of Sn 3d after Ar ion beam sputtering for 0s, 10s, 20s, 30s, 50s, 70s, 90s, 110s and 150s respectively, of which corresponding depth profile analysis is shown in Figure 4e. The binding energies were calibrated using the C 1s peak of 284.6 eV as standard. The binding energy of Sn 3d$_{5/2}$ indicated that the peak, which was in the range of 484.5 eV to 485.2 eV, is attributed to Sn, and the range of 486.4 eV to 486.9 eV is attributed to SnO$_2$. This result indicates that the surface of 97Sn3Cu nanosolder is mainly composed of SnO$_2$ which were exposed to air have been partly oxidized. After the sputtering time was larger than 110 s, the quantitative analysis of XPS wide spectrum (ESI†, Fig. S5) reveals that the 1D SnCu nanosolders reach a stable 96.8:3.2 weight ratio of Sn:Cu. This result is also the same as above EDX measurement in error. Therefore, the chemical composition of the 1D SnCu nanosolders in this work is inferred to be 97Sn3Cu alloy by weight ratio.

It is well known that Ga ion beam in SEM-FIB has a good ability to clean up surface oxides during the reflow process. In this work, this method is adopted and further combined with a thermal heating technique, which creates a novel in situ SEM-FIB thermal soldering method as far as we have known. As shown in Fig. 5, a 250 °C temperature (about 30 °C higher than its melting point) was set up to melt the nanosolder in Si/SiO$_2$ wafer in order to achieve a full reflow. Figure 5a shows a representative SEM image of a bundle of 1D 97Sn3Cu nanosolders after preheating 2 minutes at 180 °C and followed heating 3 minutes at 250 °C. One can see that the most of the nanosolders still remain their original morphology except that few protuberances along the nanowires were formed because of the impediment of surface oxides. Followed by the bombardment of weak Ga ion beam, Figure 5b shows that all solder nanowires dramatically changed into spheres because of the knock-off of surface oxides. In order to further verify the cleaning effect of ion beam irradiation, a comparison reflow experiment with and without ion beam irradiation before reflow has been done as shown in Figure 5c. The left side of Fig. 5c shows the reflow effect without Ga$^+$ beam irradiation when followed the same reflow process, where the nanowire solders nearly remain their original morphology. Whilst, the right side shows that of reflow effect with Ga$^+$ beam irradiation, which have nicely formed into spheres. From this compared reflow experiments, it is concluded that our invented method of in situ SEM-FIB thermal soldering has a powerful ability to reflow nanosolders at a specific temperature and can become a powerful new nano-soldering technique.

The wettability experiment is further carried out to verify the solderability between WO$_3$ material and the 97Sn3Cu nanosolders, insuring the success of soldering individual WO$_3$ nanowires together with the usage of 97Sn3Cu nanosolders. There are mainly three quantitative methods to measure the wettability: contact angle, the Amott method (imbibition and forced displacement) and the U. S. Bureau of Mines (USBM) method. In this work, the contact angle is employed to evaluate the wettability. The wettability experiments were carried out by directly heating the specimens in situ SEM (ESI†, Fig. S6). The results clearly confirm that the 1D 97Sn3Cu nanosolders have an excellent wettability and solderability on the WO$_3$ semiconductor material.

The example of soldering X-shaped nanopattern constructed by two individual WO$_3$ nanowires with a sacrificial 97Sn3Cu nanowire solder is demonstrated in Fig. 6, which shows a good application of the technique into soldering semiconductor WO$_3$ nano-objects. Two WO$_3$ nanowires with 300 nm in diameter and about 6 μm in length were firstly manipulated to construct an X-shaped nanopattern on a Si/SiO$_2$ wafer (Fig. 6a) by using a nanomanipulator in situ SEM-FIB platform. Then a sacrificial 97Sn3Cu nanosolder was accurately transferred onto the expected soldering junction of the X-shaped nanopattern (Figures 6b-c). Before the thermal soldering, a Ga$^+$ beam in SEM-FIB was used to remove the impurities covered on the surface of nanopattern marked by the yellow area (Fig. 6d), such as oxide, carbide or organics, to achieve a lower soldering temperature and more reliable bonding. In the subsequent
reflow process, the heating apparatus firstly preheated the nanosolder at 180 °C for 2 min, then the temperature rose up to 250 °C for 3 min to melt the nanosolder at the soldering site. Since monoclinic WO$_3$ is quite stable, up to 1000 °C, which is much higher than the soldering temperature of 250 °C,[2], the sustaining heating only causes the nanosolder melted and brings out a limited element diffusion between the nanosolder and the semiconductor WO$_3$ matrix at the welded junction. A mechanical, strong and reliable bonding was formed (Fig. 6e). The lateral profile of the soldering nanopattern imaged by tilted the SEM-FIB sample stage further proves that the two WO$_3$ nanowires has been well soldered together by the melted 97Sn3Cu nanosolder (Fig. 6f). It is known that the diffusion between the solder material and matrix deeply depends on the temperature according to the Arrhenius-like equation: $D = D_0 \exp(-Q/RT)$. During the processes of our \textit{in situ} SEM-FIB thermal soldering, the temperature and holding time can be precisely controlled and therefore realize a precision control of diffusion between solder material and semiconductor matrix at the soldering interface. It is then seen that our invented new nanosoldering technique provides an ideal way to construct nanooarchitectures of semiconductor nanomaterials which do not or less influence on their performance. In addition, this new method can easily tailor the morphology and chemistry of nanosolder to meet the requirements of different soldering sites and semiconductors (ESI†, Fig. S7).

**Conclusions**

In summary, we have realized the soldering of two WO$_3$ nanowires by using our invented \textit{in situ} SEM-FIB thermal naosoldering method. As for the performance of semiconductor materials are sensitive to the quantity of impurity atoms, this nanosoldering technique shows a prominent advantage because it can precisely control the diffusion between the nanosolder and the semiconductor nano-objects. Besides, our method also realizes a morphological and chemistry tailors for various soldering environments and semiconductor nanomatrix. We also have contributed a novel 1D 97Sn3Cu nanowire solder. Our work is believed to make the bottom-up nanooarchitecture of semiconductor nanomaterials reality, which is significant to transfer diverse semiconductor nano-objects into nano-sensors or nano-electronics.

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