Journal of Materials Chemistry C

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

aReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Here we demonstrate that the building blocks of semiconductor WO₃ 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,¹ nano-sensors² and nano-electronics.³ Nanoscale semiconductor nano-objects, made from materials like WO₃, InP, Cu₂O, ZnO, GaAs, SnO₂ etc., are essential building blocks for optoelectronic devices,⁴ photovoltaic diodes,⁵ nanowires lasers,⁶ photon- and gas-sensing nano-devices,⁷ owing to their unique optical, chemical, electrical and biological properties.⁸ Among them, WO₃ nanomaterials with outstanding electrochromic, optochromic, and gaschromic properties, have been widely utilized to manufacture various nano-structures such as high-performance flexible electrochromic device,⁹ optical switching devices,¹⁰ ultrasensitive NO₂ gas sensors,¹¹ ultraviolet (UV) photodetector with high sensitivity and precise selectivity,¹² nonvolatile memory devices,¹³ WO_{3-x}-based nanoionics device¹⁴ 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.

Nano-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,¹⁵ soldering technique,^{16,17} Joule heating,¹⁸ high-energy electron beam irradiation,¹⁹ ion beam deposition,²⁰ ultrasonic soldering²¹, thermal heating²² and electron-beam-induced deposition.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.^{16,17} One technique is to locally deposit nanoscale volumes of solder at the soldering site by electricity-induced Joule heating.¹⁶ Another approach is laser-induced heating nanosolder at the soldering site.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.^{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 $\bar{D} = D_0 \exp(-Q/RT)$, 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

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†Electronic Supplementary Information (ESI) available: supplementary figures See DOI: 10.1039/x0xx00000x

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diffusion mechanisms.²⁶ This high temperature leading to an instantaneous mild diffusion between nanosolders and semiconductor materials may have a disastrous damage on electrical characteristics of semiconductor materials, due to be that their electrical properties deeply depend on the quantity of impurity atoms inside the semiconductor materials.²⁷

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 WO₃ 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-bondings. A large number of studies have revealed that the copper has a good ability to thermally diffuse into WO₃ films beyond the temperature of 135 °C.²⁸ 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.²⁹⁻³² 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.³³⁻³⁶ Hence, there is credible to utilize 97Sn3Cu alloy nanosolders to solder semiconductor WO₃ nanowires together, in that a reliable

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.

metallurgical 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 WO₃ nanowires were prepared by electrospinning method, which is similar with other's report.¹² The obtained WO₃ nanowires were calcined at 500 °C for 2 h at the heating and cooling speed of 1 °C min⁻¹.

Figure 2. Characterization of 1D 97Sn3Cu nanowires solder and WO₃ 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 WO₃ nanowires fabricated by electrospinning. (d) HAADF-STEM image of individual WO₃ 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 CBED patterns obtained.

The morphological, chemical and structural analysis of the 1D SnCu alloy nanowire solder and WO₃ nanowires were characterized by transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDX), scanning transmission electron microscope (SEM), 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 showed 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 WO₃ nanowires fabricated by electrospinning with a diameter of approximately 300 nm. A representative EDX spectrum of the WO₃ 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 WO₃ composition. Figure 2d shows a HAADF-STEM image of WO₃ 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 WO₃ chemical phase. A representative TEM image of WO₃ 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 WO₃.¹² 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 Cu₆Sn₅; and 2.64 Å for area L matching the (101) plane of tetragonal SnO₂. The SnO₂ 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 Cu₆Sn₅, 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),³³ 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 S4. The measured melting point of 97Sn3Cu is close to that of bulk Sn3.5Ag (221 °C),³⁸ so the representative reflow temperature of 250 °C could be utilized for the reflow of

97Sn3Cu nanosolder. According to our previous work,³⁹ 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

Figure 3. Dynamic melting process of a bundle of 1D 97Sn3Cu nanosolders in situ monitored in SEM-FIB. (a) A representative DSC curve of 97Sn3Cu nanowires solder embedded in a PC template heated from 50 °C to 550 °C at the 5 °C min⁻¹. Inset, the DSC curve with full measuring range. (b) A line chart of melting process in Ni-grid by in situ SEM-FIB heating apparatus including preheating, thermal soak, reflow and cooling process. (c–j) Representative SEM images of dynamic melting process.

showed 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 showed 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 solders. This oxide was proved to come from oxidization after they are released from the PC templates,³⁹ 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

Figure 4. (a) A representative TEM image of an individual 1D 97Sn3Cu nanowire. (b) The EDX elemental mappings of O–K from the area in (a). (c) The reflowed nanosolders under electron beam irradiation in TEM. (d) The magnified images from the area marked by the yellow dotted circle in (c). (e) The XPS spectra for Sn3d after Ar ion sputtering 97Sn3Cu nanosolders for 0, 10, 20, 30, 50, 70, 90, 110, 150s, respectively.

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

Figure 5. Reflow behavior of the 1D 97Sn3Cu nanowires solder in Si/SiO₂ wafer with Ga⁺ beam irradiation. (a) Preheating at 180 °C for 2 min and then heating at 250 °C for 3 min without Ga⁺ beam irradiation. (b) After Ga⁺ beam irradiation. (c) A comparison diagram of preheating 2 min at 180 °C then heating 3 min at 250 °C: the area left is reflowed after the bombardment of Ga⁺ beam, while the right area is not.

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 SnO₂. This result indicates that the surface of 97Sn3Cu nanosolder is mainly composed of SnO₂ 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.⁴⁰ 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/SiO₂ 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 WO₃ material and the 97Sn3Cu nanosolders, insuring the success of soldering individual WO₃ 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.⁴¹ 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 WO₃ semiconductor material.

The example of soldering X-shaped nanopattern constructed by two individual WO₃ nanowires with a sacrificial 97Sn3Cu nanowire solder is demonstrated in Fig. 6, which shows a good application of the technique into soldering semiconductor WO₃ nano-objects. Two WO₃ nanowires with 300 nm in diameter and about 6 μm in length were firstly manipulated to construct an X-shaped nanopattern on a Si/SiO₂ 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 WO₃ is quite stable, up to 1000 °C, which is much higher than the soldering temperature of 250 °C⁴², the sustaining heating only causes the nanosolder melted and brings out a limited element diffusion between the nanosolder and the semiconductor WO₃ 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 WO₃ nanowires has

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 nanoarchitecture of semiconductor nanomaterials reality, which is significant to transfer diverse semiconductor nano-objects into nano-sensors or nano-electronics.

Acknowledgements

This work was supported by National Natural Science Foundation of China (51571104 and 11274145), MOST International Cooperation Funds (2014DFA91340), Program for Changjiang Scholars and Innovative Research Team in the University (Grant No. IRT1251).

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Figure 6. The thermal soldering process. (a) The 97Sn3Cu nanosolder were mechanically lifted with shovel-like tip of the nanomanipulator probe. (b, c) Accurately place the sacrificial nanosolder in the junction of the nano-pattern to be welded, then withdraw the probe. (d) Ga ion beam irradiation the soldering site marked by yellow circle area. (e) Thermal nanosoldering the WO₃ nanowires together by preheating at 180 °C for 2 min and then reflow heating at 250 °C for 3 min, causing efficient and limited material diffusion in the interface to form strong bonding. (f) The magnified lateral profile of the thermal soldering junction.

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: $\tilde{D} = D_0 \exp(-Q/RT)$. During the processes of our *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 nanoarchitectures 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 WO₃ nanowires by using our invented *in situ* SEM-FIB thermal nanosoldering method. As for the performance of semiconductor materials are sensitive to the quantity of impurity atoms, this nanosoldering technique shows a prominent advantage because

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