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Modulating the surface states of electric field assembled CuO nanowires by electrochemical deposition method

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In this paper, the electrochemical deposition and anneal method has been developed to modulate the contact performance of electric field assembled CuO nanowires. After modulation, the current increases about two orders. The *I-V* curves indicate that before and after modulation, the current transport properties are both dominated by the reverse current of Schottky barriers under image force model. The current increase results from the formation of another current pathway, i.e., the CuO nanowire@nanoparticles/Pt electrode structure, in which the surface states in metal-semiconductor interface are largely reduced by passivating dangling bonds, and the barrier height decreases about 105 meV. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3213551]

The Schottky barrier (SB) between metal and semiconductor is an important building block for electronic and optoelectronic devices,[1,2] and many SB nanodevices based on one-dimensional (1D) semiconductor nanomaterials have been prepared in the recent years, such as 1D SB rectifier,[3–5] carbon nanotube (CNT) SB field effect transistor,[6] and CNT SB light emitter.[7] In the preparation of these 1D SB nanodevices, the key basis is controlling the barrier height.[3–7] For CNT, the barrier height of SB can be effectively controlled by the work function of metals.[3] However, for semiconductor nanowires (NWs), more and more reports have indicated that the SB is caused by the surface states of NWs due to the Fermi level pinning effect.[8,9] Therefore, it is necessary to explore other methods to modulate the surface states of NWs for controlling their barrier height and developing NW SB nanodevices. The dangling bonds in the surface are the major factor for the formation of surface states,[2] therefore, the passivation of dangling bonds can effectively modulate the surface states.[10,11] For example, Wu *et al.*[10] and our group[11] have reported the preparations of NiSi–Si and Cu–Cu$_x$O metal-semiconductor nanojunctions by selective transformation using photolithography and atomic force microscopy lithography methods, respectively. In these two methods, the semiconductors and metals are developed on the homologous substance, and the dangling bonds in the interface between them can be passivated, which can effectively modulate the surface states and form Ohmic contact. However, low yield and high cost of these two methods limit their applications for the integration of nanodevices. In this paper, a simple and effective method based on electrochemical deposition has been developed to modulate the surface states of the electric field assembled CuO NWs by passivating the dangling bonds, which shows promising applications in the preparation and integration of NW SB nanodevices. After modulation, the current increases about two orders, and the barrier height of NW SB decreases about 105 meV. In addition, the mechanism of this modulation method has been discussed on

the base of the two-dimensional (2D) barrier geometry model of NW SB.

CuO is a *p*-type semiconductor with a narrow band gap (1.2 eV) and exhibits a number of interesting properties.[12,13] The preparation of CuO NWs by heat oxidation method has been described in detail in our previous report.[8] After being dispersed in ethanol, the CuO NWs were assembled on a pair of Pt electrodes by electric field assembly method.[14–16] The detailed discussion of electric field assembly has been described in our previous report,[14] and the scanning electron microscopy (SEM) image of the assembled CuO NWs is shown in Fig. 1(a), which is defined as after-assembled (AA) NWs. In the following, a layer of Cu film was deposited on the surface of Pt electrodes and CuO NWs by electrochemical deposition method. The electrolyte was composed of cupric saxlfate pentahydrate (CuSO$_4$·5H$_2$O), citric acid (C$_6$H$_8$O$_7$·H$_2$O), and potassium sodium tartrate tetrahydrate (C$_4$H$_4$O$_6$KNa·4H$_2$O), and the *p*H value was adjusted to 9 with KOH. A Pt thread was used as anode, the two Pt electrodes were electrically connected together and used as cathode, and the deposition voltage and time were 2.65 V and 2 min, respectively. After electrochemical deposition, the samples were annealed in air at 500 °C for 5 h. The SEM image of the NWs after electrochemical deposition and annealing treatment is shown in Fig. 1(b), which is defined as after-treated (AT) NWs. The x-ray diffraction pattern of AT NWs (not shown here) shows that the annealing treatment has completely oxidized the Cu film into monoclinic CuO nanoparticles (NPs) film, and the size of CuO crystal particle
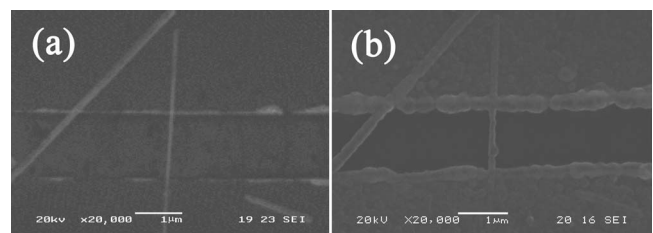

FIG. 1. The SEM image of the CuO NWs after assembly (a) and after treatment (b).

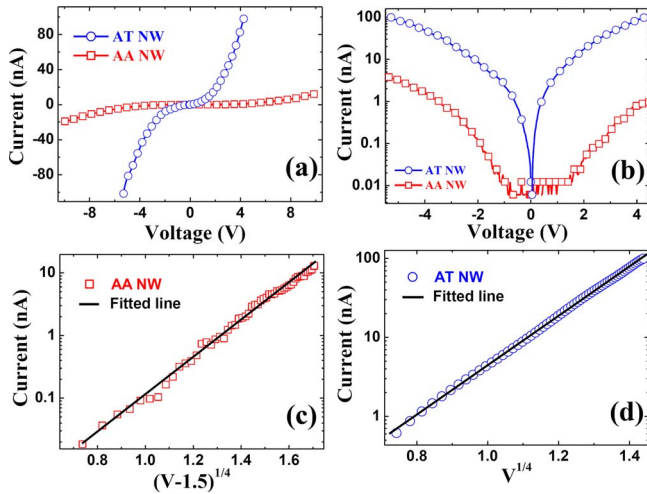[a)]Author to whom correspondence should be addressed. Electronic mail: zld@henu.edu.cn.

FIG. 2. (Color online) (a) and (b) are the *I-V* curves of AA and AT NWs in linear and log scale, respectively. (c) and (d) show the plots of ln *I* with $(V-V_0)^{1/4}$ for AA NWs using $V_0=1.5$ V and AT NWs using $V_0=0$ V, respectively. The solid straight lines are their fitted lines.
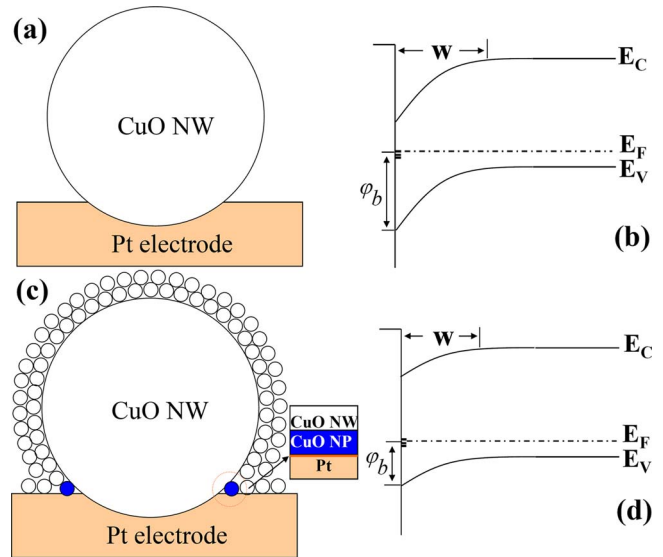

FIG. 3. (Color online) (a) and (b) show the sketch maps and the corresponding energy band diagram of AA NWs cross section, respectively. (c) and (d) are the sketch map and the corresponding energy band diagram CuO NW@NPs cross section, respectively. The right inset of (c) shows the CuO NW@NPs/Pt structure diagram.

is about 14.6 nm according to Scherrer formula. As shown in Fig. 1(b), the thickness of the CuO film on the surface of CuO NWs is about 50 nm. So AT NWs are actually the CuO NWs coated by CuO NPs, which can be marked as CuO NW@NPs.

Figure 2(a) shows the *I-V* curves of AA NWs and AT NWs measured in air at room temperature, and Fig. 2(b) shows their plots in log scale. It is clear that the current of CuO NW@NPs is obviously larger than that of AA NWs, and the current ratio between them is about 100 times in the bias range from 2 to 4 V. In addition, the positive and negative turn-on voltages for AA NWs are 1.5 and −0.8 V, respectively, while the turn-on voltages for CuO NW@NPs decrease to zero. The current transport behavior of CuO NW SB under image force model has been discussed in detail in our previous report.[8] In the image force model,[2] the effective barrier height of SB decreases with the increase of reverse bias because of the image force, and the current transport properties follow the equation $\ln(I) \propto (V-V_0)^{1/4}$, where V_0 is the turn-on voltage. As shown in Figs. 2(c) and 2(d), for the positive current of AA NWs (using $V_0=1.5$ V) and CuO NW@NPs (using $V_0=0$ V), the plots of ln *I* are both linear with $(V-V_0)^{1/4}$, which indicates that the current transport properties of AA NWs and CuO NW@NPs both follow the image force model. This indicates that for both AA NWs and CuO NW@NPs, the NWs make two SB contacts with the two Pt electrodes, and a back-to-back SBs structure[8,14,17] is formed, in which the current is dominated by the reverse current of the reverse biased SB.

In order to investigate the current increase mechanism of AT NWs, it is necessary to understand the current transport pathway of AA NWs and CuO NW@NPs. Figure 3(a) shows the sketch map of cross section of the contact between AA NW and Pt electrode. Here, we define the SB in the contact interface between CuO NW and Pt electrode as SB_{NW}, and its energy band sketch map is shown in Fig. 3(b), in which φ_b, W, E_C, E_F, and E_V are the barrier height, barrier width, conduction band level, Fermi level, and valence band level, respectively. According to the 2D partly depleted geometry model of NW SB developed in our recent report,[14] the band bending direction (the lateral axis in [Fig. 3(b)] is along the

normal direction of the interface between NW and Pt electrode, the barrier height W is smaller than the radius of NW, and an undepleted region existed in the center region of the NW cross section. When SB_{NW} is reverse biased, the holes first get across the SB_{NW} and transfer from the Pt electrode into the undepleted region in AA NW, and then transfer along the long-axis of NW [perpendicular to the cross section in Fig. 3(a)] in the undepleted region. Therefore, the current of AA NWs is dominated by the SB_{NW}.

Figure 3(c) shows the sketch map of cross-section of the contact between CuO NW@NPs and Pt electrode. In corners between CuO NWs and Pt electrode, the surface of CuO NW is also connected to Pt electrode by the CuO NPs, and then another current transport channel is formed [marked as the solid circles in the inset of Fig. 3(c)]. The control experiments indicate that, when AA NWs are only annealed under 500 °C for 5 h, there is no obvious current increase. These results indicate that the current increase of AT NWs is attributed to the added current channel, i.e., the CuO NW@NPs/Pt electrode structure. It is necessary to note that since the CuO NW@NPs structure is obtained by oxidizing the CuO NW/Cu NPs structure under high temperature, the CuO NPs can be considered as an epitaxial growth layer on the CuO NW surface, and there is no interface barrier between CuO NW and CuO NPs. So the current transport of CuO NW@NPs is only dominated by the SB in CuO NPs/Pt electrode interface, which is defined as SB_{NP}. As discussed above, the *I-V* curve of CuO NW@NPs is also in good agreement with image force model. The barrier height decrease under image force model is caused by the generation of image charges in the metal around the metal/semiconductor interface,[2] which is a characteristic transport model of SB between metal and semiconductor, and not suitable for other junctions (such as *p-n* junction and semiconductor heterostructure). Therefore, the image force transport model also confirms that the current transport of CuO NW@NPs is dominated by the SB in CuO NPs/Pt electrode interface. Figure 3(d) shows the sketch map of the energy

band of SB_{NP}, in which the band bending direction is along the normal direction of CuO NPs/Pt electrode interface.

According to above discussions, the current transport properties of AA NWs and CuO NW@NPs are dominated by SB_{NW} and SB_{NP}, respectively. Therefore, the current increase of CuO NW@NPs is mainly attributed to the barrier height decrease of SB_{NP}. The reverse saturation current I_0 and barrier height φ of SB follow the equation $I_0 = AA^{**}T^2 e^{(-q\varphi/kT)}$,[1,2] where A is the contact area of SB, A^{**} is effective Richardson constant, T is absolute temperature, q is the magnitude of electronic charge, and k is Boltzmann constant. The I_0 values for SB_{NW} and SB_{NP} are equal to the intersection point between the y-axis $[(V-V_0)^{1/4}=0]$ and the fitted lines of $\ln(I) \propto (V-V_0)^{1/4}$ in Figs. 2(c) and 2(d), respectively. According to the obtained I_0 values and assuming that the contact areas of SB_{NW} and SB_{NP} are approximately equal, we can get that the barrier height of SB_{NP} decreases about 105 meV than that of SB_{NW}.

In our previous report, it has been discussed in detail that the SB of CuO NWs is controlled by their surface states, but not by the work function difference between CuO NWs and metal.[8] For p-type metal-oxide semiconductor, the surface states induced by metal ion dangling bonds is the dominative factor for forming SB.[18,19] In the case of p-type CuO NW, the surface states of Cu dangling bonds can capture the holes in the valence band, and then form charge depletion layer and SB. In the formation process of SB_{NP} by oxidizing Cu NPs/Pt electrode structure, a PtCu alloy about several atomic layers can be formed in the interface,[20] and the Cu atoms on the surface of CuO NPs can form Cu–Cu or Cu–O–Cu chemical bonds with the Cu atoms in the PtCu alloy layer, which can passivate the Cu dangling bonds and then decrease the barrier height of SB_{NP}. In addition, the adsorbed gas (such as O_2, vapor, etc.) can form chemical bonds with Cu dangling bonds, and then partly releases the captured holes to valence band, which reduces the barrier width and barrier height of SB.[18,19,21] However, this kind affects to p-type semiconductor must be much smaller than to n-type semiconductor, in which the adsorbed O_2 is main reason for forming the charge depletion layer and SB.[9] Moreover, in our experiment the electrical measurement of SB_{NW} and SB_{NP} are both carried out in air with same O_2 pressure, so we consider that the barrier height decrease of SB_{NP} is mainly attributed to the passivation of Cu dangling bonds.

We have recently reported the preparation of Cu/CuO metal/semiconductor nanoscale heterostructure by atomic force microscopy lithography, in which the dangling bonds of CuO NPs in Cu/CuO interfaces can be largely passivated by forming chemical bonds, and the Ohmic contact with linear I-V curve can be obtained.[11] While, in CuO NW@NPs the I-V curve is nonlinear, and a barrier is still existed for SB_{NP}. This result indicates that the dangling bonds of CuO NPs in SB_{NP} have not been completely passivated, and the surface states density has not been reduced to a threshold value for forming Ohmic contact. Increasing the Cu atom ratio in PtCu alloy layer may be an effective method for completely passivating dangling bonds and forming Ohmic contact.

In conclusion, the current of electric field assembled CuO NWs increases about two orders after treatment by electrochemical deposition and anneal. Before and after treatment, the current transport properties of the NWs are both dominated by the reverse current of SB under image force model. The current increase of AT NWs mainly results from the formation of another current channel, i.e., the CuO NW@NPs/Pt electrode structure, which has a barrier about 105 meV lower than that of AA NWs. The decrease of barrier height is mainly attributed to the reduction of surface states of CuO NPs caused by the passivation of Cu dangling bonds. This passivation is closely associated with the formation of Cu–Cu or Cu–O–Cu chemical bonds and PtCu alloy at the interface between Cu atoms on the surface of CuO NPs and Pt electrode during the process of electrochemical deposition and anneal. The combination of electric field assembly and electrochemical deposition supply a simple and effective method to modulate the surface states and barrier height of NW SB, which show promising applications in the preparation and integration of NW SB nanodevices.

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