Interfacial effect on metal/oxide nanowire junctions

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An interface in metal/oxide nanowire junctions plays a crucial role on the electronic device applications, especially two-terminal devices. Here we demonstrate the crucial role of interfacial effects on oxide ($SnO_{2-\delta}$) nanowire/Pt junctions. The resistivity estimated from the *I-V* data of the junctions was four orders of magnitudes higher than that measured by a noncontact microwave conductivity method. We found that such apparent discrepancy is due to the presence of insulating oxidized interfacial layer. Since most conductive oxides are typically *n*-type semiconductors via oxygen vacancies, above implications will be rather universal and crucial for reproducible emerging nanodevices using oxide nanowires. © *2010 American Institute of Physics*.
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Recently metal oxide nanowires are attracting much attention due to not only the fundamental nanoscale physical properties but also various device applications, including for example a transparent field effect transistor,[1] a power generator,[2] and a resistive switching memory[3] by utilizing various metal oxide nanowires. In such electronic device applications, a contact with metal electrodes must play an important role on the transport properties of such devices, especially for two-terminal devices including a resistive switching memory.[4,5] Recent investigations as to a contact between metal electrodes and semiconducting nanowires have demonstrated the impact of nanocontact on the transport properties.[6–17] Several important factors, including nanosize-dependent Schottky barriers,[6,7] oxidations of metal electrodes and/or nanowires,[8,9] fringing field effects,[10] interfacial trap states,[11–14] and others,[15–17] have been demonstrated. Since a carrier in many oxide materials typically originates in a crystallographic imperfection including oxygen vacancies (*n*-type) and cation vacancies (*p*-type),[18] a local stoichiometry at the interface should affect significantly the carrier injection from electrodes to oxide nanowires. However, knowledge as to such interfacial effects on oxide nanowire/metal junctions is still much scarce compared with those of carbon nanotube,[7,19–22] Si nanowires,[23,24] and compound semiconductor nanowires.[9,11,13,16] In this letter, we investigate the interfacial effect on the transport properties of Pt electrode/$SnO_{2-\delta}$ nanowire junctions by utilizing and comparing both a contact dc transport measurement and a noncontact ac microwave conductivity measurement.

SnO_2 nanowires were grown on Al_2O_3 (110) single crystal substrate by Au catalyst-assisted pulsed laser deposition technique.[25] Prior to the nanowire growth, Au catalysts were deposited on single crystal substrate. The background pressure of the chamber was 10^{-6} Pa. ArF excimer laser (Lamda-Physik COMPex 102, $\lambda = 193$ nm) operating at the pulse repetition rate of 10 Hz and the laser energy of 40 mJ was used for the laser ablation. Sn metal target was used as the source of Sn species during the nanowire growth. Oxygen and argon mixed gas was introduced into the chamber with controlling the ambient total pressure. The ambient total pressure was 10 Pa with the flux ratio of oxygen and argon (1:1000). The oxygen partial pressure was optimized to maintain untapered nanowire morphology by suppressing sidewall growth.[26] Prior to the laser ablation, the Au-coated Al_2O_3 substrate was preheated at 750 °C for 20 min. The typical growth temperature was 750 °C. After the nanowire

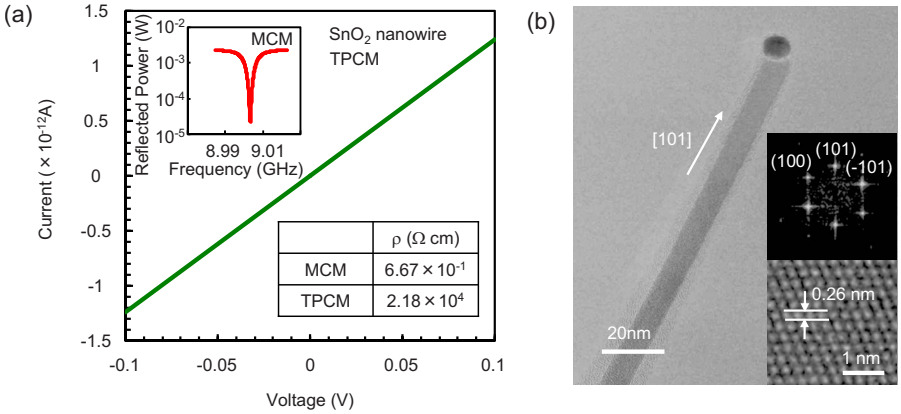

FIG. 1. (Color online) (a) *I-V* characteristics of individual SnO_2 nanowire measured by TPCM. Insets show the resonant curve obtained from MCM measurement and the table of resistivity data. (b) HRTEM image of fabricated SnO_2 nanowire. Inset shows the magnified images and the fast Fourier transform pattern.

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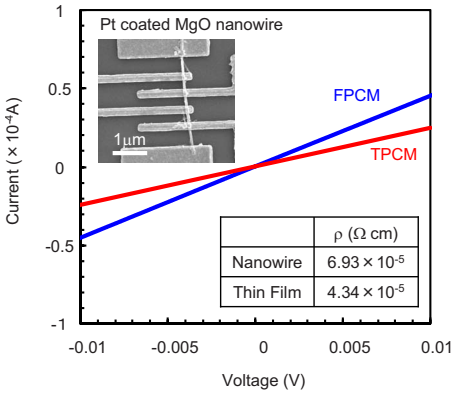

FIG. 2. (Color online) *I-V* characteristics of individual Pt coated MgO nanowire measured by TPCM and FPCM. Insets show the FESEM image of FPCM device and the table of resistivity data of Pt-coated MgO nanowire and Pt thin film.

growth, the samples were annealed in oxygen atmosphere for 30 min and cooled down to room temperature (RT) for 30 min. The nanowire morphology was characterized by field emission scanning electron microscopy (FESEM: JEOL JSM-6330FT) at an accelerating voltage of 30 kV. High-resolution transmission electron microscopy (HRTEM: JEM-3000F) was used to evaluate the diameter, the crystallinity, and the composition of the fabricated nanowires. HRTEM measurement was performed at an accelerating voltage of 300 kV. We employed several different methods to measure the transport properties of nanowires, including a microwave conductivity measurement (MCM), a two-probe conductivity measurement (TPCM), and a four-probe conductivity measurement (FPCM). The other details of the set of apparatus were described elsewhere.[27,28] For TPCM and FPCM, we utilized devices composed of individual nanowire, which were fabricated on degenerately doped *n*-type silicon substrate capped with a 200 nm silicon dioxide SiO_2 layer. Combining photolithography and electron-beam lithography processes enables us to define electrode patterns on the SiO_2/Si substrate, followed by metal deposition of Pt/Au 10/100 nm. Rapid thermal annealing (RTA) was performed to modify the contact conditions by varying temperatures 300–700 °C in Ar atmosphere of 10 Pa for 90 s. Pt films for RTA experiment were prepared by rf sputtering. Prior to the sputtering, the chamber was evacuated to be less than 10^{-4} Pa and then Ar gas with 1 Pa was introduced. The growth rate was approximately 10 nm/min. The rms roughness of fabricated Pt films was found to be less than 1 nm. The transport properties were measured by using semiconductor analyzer (Keithley 4200).

Figure 1 shows the comparison between TPCM and MCM on the resistivity of SnO_2 nanowires. The resistivity of TPCM was found to be four orders of magnitudes higher than that measured by MCM. Note that performing FPCM was not possible due to the high resistance. The methodological differences between TPCM and MCM are a measurable length scale due to the difference of the used high frequency range and a contact with metal electrodes. The frequency dependence on the resistivity of SnO_2 nanowires was found to be negligible considering the mobility range of SnO_2 nanowires.[25] Thus the observed discrepancy between them must be related to such interfacial contact issues. Here we examine several possible scenarios, which might explain the origin of the observed discrepancy. First, some previous reports[8,9] as to a contact between nanowires and Ti/Au metal electrodes highlighted the importance of the electrode oxidation in the presence of TiO_x at the contact interface on the transport properties. However, such electrode oxidation scenario should not be applicable for our case since our devices utilize a Pt/Au electrode. Second, residual organic resists at the interface might be detrimental for the carrier injection from the electrodes. To examine this effect, we performed TPCM and FPCM measurements for Pt-coated MgO nanowires by utilizing the same procedure of lift-off resist process, as shown in Fig. 2. We compare the transport properties of Pt-coated nanowires with that of Pt thin films without resist process. The resistivity data of both nanowires and thin films were consistently found to be close to the Pt bulk resistivity-10^{-5} Ω cm at RT,[29] and the resistance ratio of FPCM to TPCM, which is related to a contact resistance, was around 0.45–0.54 for both nanowires with resist process and thin films without resist process. Thus the scenario based on the presence of residual resists alone cannot explain the substantial discrepancy (four orders of magnitudes) between TPCM and MCM. Third, a point contact between granular metal electrodes and nanowires might exhibit an electric barrier at the contact interface. To address this issue, we have performed a RTA to modify the contact conditions. RTA treatments for various temperatures (300–700 °C in Ar 10 Pa for 90 s) were performed for Ta(5 at. %)-doped SnO_2 nanowires. We confirmed that increasing RTA temperature resulted in smoother electrode surfaces as shown in Fig. 3(a). This indicates that RTA treatments modify the contact area between electrodes and nanowires. Figure 3(b) shows the resistivity and the contact resistance extracted from TPCM

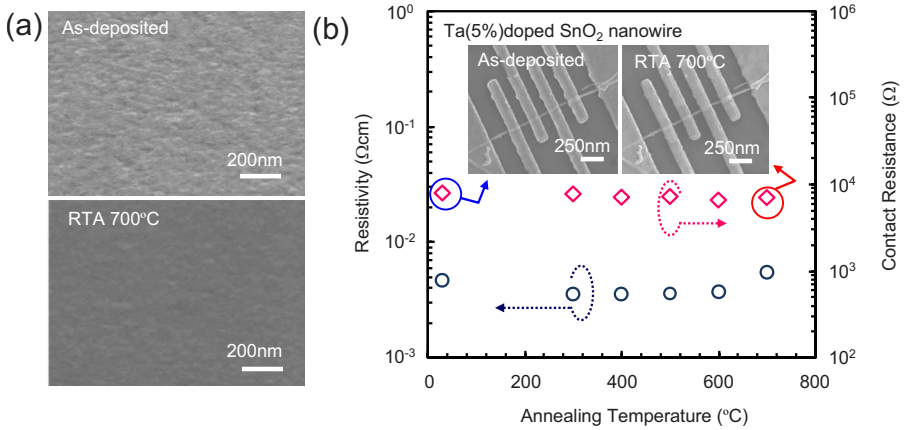

FIG. 3. (Color online) (a) FESEM image of the Pt thin film, upper: as-deposited, lower: after RTA at 700 °C. Pt films were fabricated by rough dc sputtering to show the effect of RTA clearly. (b) RTA temperature dependence of the resistivity and the contact resistance of the Ta(5 at. %)-doped SnO_2 nanowire. Pt/Au contact was prepared by rf sputtering. Insets show FESEM images of before and after RTA process.

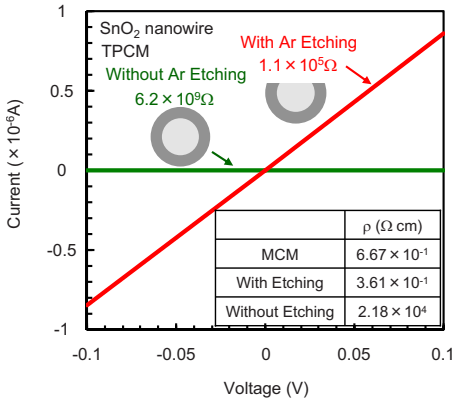

FIG. 4. (Color online) *I-V* characteristics of the SnO_2 nanowire with and without dry etching. Inset shows the table of resistivity data of MCM and TPCM with and without dry etching.

and FPCM data when varying the RTA temperature. The contact resistance was rather insensitive to the variation of RTA temperatures. Thus the scenario based on the point contact between granular metal electrodes and nanowires alone cannot explain the discrepancy between TPCM and MCM. Fourth, the insulative SnO_2 interfacial layer might exist and cause an electric barrier for carrier injections from electrodes into nanowires. To address this issue, we have performed a dry etching of nanowire surface to remove such insulative surface layer prior to metal electrode depositions. Note that the dry etchings were performed on only the area for metal electrode depositions in the presence of resists. Figure 4 shows the TPCM data of both dry-etched and virgin nanowires. The resistance of dry-etched nanowires was found to be four orders of magnitudes lower than that of virgin nanowires. More importantly, the resistivity of etched nanowires reasonably agrees with the MCM data. Thus the results demonstrate the existence of insulative interfacial layer. The further remained issue is to clarify what is and causes such insulative interfacial layer. Previous experimental studies have demonstrated that a conductivity of *n*-type SnO_2 originates in an oxygen vacancy,[30] and there were several theoretical interpretations as to the origins of carriers within SnO_2, including hydrogen incorporation model,[18] oxygen vacancy model,[30] and tin interstitial model.[31] A surface oxidation might occur during the fabrication process of nanowire devices due to atmospheric exposure. In fact, the gas sensitivity of SnO_2 nanowires has been reported.[17] There are two scenarios to explain the existence of insulating SnO_2 layers. First scenario is based on an oxygen adsorption onto the nanowire surface, which traps a mobile carrier on the surface. Second scenario assumes the change of local stoichiometry by surface oxidations. Although there are no direct experimental evidences to distinguish the two, the results in Fig. 4 seem to support the second scenario since an oxygen adsorption must occur even after the *ex situ* dry-etching treatments. To validate the existence of the insulating interfacial layer, we roughly estimated the resistivity of the insulating layer by assuming 1 nm thickness (considering the dry-etching rate). The value is around 10^4–10^5 Ω cm, which is not far from insulating bulk SnO_2 since a stoichiometry SnO_2 should be an insulator with the band gap 3.6 eV.[18]

In summary, we have demonstrated the importance of interfacial effects on $SnO_{2-\delta}$ nanowire/Pt junctions. The resistivity value estimated from the *I-V* data of junctions was four orders of magnitudes higher than that measured by a noncontact microwave conductivity method. We found that such apparent discrepancy is due to the presence of insulating oxidized interfacial layer. Since a conductivity of various reduced *n*-type oxides originates in oxygen vacancies, these implications will be rather universal for oxide nanowire/metal junctions and also crucial to realize reproducible emerging nanodevices by utilizing oxide nanowires.

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