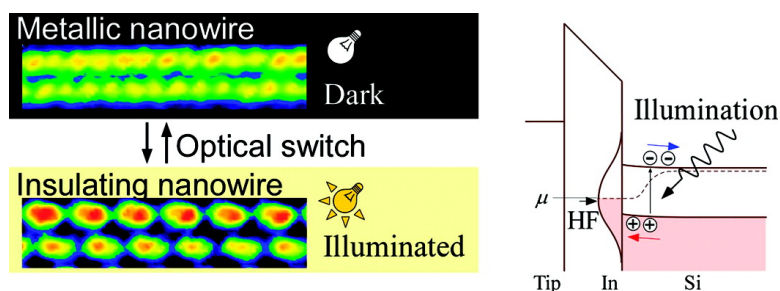# NANO LETTERS

Letter

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Optical Doping: Active Control of Metal−Insulator Transition in Nanowire

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ABSTRACT

The reversible control of metal−insulator transition (MIT) in In/Si(111) nanowires is demonstrated by tuning the band filling of the one-dimensional surface state by optical doping. The control of MIT is carried out by regulating the Fermi level in the surface state around the half-filled position, depending on the carrier density introduced at the interface. We successfully achieved the reversible and active control of MIT via the charge doping by regulating the intensity of photoexcitation. This method is widely applicable to other low-dimensional systems and makes MIT more controllable and suitable for use in nanowires as an active element in future architectures of nanosized functional devices as well as nanoscale interdevice wiring.

One-dimensional (1D) nanowires are nanoscale building blocks that can efficiently transport electrical charges that constitute information in nanoelectronics. Recently, they have attracted considerable interest in terms of their use as an active element in the future architectures of nanosized functional devices as well as nanoscale interdevice wiring. An important direction in this context is to exploit the unique properties of nanowires arising from the reduced dimension to provide a function that cannot be performed by existing devices. In designing such devices, the modulation and control of unique 1D electronic structures by, for example, external electric, magnetic, or optical field are essential for obtaining various functions, as has been reported for the cases of the field-modulated carrier transport in carbon nanotube transistors,[1] switching of semiconductor nanowire emitters,[2] and photovoltaic power sources in silicon nanowires.[3]

In this paper, we demonstrate a new methodology to modify the electronic properties of a quasi-1D nanowire formed on a semiconductor, that is, the active control of metal−insulator transition (MIT) by optical doping. In general, a quasi-1D metal shows a characteristic Peierls-type transition at low temperatures, which is accompanied by a marked change in electric conductance.[4,5] The transition temperature is known to be governed by the balance between the degree of Fermi surface contour nesting and the strength of electron−phonon coupling. However, the thermal control of MIT, which is related to electron−phonon coupling, is unfavorable to device application because, for example, of low switching speed and lack of local controllability. Here,

we introduced a new method to control MIT, namely, we modified the nesting of the Fermi surface contour by regulating the Fermi level position using optical doping. For the sample, a typical quasi-1D metal system formed on a semiconductor, that is, an indium quasi-1D nanowire array self-organized on a Si(111) surface[6−10] was used. The optical control of the In Fermi level position was realized by regulating the amount of photocarriers transferred to the In nanowires from the Si substrate at the interface. This method is suitable for the dynamical control of MIT in nanowires at a high switching speed. In addition, with the combination of the optical control with the electrical field applied by a scanning tunneling microscopy (STM) tip, the local controllability of MIT within a narrow area was also demonstrated. Since the optical control method is widely applicable to other 1D metal/semiconductor systems, it is expected to open up new possibilities for the development of future nanoscale devices, such as optical switching, memory, and sensors.

An In/Si(111) sample was prepared by the in situ deposition of In onto a Si(111) 7 × 7 clean surface at 700 K under ultrahigh vacuum (1 × 10^{-8} Pa). Angle-resolved photoemission,[6,7] STM,[6,8−10] and reflection high-energy electron diffraction (RHEED)[6] studies have revealed that the MIT in this system occurs with the structural change from the high-temperature metallic 4 × 1 phase to the low-temperature insulating 8 × 2 phase at a transition temperature (T_c) of approximately 125 K. The In/Si-4 × 1 structure has a quasi-1D metallic band, and the MIT is associated with the formation of charge density wave (CDW) with a double periodicity along the In nanowires. Because of the perfect Fermi surface nesting with $2k_F = \pi/a_0$ ($a_0 = 0.384$ nm), the

CDW phase is strongly locked with the lattice potential and stabilized.[10]

A variable-temperature STM was used with a chemically etched tungsten tip. For the optical control of MIT, an optical beam from a laser diode (635 nm, 1 mW) was focused onto the sample surface below the STM tip with a spot diameter of 0.02 μm, and was turned on and off to provide a dark condition and an illuminated condition, respectively. The electric properties of the reconstructed structures were determined by the current−voltage (I−V) curve taken by STS measurement. Light-modulated scanning tunneling spectroscopy (LM-STS)[11,12] was used to investigate the band structure for analyzing the mechanism of the light-intensity-dependent phase transition.

First, we show the characteristics of the In nanowire array formed on a Si(111) surface, which has been veiled until now. Figure 1a is an STM image of the In/Si(111) surface (n-type, 0.001 Ωcm) obtained at 61 K under dark condition at the sample bias voltage of $V_s = +0.4$ V. Surprisingly, the surface is dominated by the 4×1 phase with a metallic feature, as shown by the I−V curve (red line in Figure 1c), even at 61 K, which is much lower than the T_c of 125 K reported in the literature.[9] A previous study[9] also showed the coexistence of metallic and insulating domains. However, since the temperature was only slightly below T_c, in the range of 100−125 K, it was concluded that the entire surface was divided into domains of different sizes with different effective T_c values owing to the random distribution of defects and steps. In contrast, in the case we observed here the area of the metallic phase is much larger (Figure 1a), which strongly suggests the existence of some inherently different mechanism. Here we attribute the presence of the metallic phase at 61 K to the decrease in T_c. Indeed, the surface undergoes MIT upon further cooling as shown below.

Figure 1b shows an STM image of the In/Si(111) surface at 47 K under dark condition. Since the conductivity of the Si substrate decreases, a higher bias voltage, $V_s = -1.0$ V, was used for measurement. Here, the surface is completely dominated by the insulating 8×2 phase. The insulating feature of the 8×2 phase was confirmed by I−V curve measurement (blue line in Figure 1c), and the double periodicity of the 8×2 phase along the nanowires is attributed to the formation of the insulating CDW. Figure 1d shows the temperature dependence of the area ratio of the four domains: (1) 4×1 metallic domain, (2) crossover domain, (3) 8×2 insulating CDW domain, and (4) defects. Here the crossover domain corresponds to the defect-induced structure discussed in detail in ref 8. From Figure 1d, T_c is estimated to be 47 K, where the metallic phase vanishes.

The origin of the decrease in T_c is the shift of the Fermi level in the In band from its half-filled (HF) position.[13,14] The Fermi level shift is caused by charge transfer, which is expected to occur in a metal/semiconductor system, but has not been discussed until now for low-dimensional metal/semiconductor systems. Figure 1e shows the band structure of the STM tip/tunneling junction/In layer/Si substrate system under dark condition, where the HF position is indicated by an arrow and the In surface band is drawn with the absence
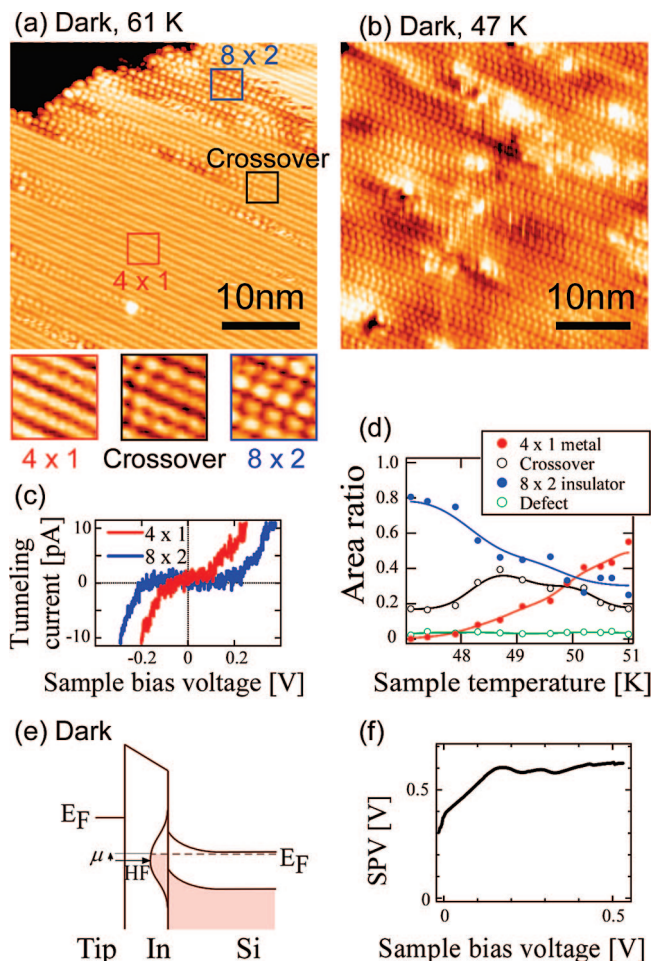

Figure 1. STM images of In nanowires on n-type Si(111) obtained under dark condition at (a) 61 K ($V_s = +0.4$ V) and (b) 47 K ($V_s = -1.0$ V). (c) I−V curves obtained for the 4×1 and 8×2 structures. The setpoint current and voltage were 200 pA and $V_s = -0.6$ V, respectively. (d) Ratio of the areas with different phases as a function of sample temperature, obtained from a series of STM images for different temperatures. (e) Schematic illustration of the band structure profile of STM tip/In surface layer/n-type Si substrate for $0 < V_s$ under dark condition. E_F denotes the Fermi level position of the tip and Si. The half-filled (HF) position is indicated by an arrow. The band gap opens if the system becomes insulating, which is not shown in the figure for simplicity. (f) SPV as a function of V_s obtained for the relative laser intensity of 12.5%. (see Supporting Informaton, Figure S1 for details).

of potential band gap opening for simplicity. Here, μ is defined as the Fermi level of the In band measured from the HF position. At the metal/semiconductor interface, charge transfer occurs to equalize the Fermi levels in both sides, the In layer and Si substrate in this case, resulting in band bending, as shown in Figure 1e. To analyze the band structure, surface photovoltage (SPV) was measured using LM-STS.[11,12] As shown in Figure 1f, a positive SPV clearly exists even at zero-bias voltage (see Supporting Informaton, Figure S1 for details). Thus, the Si band bends upward in this system under dark condition.[12,15] The upward band bending is a result of the electron transfer from the substrate to the surface layer. Therefore, the In layer is negatively charged, which causes a shift of μ from the HF position in the direction in which electrons are excessively supplied (μ

> 0). In the 1D electron system, when its band structure has an HF state, that is, $\mu = 0$, the wavenumber ($Q = 2k_F$) of CDW is equal to $a*/2$, where k_F is the Fermi wavenumber and $a*$ is the reciprocal lattice vector.[6,7] In this case, CDW is commensurate with the lattice potential and is strongly locked with the lattice, making the system insulating with the gap opening in the In band. In contrast, for $\mu > 0$ (Figure 1e), Q deviates from $a*/2$, and is incommensurate with the lattice potential. In this case, the energy gain obtained by the formation of an incommensurate CDW is low. Therefore, when the deviation is small, the formation of a commensurate CDW accompanied by the decrease in the transition temperature T_c may be energetically favored.[13,14] This is the case observed for the current system.

Next, we demonstrate a new methodology to control MIT by optical doping. When the In/Si surface with the band structure shown in Figure 1e is photoilluminated with an energy higher than the band gap of silicon, electron−hole pairs are generated in the silicon substrate, and the photo-generated holes drift to the surface owing to upward band bending, which neutralizes the excess electrons in the In band (Figure 2b). Thus, μ approaches zero, namely, the In band changes closer to the HF state, resulting in the change in T_c to the value close to the original T_{c0} (~125 K). Through this mechanism, optical doping is expected to increase the total area of insulating domains.

Figure 2a shows an STM image at 61 K under illuminated condition obtained over the same area shown in Figure 1a ($V_s = +0.4$V). When the surface is illuminated, the 4×1 metallic phase (Figure 1a) changed into the surface with the 8×2 insulating phase (Figure 2a), and vice versa, indicating that MIT can be reversibly controlled by optical doping. The phase transition may be caused by the sample temperature increase as a result of local heating upon laser illumination. If this is the case, the metallic high-temperature phase may dominate under illumination. However, this is not the case; therefore, the observed change in the MIT induced by optical illumination is not due to laser-induced heating.

To quantitatively investigate the effect of optical doping on the phase transition, we measured the ratio of the area of each domain, as a function of laser intensity ($V_s = +0.4$ V). As shown in Figure 3a (see also Supporting Informaton, Figure S2), the area of the metallic (insulating) phase decreases (increases) as the light intensity increases, but there exists a stepwise change around 1.7%. Namely, MIT occurs within an extremely narrow intensity range (1.1−2.5%), indicating that MIT is highly sensitive to the light intensity. As the light intensity increases, the amount of doping charge increases, and eventually μ decreases. Therefore, the observed characteristic is attributed to a strong dependence of T_c on μ. To observe the mechanism in more detail, we performed SPV measurement. As shown in Figure 3b, an abrupt change in SPV was observed at around 1.3%. In general, as the light intensity increases, SPV increases linearly, followed by saturation at high intensities. At moderate intensities, the dependence of SPV on the light intensity is approximately expressed by SPV $= A \ln(1 + CP)$, where A and C are constants, and P is the light
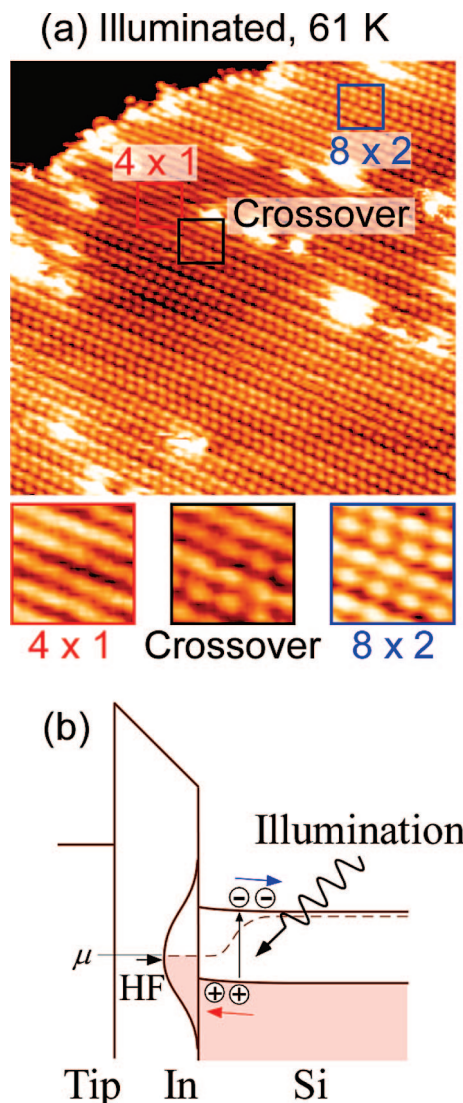
Figure 2. (a) STM images of In nanowires on n-type Si(111) obtained at 61 K and $V_s = +0.4$ V under photoilluminated conditions. Magnified images of the color-squared areas are shown together. (b) Schematic illustration of the band structure profile of STM tip/In surface layer/n-type Si substrate for $0 < V_s$ under illumination.

intensity.[16] However, the abrupt change in SPV cannot be explained by this equation. We attribute the observed anomalous characteristic to the gap opening caused by MIT. The gap opening results in the marked change in the density of states (DOS) of the In band. Since the constant C depends on the DOS, the gap opening in the In DOS is considered to produce the abrupt change in SPV. Indeed, the intensity at which the abrupt change occurs is close to the critical value at which MIT occurs. At higher intensities, after the gap opening, the SPV curve gradually saturates as in the typical case.

In the last part, to understand the mechanism in more detail and consider a more efficient and local control we discuss the V_s dependence on MIT. Figure 3b shows the laser intensity dependence of the ratio of the domain area with different phases obtained for $V_s = -0.7$ V. The laser intensity at which the ratio of the area of the insulating phase becomes
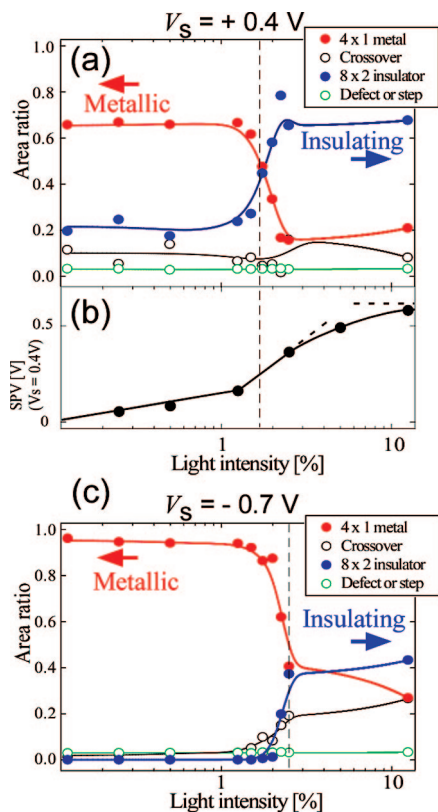
Figure 3. (a,c) Ratios of the domain areas with different phases as a function of laser intensity. The bias conditions are (a) +0.4 and (c) −0.7 V, respectively. (b) SPV as a function of laser intensity measured by LM-STS for $V_s = +0.4$ V (see also Supporting Informaton, Figure S2).
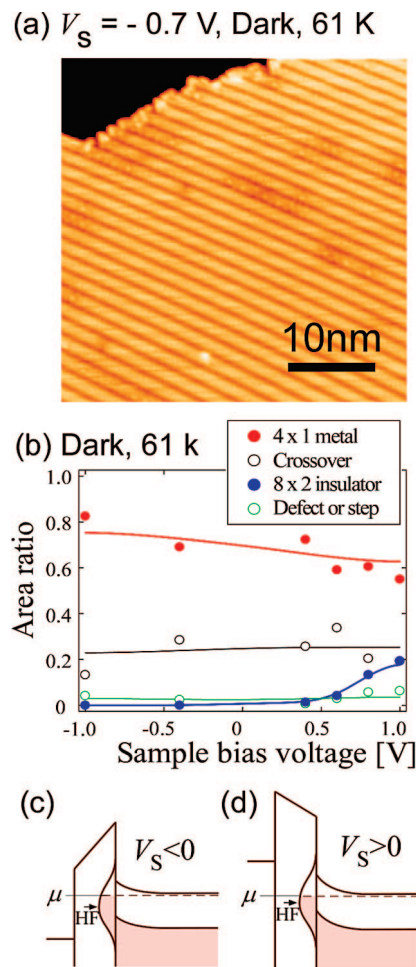

Figure 4. (a) STM images of In nanowires on n-type Si(111) obtained at 61 K and $V_s = -0.7$ V under dark condition. (b) Ratios of the domain areas with different phases under dark condition as a function of V_s. Schematic illustrations of band structure profiles of STM tip/In surface layer/n-type Si substrate for (c) $V_s < 0$ and (d) $0 < V_s$ conditions. The HF positions are indicated by arrows. The band gap opens if the system becomes insulating, which is not shown in the figure for simplicity.

50% increases from 1.7% for $V_s = +0.4$ V (Figure 3a) to 2.3% for $V_s = -0.7$ V (Figure 3c). This indicates that the MIT is more easily induced for positive V_s than for negative V_s. Indeed, an STM image taken at $V_s = -0.7$ V under dark condition (Figure 4a) shows that the 8×2 insulating phase area is smaller than that of $V_s = +0.4$ V (Figure 1a). This difference is attributed to V_s-dependent band bending.[15] SPV gradually increases with V_s (Figure 1f) and is larger for positive V_s than for negative V_s, indicating that the magnitude of the band bending is larger for positive V_s than for negative V_s. Thus, μ is closer to zero for positive V_s (Figure 4d) than for negative V_s (Figure 4c). Therefore, for positive V_s the system is expected to be more insulating and a weaker light intensity induces the insulating 8×2 phase. Figure 4b shows the area ratio of the phases as a function of V_s. The insulating area with the 8×2 phase increases with V_s, but the total change is less than 20%, indicating that the effect of V_s on MIT is not negligible but is small. This is in contrast to the optical doping shown in Figure 3, which enables a much more efficient control of MIT. However, since the bias voltage can locally be applied, the combination of optical doping with V_s has the potential to realize an efficient and local control of MIT.

Depending on the doping type and concentration of the semiconductor substrate, the position of the substrate Fermi energy shifts and, hence, the amounts of band bending and charge remaining in the In layer change. Accordingly, the phase area and transition temperature, both of which depend on the charge amount, are expected to change. This mechanism was confirmed by performing similar measurements on a p-type substrate (0.02 Ωcm), where SPV was zero independent of V_s, indicating the absence of band bending and thus the absence of charge transfer between the substrate and the In layer. In fact, for this sample the transition temperature was close to T_{c0}, and no change was observed for MIT by either voltage or optical excitation. These observations are consistent with the fact that the In band on p-type Si is HF.

The optical control of MIT can be applied to other low-dimensional systems formed on a semiconductor surface. If the doping level of the semiconductor is prepared as the band bending occurs under dark condition, that is, the Fermi level in the low-dimensional system differs from that of the substrate semiconductor, the T_c of the system is decreased from the original value and can be modified using optical

doping. To realize a high efficient control, proper selection of the doping level of the semiconductor substrate is important.

The electronic structures of low-dimensional structures on semiconductor surfaces are widely studied experimentally using optical excitation methods, such as X-ray diffraction, photoemission, and Raman spectroscopy. Clearly, it is important to consider the optical perturbation that modifies the electronic structure of a probed low-dimensional structure through a charging or discharging effect.

In summary, the reversible control of the MIT in In/Si(111) nanowires was demonstrated by tuning the band filling of the one-dimensional surface state by optical doping. We found that the MIT in the In/Si(111) nanowire system can be controlled by external photoexcitation. We demonstrated that MIT is controllable by adjusting the amounts of band bending and band filling by regulating the laser intensity and the voltage applied between the STM tip and the substrate. This method is widely applicable to other low-dimensional systems and makes MIT more controllable and suitable for use in nanowires as an active device element in future architectures of nanosized functional devices as well as nanoscale interdevice wiring.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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