Observation of room-temperature negative differential resistance in Gd-doped Si nanowires on Si(110) surface

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The massively parallel arrays of highly periodic Gd-doped Si nanowires (SiNWs) self-organized on Si(110)- 16×2 surface were investigated by scanning tunneling microscopy and spectroscopy. These periodic Gd-doped SiNWs are atomically precise and show equal size, periodic positions, and high-integration densities. Surprisingly, the scanning tunneling spectroscopy results show that each metallic-like, Gd-doped SiNW exhibits room-temperature negative differential resistance (RT-NDR) behavior, which can be reproducible with various Gd dopings and is independent of the tips. Such massively parallel arrays of highly ordered and atomically identical Gd-doped SiNWs with one-dimensional laterally confined RT-NDR can be exploited in Si-based RT-NDR nanodevices. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739947>]

Negative differential resistance (NDR) is an important nonlinear electron transport property and is essential for device applications in current rectification, fast switching, logic circuits, high-frequency oscillators, and low-power memory circuits.^{1–3} Motivated by the urge for electronic device miniaturization, NDR has been detected in tunneling conductance measurements for various low-dimensional systems, such as carbon nanotubes (CNTs),^{4,5} semiconductor nanowires (NWs),^{6–8} doped semiconductor surfaces,^{9–11} and organic molecules,^{12,13} by using scanning tunneling microscopy and spectroscopy (STM/STS). Several mechanisms have been proposed to explain the observed NDR.^{4–13} From a technological perspective, the achievement of NDR nanoelectronics based on one-dimensional (1D) nanomaterials can efficiently be implemented in logic and memory nanocircuits.^{14,15} Therefore, CNTs and NWs are promising 1D nanomaterials as active components in NDR nanoelectronic devices. However, NDR nanodevices based on a single NT or NW are not suitable for semiconductor manufacturing purposes, as it is difficult to control the electronic properties, growth, and alignment of individual NTs or NWs on an industrially reliable scale. For practical device applications, it is necessary to fabricate a large-area and well-ordered parallel array of periodically spaced and identical-size NTs/NWs for wafer-scale integration into an active parallel nanoarchitecture in real-world devices.¹⁶

Recently, we have shown that the long-range, periodic upper Si terraces of 16×2 reconstruction on a Si(110) surface can be recognized as massively parallel silicon NWs (SiNWs) grown naturally on a Si(110) surface.¹⁷ SiNWs have been widely used as the basic building blocks of several nanodevices (e.g., field-effect transistors, logic gates, and biochemical sensors),^{18–20} and they can be directly integrated into Si-based chips by means of Si-compatible nanofabrication technology. Moreover, transition-metal doped SiNWs have been shown to exhibit room-temperature (RT) ferromagnetism or half-metallic ground state.^{21–23} Because doped zigzag nanoribbons

have been predicted to possess the NDR effect and magnetic properties simultaneously using the density-functional theory,^{24,25} it is highly desirable to grow high-quality heterojunctions of massively parallel-aligned, doped SiNWs on Si(110) surface for wafer-scale integration into NDR nanoelectronic or magnetoelectronic devices.

Here, we report the observation of apparent NDR behavior at RT in large-area parallel arrays of highly integrated and atomically precise Gd-doped SiNWs on a Si(110) surface using STM/STS. Our STM/STS studies clearly show that the apparent RT-NDR feature can be repeatedly obtained in the uniformly spaced and atomically precise Gd-doped SiNWs with various dopings and is reproducible with different tips. Notably, most NDR effects were observed at low temperatures.^{4,5,8–12} The presence of NDR in massively parallel arrays of periodic and atomically identical Gd-doped SiNWs on a Si(110) substrate at RT allows for many practical applications of a Si-based RT-NDR nanodevice that utilizes Gd-doped SiNWs as the active component.

Our experiments were performed in an ultrahigh-vacuum, variable-temperature STM system with a base pressure of $\sim 4 \times 10^{-11}$ mbar. Atomically clean Si(110)- 16×2 surfaces (heavily n-type doped, $\sim 1 \Omega \text{ cm}$) were prepared by using well-established annealing procedures¹⁷ and confirmed by STM observations. The massively parallel Gd-doped SiNW arrays were formed by depositing 0.01–0.1 ML (1 ML = 9.59×10^{14} atoms/cm²) of high purity (99.95%) Gd onto a single-domain Si(110)- 16×2 surface at 750 °C at a deposition rate of ~ 0.035 ML/min and subsequently annealing at 800 °C for 30 min. The Gd coverage was determined *in situ* by using a quartz-crystal thickness monitor. The STM measurements were acquired in the constant-current mode at RT with electrochemically etched nickel (Ni) tips. I-V curves were obtained at a constant tip-sample separation and then were numerically differentiated to derive differential conductance (dI/dV) curves (i.e., STS spectra). Spatially resolved dI/dV maps were acquired in the current imaging tunneling spectroscopy mode at RT.

Figures 1(a)–1(d) show the representative STM topographic images of the parallel Gd-doped SiNW array at

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FIG. 1. [(a)–(d)] STM topographic images of the parallel Gd-doped SiNW array with a doping of 0.05 ML Gd on Si(110)- 16×2 surface taken at different magnifications: (a) $500 \times 500 \text{ nm}^2$ (bias voltage $V_b = +1.5 \text{ V}$, tunneling current $I_t = 50 \text{ pA}$), (b) $250 \times 250 \text{ nm}^2$, (c) $125 \times 125 \text{ nm}^2$, and (d) $35 \times 35 \text{ nm}^2$ ($V_b = -1.2 \text{ V}$, $I_t = 10 \text{ pA}$).

different magnifications. In Figs. 1(a) and 1(b), two different types of NWs with various contrasts can be observed in the two regions labeled I and II, which are divided by a white dashed line. The parallel SiNW array with low contrast was formed within Region I; the parallel Gd-doped SiNW array with bright contrast was self-organized within Region II. As seen in Fig. 1, these parallel-aligned, straight, and defect-free Gd-doped SiNWs cover a mesoscopic area exceeding $250 \times 250 \text{ nm}^2$ and are elongated along the $[1\bar{1}2]$ direction. The width of these NWs remains atomically smooth along the NW. All individual Gd-doped SiNWs are atomically precise, essentially identical one to other in the whole macroscopic area on the sample surface. Such a 1D self-organized

parallel NW array with good uniformity and alignment over a mesoscopic area demonstrates long-range spatial ordering. Additionally, this microscopically ordered doped-SiNW array exhibits a high NW density that can be applied for the wafer-scale integration of ultrahigh-density nanoelectronic devices. Figure 1(c) clearly shows the zigzag chain formed on each Gd-doped SiNW, similar to the appearance of clean SiNWs.²⁶ However, the high-resolution filled-state image of Fig. 1(d) clearly shows that the elemental structure of Gd-doped SiNWs is completely different from that of clean SiNWs. A detailed comparison of the elemental structures of Gd-doped SiNWs and clean SiNWs are clearly depicted in a series of bias-dependent STM images of Gd-doped SiNWs in Region II and clean SiNWs in Region I,²⁶ which were obtained with the same Ni tip. As displayed in Fig. 1(d), the typical width of these periodic Gd-doped SiNWs is $2.3 \pm 0.1 \text{ nm}$, and the pitch is $5.0 \pm 0.1 \text{ nm}$. These dimensions are equal to those of clean SiNWs.¹⁷ These results suggest that the dimensions and appearances of the SiNWs did not change after Gd doping, but the atomic structure of the doped SiNWs is different from that of the clean SiNWs.

Interestingly, a set of five dI/dV curves acquired at five different positions (A–E) along a Gd-doped SiNW [marked by the black points in Fig. 2(a)] shows an energy gap smaller than 0.1 eV and represents a negative differential conductance at $-1.35 \pm 0.05 \text{ V}$, indicating that Gd-doped SiNWs are metallic-like and that NDR behavior appears in the Gd-doped SiNWs, as shown in Fig. 2(b). Also displayed is the 6th dI/dV curve taken on clean SiNWs (indicated by a black dashed line) for comparison. Each representative dI/dV curve was averaged over 10 repeated measurements at the same locations in Fig. 2(a). We find that although the detailed features of each curve varied slightly due to the different electronic structure of the various positions, NDR always appears at nearly the same energy position of $-1.35 \pm 0.05 \text{ V}$. However, weaker NDR behavior was observed at the substrate between the neighboring Gd-doped

FIG. 2. (a) The STM topographic image ($+1.2 \text{ V}$, 20 pA , $15 \times 10 \text{ nm}^2$) of a Gd-doped SiNW. (b) A set of five dI/dV curves acquired at different positions (A–E) along a Gd-doped SiNW, as indicated in (a). (c) A set of five dI/dV curves acquired at different positions (F–J) within the adjacent substrate. All dI/dV curves in (b) and (c) were acquired at $V_b = 1.5 \text{ V}$, $I_t = 20 \text{ pA}$. (d) Six dI/dV curves on the site K taken at different tip-sample distances set by $I_t = 50\text{--}100 \text{ pA}$ at $V_b = 1.0 \text{ V}$.

SiNWs, as displayed in the five dI/dV curves taken at different positions (F-I) within the adjacent substrate [Fig. 2(c)], and NDR always appears at -1.3 ± 0.05 V. The larger NDR signal of the Gd-doped SiNWs compared to that of the adjacent substrate is ascribed to the strongly selective reaction of Gd atoms with the SiNWs, which is similar to the preferential formation of Gd-silicide NWs on the upper terraces of the Si(110) surface.²⁷ The adjacent substrate exhibits semiconducting character with an energy gap of ~ 0.28 eV that is smaller than the ~ 0.4 eV energy gap of clean SiNWs (the black dashed curve), indicating that the Si(110) substrate also reacted with Gd. Figure 2(d) shows a set of six STS dI/dV curves measured on site K [indicated in Fig. 2(a)] at different tip-sample distances, as specified by various tunneling currents (I_t) of 50, 60, 70, 80, 90, and 100 pA at a bias voltage (V_b) of 1.0 V. Each dI/dV curve was averaged over 10 repeatedly measured curves on site K at a constant tip-sample separation. As seen in Fig. 2(d), six dI/dV curves measured on site K clearly exhibit NDR at nearly the same energy position of -1.38 ± 0.05 eV, which is in contrast to prior results that show the NDR position shifting toward the Fermi energy (i.e., the zero bias) by decreasing the set-point current.¹⁰ Note that the decrease of the vertical distance between the Ni tip and the Gd-doped SiNWs (via increasing the set-point current while keeping the set-point voltage unchanged) results in the strong NDR effect, which can be ascribed to the larger tunneling probability at the smaller tunneling distance. Because all of the NDR features of the six dI/dV curves obtained at different tip-sample distances appear at nearly the same energy position and the NDR effect in Gd-doped SiNWs is reproducible with different Ni tips, we can further rule out the contributions from the possible defect states caused by the roughness of the tip surface. Such an NDR is not observed in the clean SiNWs [the black dashed curve in Figs. 2(b) and 2(c)] and is specific to the Gd-doped SiNWs. The NDR effect was reproducible for different Gd-doped SiNWs prepared at various doping levels

[Fig. 3]. Ideally, NDR-based nanodevices should be developed for operation at a lower bias. The magnitudes of the NDR voltage detected in different doped SiNWs are within a range from 1.0 V to 1.6 V [Figs. 2(d), 3(b), and 3(d)], which are much smaller than those of GaN NWs, ZnO NWs, and organic molecules.^{7,8,12} Thus, our fabricated massively parallel Gd-doped SiNW arrays can enable low-voltage nanoelectronic components used for logic circuits and memories.

Additional insight into the laterally confined NDR behavior of these parallel-aligned Gd-doped SiNWs was obtained by measuring the lateral distribution of NDR by using a two-dimensional spatially resolved dI/dV map, as shown in Fig. 4. Figures 4(a) and 4(b) depict the dI/dV map and the corresponding topographic image of the parallel Gd-doped SiNW array, which clearly show that each Gd-doped SiNW exhibits 1D laterally confined negative dI/dV with black contrast, as evidenced by the comparison of the dI/dV profile and topographic profile of the periodic doped SiNWs [Figs. 4(c) and 4(d)]. The 1D RT-NDR behavior in each NW has never been reported. Thus, such massively parallel arrays of periodic and atomically smooth Gd-doped SiNWs with 1D RT-NDR behavior on a Si(110) substrate have great potential as promising candidates for the active component in a massively parallel nanoarchitecture of RT-NDR devices.

In contrast to the resonant tunneling mechanism of the semiconductor-molecule-metal junctions (i.e., the double-barrier tunnel junction),^{8,12} the noticeable NDR behavior of Gd-doped SiNWs can be attributed to the resonant tunneling between a broad $3d$ state of the Ni tip apex and the localized Gd $5d$ -induced surface state (SS) in the Gd-doped SiNWs, which is similar to the “local-orbital symmetry matching” proposed for the cobalt phthalocyanine (CoPc) molecule with a nonatomic sharp Ni tip.¹³ The localized Gd $5d$ -induced SS results from chemical bonding between the sharper $5d$ orbitals of the Gd atoms and the narrow sp^3 orbitals of the Si atoms. The smaller the Gd doping is, the stronger the magnitude of the NDR will be (see the comparison of

FIG. 3. STM topographic images (-1.0 V, 10 pA, 33×20 nm²) and of two different parallel Gd-doped SiNW arrays obtained by depositing Gd of 0.1 ML (a) and 0.01 ML (c), respectively. [(b), (d)] Different dI/dV curves of the individual Gd-doped SiNWs in (a) and (c), taken at various tip-sample distances set by various I_t of 50 – 100 pA at $V_b = 1.0$ V.

FIG. 4. (a) The dI/dV map (250×50 pixel²) taken at $V_b = -1.380$ V and (b) the corresponding topographic STM image (21×4 nm²) of the parallel Gd-doped SiNW array shown in Fig. 1(d). (c) Intensity profiles of the dI/dV map along the dashed line in (a). (d) Cross-sectional profiles across the parallel Gd-doped SiNWs along the dashed line in (b).

the magnitude of NDR in Figs. 2(d), 3(b), and 3(d)). In lightly doped SiNWs, small amount of isolated Gd dopant atoms show atomic-like $5d$ orbitals that create the highly localized, Gd $5d$ -induced SS. Unlike the NDR mechanisms of CNTs and GaN NWs,^{5,7} the origin of NDR in Gd-doped SiNWs does not require a local defect (<1 nm) to produce the sharp electronic states. The NDR behavior of Gd-doped SiNWs is also irrespective of the tip status. This large-scale self-organization of parallel-aligned Gd-doped SiNWs can simplify the design of highly integrated nanocircuits in Si-based NDR nanodevices.

In conclusion, large-area parallel arrays consisting of highly periodic and atomically identical Gd-doped SiNWs have been self-organized on a Si(110) surface and each Gd-doped SiNW exhibits 1D RT-NDR behavior. The laterally confined RT-NDR behaviors were reproducible with different samples at various Gd doping levels. From a technological perspective, such mesoscopically ordered Gd-doped

SiNW arrays with 1D RT-NDR effects on a Si(110) substrate have important potential applications for the wafer-scale integration into Si-based RT-NDR nanodevices that utilize massively parallel Gd-doped SiNWs as the active component.

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