Robust One-Dimensional Metallic Band Structure of Silicide Nanowires

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Angle-resolved photoemission (ARP) is employed to investigate the electronic structure of an extremely anisotropic form of nanocrystals—$GdSi_{2-x}$ nanowires on Si(100). Using a stepped Si(100) surface, a well-ordered and uniformly oriented array of nanowires is formed along the step edges as confirmed by diffraction and microscopy. The ARP measurement discloses two distinct electronic bands near the Fermi level, which disperse one dimensionally along the nanowires. These bands are metallic with the electron filling of $1/4$ and $2/5$, respectively, and with the effective mass close to that of a free electron along the wires. The metallicity is robust down to 20 K, in contrast to metallic surface atomic chain systems, paving a way to further studies on one-dimensional physics of metallic nanowires.

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Nanowires (NW's), a highly anisotropic form of nanocrystals, have attracted great interest recently due to their unusual physical properties and potential applications in nanoscale devices and interconnections [1]. Various forms of NW's have been fabricated so far such as carbon nanotubes, semiconductor NW's, and metal NW's. However, important issues remain to be solved not only for applications but also for understanding the exotic quantum properties of NW's. Metallic NW's are of particular interest since one-dimensional (1D) metallic electrons would exhibit various intriguing physical properties, for example, the broken-symmetry ground states and the non-Fermi liquid behavior [2].

The detailed characterization of electronic band structures as well as atomic structures is crucial in understanding any exotic physics of the metallic NW's. However, a direct experimental investigation of electronic band structures of NW's is very much limited since the conventional probes require a macroscopic amount of uniformly oriented and uniformly sized NW's, which is often very difficult to obtain in practice. Indeed, there have been very few successful measurements of 1D band structures of NW's like the scanning tunneling spectroscopy measurements of the energy-dependent electron wavelength in carbon nanotubes [2,3].

In the present work, we have prepared a uniformly oriented regular array of rare earth (RE) silicide NW's on a vicinal-cut (stepped) Si substrate, as characterized by low-energy-electron diffraction (LEED) and scanning tunneling microscopy (STM), and successfully measured their electronic band structure with angle-resolved photoemission (ARP). The system indeed exhibits two metallic electron bands, which disperse one dimensionally along the wires. These bands are nearly quarter and $2/5$ filled and stably metallic down to 20–70 K making this system promising for a further quest of the exotic 1D physics.

Formation of RE silicide NW's on a silicon substrate, Si(100), was reported only very recently for Dy [4–8], Gd [9,10], Ho [4,11], and Er [12,13]. The average size of resulting wires is about 2–3 nm in width (typically forming much wider "bundles") and several hundreds nm in length. Several STM studies have been performed on growth behaviors of the NW's, which suggested a decisive role of the very anisotropic lattice mismatch between the hexagonal RE silicide and Si in this extremely anisotropic crystallization [4,12]. The electronic properties of RE silicide NW's are obviously important not only for their potential applications, but also for fundamental studies [14]. The recent scanning tunneling spectroscopy studies indicated some hint of metallic properties, i.e., the finite density of states near Fermi level, for Dy- [11] and Gd-silicide [15] NW's. However, no further details of electronic structures of the NW's are disclosed.

Gd was thermally evaporated onto Si(100) kept at 600 °C. This specific temperature was reported as an optimum condition for the NW growth [10]. The ARP measurements were performed with He-I [$h\nu$(photon energy) = 21.2 eV] or a soft x-ray ($h\nu$ = 130 eV) radiation at Pohang Accelerator Laboratory using high-resolution angle-resolved electron analyzers (Gamma Data, Sweden). A variable-temperature STM system (Omicron, Germany) was used for microscopy measurements. The sample could be cooled cryogenically to 70 and 20 K in the ARP and STM systems, respectively.

The usual flat Si(100) surface is composed of wide alternating terraces of 90°-rotated dimer rows. This leads to the nucleation of NW's with two orthogonal orientations since the NW's preferentially grow perpendicular to a Si dimer row [9,10]. A vicinal-cut Si(100) substrate, however, can have much narrower terraces, which may act as a proper template for the growth of oriented NW's. Indeed, a very recent STM study showed that NW's can grow with a unique orientation along the step edges of a Si(100) substrate with a miscut of 4° [9], but the surface uniformity and the interwire ordering were not guaranteed. In the present study, a 2°-miscut (toward [011]) Si(100) substrate with slightly wider terraces was found to be superior in both the uniformity and the lateral ordering. Nevertheless,

the surface preparation and the surface band structure of this stepped substrate is essentially the same as a flat one.

At first, the growth of NW's was monitored by a diffraction technique. Figures 1(a) and 1(b) show the LEED patterns at the Gd coverages of 0.3 and 0.7 ML, respectively. It is clear that the Gd-induced superstructures are very anisotropic and almost ideally single domain for both coverages; the streaky $\times 2$ features and the higher order "$\times n$" spots (arrows in the figure) run only along [011]. A closer look of the "$\times n$" superstructure indicates a systematic evolution with respect to the Gd coverage; the $\times 7$ spots grow up to $\sim$0.3 ML and mix gradually with the $\times 5$ spots for a higher coverage, which fully develop at $\sim$0.7 ML. This indicates that a 2×7 phase is formed at 0.3 ML but the domains of a 2×5 phase grow and dominate as the coverage increases up to 0.7 ML. The LEED observation is partly consistent with the previous STM study on a flat substrate; the dominating domains of the 2×7 structure at about 0.3 ML and the formation of NW's at a higher coverage [16]. The 2×7 structure was interpreted as a Si surface reconstruction induced by Gd adsorbates [16]. However, the 2×5 phase was not noticed previously although its growth condition corresponds to a regime where the NW's dominate the surface [9,10,15,16].

In order to characterize the NW formation on the stepped substrate further, especially for the newly found 2×5 phase, we performed the STM investigation. At an intermediate Gd coverage of $\sim$0.5 ML [Fig. 1(e)], the 2×7 reconstruction and the NW bundles (brighter part in the figure) are observed together. The NW bundles with a length of typically 300–800 nm are composed of 2–7 unit wires separated by the trench structure, and their width is mainly limited by the step edges [17]. At a higher coverage the density of NW bundles increases [Fig. 1(f)]. As shown in the inset of Fig. 1(e), the NW superlattice within each bundle has a $\times 5$ (19.2 Å) periodicity. This is only qualitatively consistent with the previous studies reporting 21- [15] or 33-Å [10] periodicity (or width) but matches with the 2×5 LEED pattern observed presently. A reasonable guess is that each NW is composed of four unit cells of Gd silicide ($4.18 \times 4 = 16.7$ Å) and a trench corresponds to a misfit dislocation. Small multilayer *islands* of NW's are also observed but with a very minor population [17]. Irrespective of the atomistic details of the NW structure, the LEED and STM studies clearly indicate that they, as grown on 2°-off Si(100), are not only oriented uniquely but also arranged into a relatively well-ordered array.

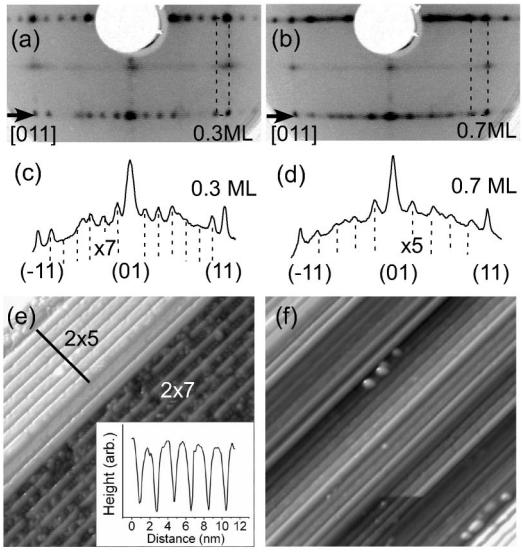

FIG. 1. LEED patterns for Gd/Si(100) prepared at 600 °C with the Gd coverages of (a) 0.3 and (b) 0.7 ML. The detailed LEED intensity profiles of the "$\times n$" superspots along [011] [arrows in (a), (b)] are also shown for (c) 0.3 and (d) 0.7 ML. The corresponding STM images with (e) 0.5-ML (500×500 Å^2) and (f) 0.7-ML Gd (620×620 Å^2). The sample bias voltages are +1.5 and +1.6 V for (e) and (f), respectively. The inset in (e) shows the line profile across a silicide nanowire bundle (along the bar in the image).

With the well-developed parallel NW's, we could characterize the band structure using ARP. In fact, on a flat substrate, where the NW's grow in two different orientations, we could not observe any dispersive features except for those from Si bulk bands. The situation is markedly different in case of the oriented NW's on the stepped substrate. Figure 2 shows the ARP spectra for the uniquely oriented NW array at 0.7 ML (the 2×5 NW phase with possibly minor 2×7 domains). In those spectra, the difference of the spectral features between the directions parallel (wire$_\parallel$) and perpendicular to the wires (wire$_\perp$) is evident. Especially near the Fermi level two parabolically dispersing bands are observed only along wire$_\parallel$, denoted as $m1$ and $m2$. A few other spectral features are also observed at higher binding energies, such as S1-S4 (Fig. 3). Since all these features are within the Si bulk band gap, extending from 0.6 eV at $\bar{\Gamma}$ down to 1.8 eV at $\bar{J}$ and $\bar{J}'$ of the 1×1 surface Brillouin zone [18], they are assigned as due to the surface electrons or the electrons localized within the NW's.

The two high-binding-energy features S2 and S3 have similar dispersions to the dangling bond surface states of clean Si(100)2×1 with a rigid energy shift of 0.2 eV. These two states and another nondispersive feature S1 are enhanced for the 2×7 phase (data not shown here). Thus, the S1-S3 states are tentatively interpreted as due to the low-coverage Gd-induced surface reconstruction and their appearance here plausibly as due to the coexisting 2×7 domains. From a detailed comparison to 2×7-Gd, it is straightforward that the characteristic spectral features of the 2×5 NW phase are the $m1$ and $m2$ bands around $\bar{J}$ near Fermi level. In particular, the 2×7 phase has no dispersing bands near the Fermi level and no spectral weight on the Fermi energy. The apparent and huge anisotropy of the band dispersions of $m1$ and $m2$ corroborates

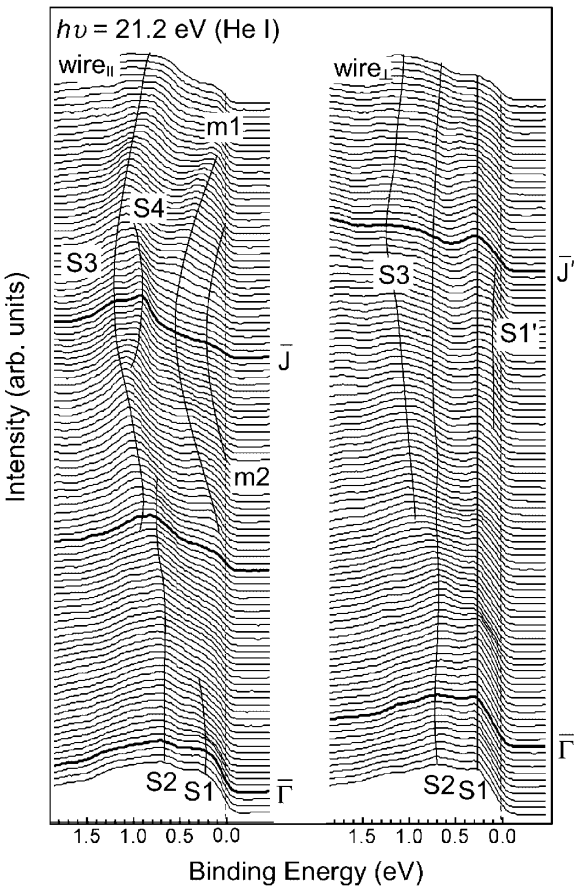

FIG. 2. Angle-resolved photoelectron spectra taken for Gd/Si(100) at 0.7 ML [Figs. 1(b) and 1(f)] along (wire $_{\parallel}$ or $\bar{\Gamma} - \bar{J}$) and perpendicular (wire $_{\perp}$ or $\bar{\Gamma} - \bar{J}'$) to the NW's. The surface Brillouin zone used here is based on a 1×1 unit cell. The He-I radiation ($h\nu = 21.2$ eV) was used and the sample temperature was 300 K. The step in the emission angle sampled here is 0.36° for clarity reasons and a smooth monotonic background was subtracted. The major spectral features are indicated by solid lines (see text for explanation).

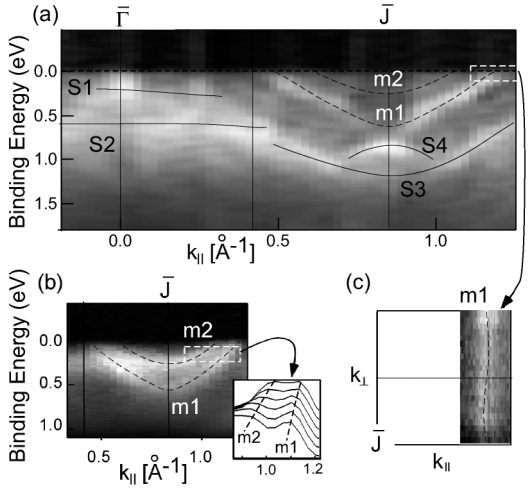

FIG. 3. (a) ARP intensity map in gray scale along the $\bar{\Gamma} - \bar{J}$ (wire $_{\parallel}$) direction for the 2×5 nanowire phase, which is constructed from the data shown partly in Fig. 2. (b) Similar ARP intensity map for the metallic bands but taken with a higher photon energy of $h\nu = 130$ eV. A few line profiles along $k_{\parallel}$ (the momentum distribution curves), for the area enclosed by white dashed lines, are also displayed in order to show the two dispersing bands more clearly. (c) ARP intensity map at the Fermi energy around the Fermi momentum of $m1$ [for the $k_{\parallel}$ region shown by the white dashed rectangle in (a)] as measured at $h\nu = 21.2$ eV. The bright part (guided by the dashed line) corresponds to the Fermi contour of the $m1$ band.

firmly their origin in the NW's. What is most important is that these bands have nearly free-electron-like (*parabolic*) dispersions up to the Fermi level indicating a strongly metallic character. Indeed, the parabolic fits of the observed band dispersions give the effective mass values close to or even much smaller than that of a free electron (m_e): $(0.91 \pm 0.05)m_e$ and $(0.63 \pm 0.05)m_e$ for $m1$ and $m2$, respectively. The $m1$ band has an electron filling of 0.41 ± 0.05 (a fully filled band is set to 1), smaller than a half filling, while $m2$ band is an almost quarter-filled band with a filling of 0.24 ± 0.07.

The Fermi contour mapped by the ARP intensity at the Fermi level [Fig. 3(c)] indicates not only the dominating 1D anisotropy of the band structure but also a small but finite interwire dispersion, in particular, for $m1$. The Fermi contour for $m2$ is not obvious in this measurement due to its low intensity. The Fermi contour exhibits a small curvature along wire $_{\perp}$ (the dashed line) and, more quantitatively, the band anisotropy at the Fermi level, the ratio of bandwidths along and perpendicular to the wires, of the metallic $m1$ band is as large as ~ 10. This could be important for the transport property of NW bundles [14] since the close-packed NW's would have a small but finite interwire electron-hopping channel and no single isolated wire is stably formed in practice. In summary, the Gd-silicide NW has a metallic band structure with two fractionally filled quasi (but nearly ideal) 1D bands. It is noted that similar but 2D metallic bands near the Fermi level were also observed for the epitaxial Gd (Er) silicide films on Si(111), which involve RE d and Si $3p$ electrons [19]. Although it is tempting to suggest a similar origin for the $m1$ and $m2$ states, a further comparison is limited by the uncertainty in the atomic structure of a NW.

It is worthwhile to compare the RE NW system with the surface atomic chain structures induced by metal (In or Au) adsorbates on flat or vicinal Si(111) surfaces, which happen to have very similar band structures, multiple 1D metallic bands centered on the zone boundary with $1/2$ and smaller fillings [20–23]. The recent ARP studies observed metal-insulator transitions for the above metallic chain systems at 130–270 K due mainly to the Peierls instability without an exception [20,22,23]. Such a substantial electron-lattice interaction may generally suggest the *soft* nature of the lattice for those surface systems composed

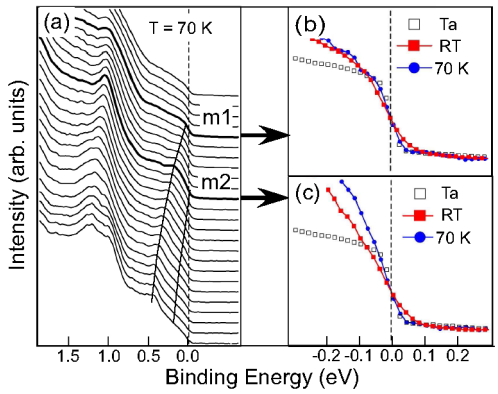

FIG. 4 (color online). (a) Detailed ARP spectra for the two metallic bands, $m1$ and $m2$, near their Fermi momenta, k_F's, taken at 70 K with a photon energy of $h\nu = 21.2$ eV. The spectra at the Fermi level crossings of $m1$ and $m2$ [thick lines in (a)] are compared for 70 and 300 K in (b) and (c), respectively. The spectrum for the well-defined metal of polycrystalline Ta at 70 K is also given (squares) for comparison.

basically of a single atomic layer possibly with a large electron-phonon coupling. Note that all these systems have almost ideally nested $1/2$-filled bands providing the substantial electronic instability. While the instability of the metallic phase would have its own scientific importance, it could obscure other low-energy characteristics of the 1D metallic system such as the collective excitations of a non-Fermi liquid.

The present system of $GdSi_{2-x}$ NW's has largely different structural characteristics as basically epitaxial nanocrystals with its own in- and out-of-plane lattice structure. Thus, the NW's might naturally be expected to have a significantly more rigid lattice against the Peierls instability. The fractional electron fillings in $GdSi_{2-x}$ NW's, the lack of a $1/2$-filled band for the maximized Peierls instability, would drive a metal-insulator transition less probable in clear contrast to the surface atomic chain systems. We have checked the possible metal-insulator transition of $GdSi_{2-x}$ NW's by ARP (Fig. 4) and LEED down to 70 K as well as by STM down to 20 K. All these experiments consistently indicate that there is no metal-insulator transition and no lattice distortion at least down to 20 K. For example, the ARP data for the Fermi edges of both $m1$ and $m2$ exhibit only the normal metallic behavior, clear Fermi-Dirac-type spectral functions with a reduced thermal broadening at low temperature (Fig. 4). This robust 1D metallic property of $GdSi_{2-x}$ NW's poses them as a good candidate to explore the exotic low-energy excitations of 1D metals, with electron spectroscopy and microscopy.

In conclusion, on a stepped Si(100) surface, a well-ordered and uniformly oriented array of $GdSi_{2-x}$ nanowires is formed along the step edges. Detailed ARP study establishes that this NW system is indeed one-dimensional metallic with fractionally filled bands with an effective mass close to that of a free electron. A small but finite interchain coupling between the close-packed NW's is also disclosed. The metallic phase is shown to be stable down at least to 20 K in clear contrast to other surface 1D metallic systems. The quest for the exotic 1D many-body physics at a sufficiently low temperature would be promising and in order.

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