

Uniform Pb nanowires of magic thickness on Si(111) controlled by elastic interaction and quantum size effects

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An ordered array of uniform single crystal Pb nanowires with a magic thickness of 9 monolayers (ML) was obtained on Si(111) by a two-step method. The coverage of 6.4 ML is critical for the formation of uniform nanowires at the deposition temperature of 200 K and the flux rate of 1.2 ML/min, while at other coverages elongated islands or interconnected stripes with various thicknesses are formed. The width ratio of the nanowires to the Si(111) substrate terraces is found to be a characteristic value of 0.54. *In situ* low-temperature scanning tunneling microscopy study reveals that the magic thickness and uniform distribution of the Pb nanowires are governed by the interplay between the electronic quantum size effects along the normal direction and the lateral elastic interaction induced by strain.

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I. INTRODUCTION

Nanowires have recently attracted much attention for both basic research and technological applications because of the dramatic differences in electronic,^{1,2} transport,^{3,4} and magnetic⁵ properties from their bulk partners. To fabricate the array of regular nanowires, self-organization growth on vicinal substrates by molecular beam epitaxy (MBE) has been often used.⁶ At appropriate substrate temperatures, the mobility of adatoms on substrate surfaces is high enough to allow adatoms migrate and attach to the steps, since the binding energies at step sites with more unsaturated bonds are in general larger than those on terraces. As a consequence, quasi-one-dimensional (1D) wires preferentially grow at steps when the average diffusion length of adatoms is larger than the terrace width, which is referred to as step decoration effect or step flow growth mode. In this case, the wire width and spacing can be controlled via the coverage and step spacing or miscut angle of the vicinal surface independently. Sometimes, the strain resulting from lattice mismatch can have a strong impact on surface diffusion and nucleation,⁷ and induce a long-range elastic interaction between adjacent strain domains, which defines the distribution of strain domains.^{8,9} Without good control of uniformity, the energy levels of the nanostructured materials will spread out because of their strong size dependence and change to bulklike quasicontinuum energy bands. For example, quantum well states have only been observed in a small group of thin films.¹⁰⁻¹²

Here we report on the growth of uniform single crystal Pb nanowires on Si(111). The nanowires exhibit an atomically flat surface and a singular thickness of 9ML above a uniform but amorphous Pb wetting layer, and are evenly separated, which forms a unique system for the study of 1D superconductivity. The detailed scanning tunneling microscopy (STM) studies indicate that the magic thickness of nanowires is a result of electron confinement along the surface normal direction, while the uniform distribution results from the lateral elastic interaction induced by lattice-mismatch strain between Pb and Si. The Pb nanowires are metastable and evolve into big flat-top islands with steep edges to decrease

step energy and interface strain energy after the annealing for several hours. The quantum force associated with the confinement also plays a role in the evolution process and determines the preferential thickness of islands.

II. EXPERIMENT

The experiments were performed in a Unisoku ultrahigh vacuum low-temperature scanning tunneling microscopy (LT-STM) system with a MBE chamber for *in situ* preparation of thin films. The base pressure of the system is better than 2.0×10^{-10} Torr. The substrates are *n*-type Si(111) wafer with a resistivity of 20 m Ω cm and a miscut angle of 0.2° towards the $[\bar{1}\bar{1}2]$ direction. By the well-established flashing procedure,¹³ the clean 7×7 reconstructed surfaces with an average terrace width of about 110 nm separated by monoatomic steps (0.31 nm) were obtained. Pb with purity of 99.999% was evaporated from a pyrolytic boron nitride (PBN) crucible onto the Si substrate at a flux rate of 1.2 ML/min in the MBE chamber. During evaporation, the Si substrate was cooled down to 200 K by a liquid nitrogen reservoir through copper braids. The temperature was measured with an AuFe-Cr thermocouple close to the Si substrate, with an error of ± 5 K for any given temperature. After growth, the samples were directly transferred to the LT-STM chamber where the STM topographic images were taken at 80 K. In the annealing experiment, the cooled sample at 80 K was transferred out of the LT-STM chamber, held on a room-temperature sample holder for 3 h, and then sent back to be imaged again. All STM images were acquired at a positive bias of 3 V and a tunneling current of 100 pA.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical STM image of the sample deposited with 6.4 ML Pb. The stripes along the step running direction are formed. Although some of the top-layer stripes are still narrower than the Si terrace, the dominating thickness of the stripes is 5 ML above the wetting layer. Pb islands with magic thicknesses were reported in the previous

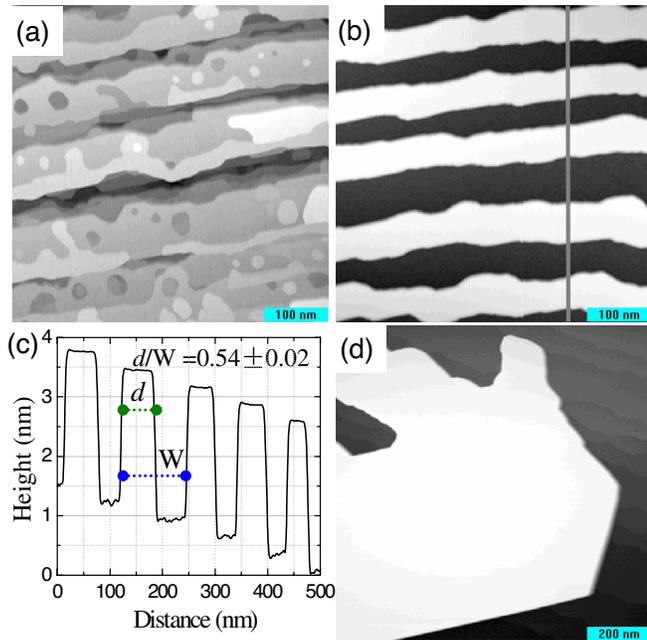


FIG. 1. (Color online) STM images ($500 \text{ nm} \times 500 \text{ nm}$) obtained after (a) 6.4 ML Pb deposition at the substrate temperature of 200 K and the flux rate of 1.2 ML/min on Si(111), (b) the room-temperature annealing of the sample in (a) for 3 h. (c) The corresponding line profile of that indicated by the black line in (b). (d) STM image ($1000 \text{ nm} \times 1000 \text{ nm}$) obtained after the room-temperature annealing of the sample in (b) for 12 h.

studies and the formation of these islands was attributed to the quantum size effects (QSE).^{14–20} On Si(111), about 1.5 ML Pb is consumed initially to form a homogeneous and amorphous wetting layer, and then islands with preferential thicknesses of 5 ML, 7 ML, and 9 ML grow on top of the wetting layer during subsequent deposition.^{16–20} These islands of odd-numbered layers are more stable than those of the adjacent even-numbered layers because of their higher concentrations of surface charge density, which induces lower surface energy in turn.¹⁹ We believe that the preferential 5 ML thickness comes from the same reason, and we attribute the different morphologies to the different kinetic processes, which will be discussed below.

More interesting features were observed when the sample was subsequently annealed at room temperature for several hours. Figures 1(b) and 1(d) show the sample morphologies after annealing for 3 h and another 12 h, respectively. In the case of 3 h annealing, well-ordered Pb(111) nanowires are formed along the upper terraces of the Si(111) substrate. According to the line profile in Fig. 1(c), all nanowires are singular 9 ML thick. Depending on the Si terrace size, the width of the nanowires varies from 45 to 65 nm, while the width ratio of the nanowires to substrate terraces is essentially a constant of 0.54 ± 0.02 . This observation indicates that there is a mass conservation during the annealing process. In other words, the atom diffusion during the evolution from the stripes to the nanowires is limited within the same terrace. Required by minimizing step energy and interface strain energy, nanowires merge together to form big Pb islands with flat tops and steep edge after the further annealing

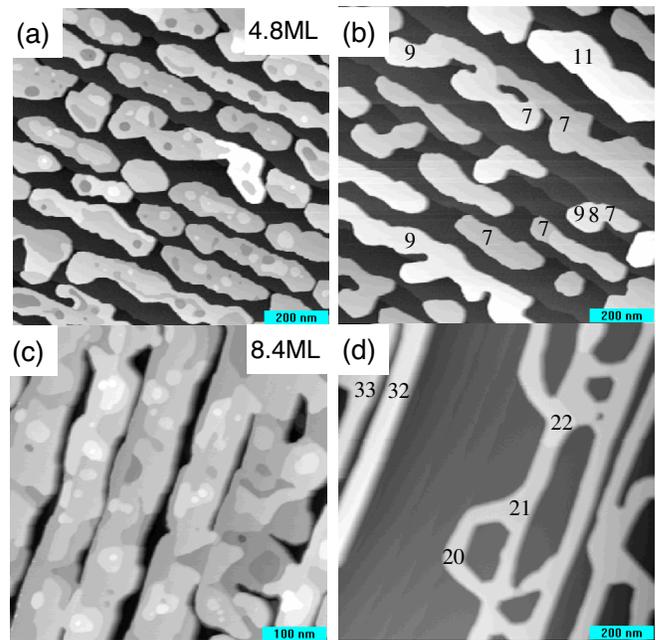


FIG. 2. STM images ($1000 \text{ nm} \times 1000 \text{ nm}$) obtained after (a) 4.8 ML Pb deposition on Si(111), and (b) the room-temperature annealing of the sample in (a) for 3 h. STM images obtained after (c) ($500 \text{ nm} \times 500 \text{ nm}$) 8.4 ML Pb deposition on Si(111), and (d) ($1000 \text{ nm} \times 1000 \text{ nm}$) the room-temperature annealing of the sample in (c) for 3 h. The numbers labeled on the islands and stripes indicate the thickness as a form of atomic layers.

for 12 h, as shown in Fig. 1(d). The size of the island is larger than $1 \mu\text{m} \times 1 \mu\text{m}$, the maximum scanning area of our STM at liquid nitrogen temperature.

Different morphologies were observed for both below and above 6.4 ML. Figures 2(a) and 2(c) show the STM images of as-deposited samples at a nominal coverage of 4.8 ML and 8.4 ML, respectively. The corresponding STM images after room temperature annealing for 3 h are shown in Figs. 2(b) and 2(d). The numbers in images of Figs. 2(b) and 2(d) indicate the island thickness in terms of atomic layers. At 4.8 ML, the surface is covered by elongated Pb islands near the substrate steps, most of which are the same thickness of 5 ML as observed above. In the following annealing process, the islands merge together, and become more anisotropic. The thicknesses of most islands are 7 ML and 9 ML. A few islands of 8 ML thick appear, but it happens only when the islands cross the Si step [Fig. 2(b)]. In the case of 8.4 ML, compared to Fig. 1(a), similar Pb stripes with the preferred thickness of 7 ML along the substrate steps are formed, but some of the stripes on the neighboring terraces are connected [Fig. 2(c)]. Consequently, many interconnected nanowires of more than 20 ML thick are formed after annealing [Fig. 2(d)].

Note that the array of uniform Pb nanowires with the magic thickness of 9 ML is only obtained at the special deposition condition and annealing process, i.e., 6.4 ML Pb at a deposition flux rate of 1.2 ML/min on Si(111) at 200 K, followed by a room-temperature annealing for 3 h. To prepare the array of uniform nanowires, the formation of stripes is the first and most important step. Three factors are crucial for

such a preparation, i.e., the deposition temperature, the flux rate, as well as the coverage. The cross-step diffusion is suppressed to some extent at the substrate temperature of 200 K,²¹ that is, the adatoms are confined and diffuse only in the same terrace [Figs. 1(a) and 2(a)]. As compared to the previous studies,^{18,19} a higher flux rate of 1.2 ML/min was adopted during the deposition. The diffusion that favors aggregation and formation of multilayer islands is suppressed at the high flux rate, so that elongated islands and stripes along the substrate steps are formed, while isolated islands with circular shape are formed at a relatively lower flux rate of 0.32 ML/min.²¹ Depending on the coverage, elongated islands are formed below 6.4 ML [Fig. 2(a)], while long stripes along the substrate steps are formed at and above 6.4 ML [Figs. 1(a) and 2(c)]. But when the coverage is larger than what is needed for the 1.5 ML wetting layer and the complete 5 ML film, merging of the stripes cannot be avoided. Therefore, 6.4 ML is the critical coverage for the preparation of the uniform Pb stripes under the certain deposition condition.

When the samples are annealed at room temperature for 3 h, elongated islands and stripes become narrower and higher. In the case of 6.4 ML, the array of uniform Pb nanowires is characterized by the magic thickness of 9 ML and the width ratio of 0.54. According to Ref. 9, the total energy of the stripes array E_{stripe} can be written as

$$E_{\text{stripe}} = \frac{1}{W} \left[C_i + C_1 - 2C_2 \ln \left(\frac{W}{2\pi a} \sin \pi \theta \right) \right], \quad (1)$$

where C_i and C_1 are the energy per unit length of the inter-step edge and free edge of the stripe, respectively. The last term is the strain contribution which depends on the area fraction θ , as defined as the fraction of the total surface area that is covered by single crystal Pb. At low area fraction, the total energy is large because of the strong intrastripe repulsion between the monopoles on the opposite edges of the same stripe. It decreases with increasing area fraction and reaches a minimum at the value of 0.5. At higher area fraction, the total energy becomes large again because of the strong interstripe repulsion between the monopoles on the opposing edges of two neighboring stripes. The competition between the intrastripe repulsion and the interstripe repulsion determines the preferential width ratio of stripes to substrate terraces in the deposition process, for example, in the case of CaF_2 on vicinal $\text{Si}(111)$.⁹ In the present case, this thermodynamic effect is suppressed due to limited atom diffusion at the low deposition temperature of 200 K. But it becomes important in the thermal annealing induced morphology evolution process. Driven by the strong interstripe repulsion, Pb atoms move upward to reduce the interface strain associated with the mismatch. This cannot happen at low temperatures where the necessary kinetics is frozen. After annealing for 3 h, the width ratio decreases to 0.54 ± 0.02 , a value very close to the theoretical one of 0.5, which suggests that the uniformity is determined by the lateral elastic interaction. The difference between the experimental area fraction of 0.54 and the theoretical value of 0.5 deduced from Eq. (1) can be understood by the fact that the total energy should include the surface energy, and the boundary energies C_i and

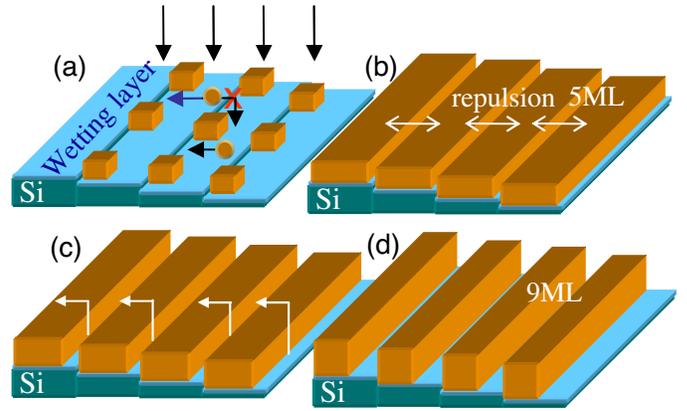


FIG. 3. (Color online) Schematic diagram showing the formation process of the array of uniform Pb nanowires. (a) during the deposition, (b) at completion of the deposition, (c) during the room-temperature annealing, and (d) after the room-temperature annealing for 3 h.

C_1 should change with boundary height, both of which are ignored in Eq. (1).

In the case of 4.8 ML, the coverage is too low to cover the $\text{Si}(111)$ substrate completely with the magic thickness of 5 ML. Due to the repulsions between islands along steps and between islands on neighboring terraces, the subsequent annealing process makes the distances between islands both along and perpendicular to the steps become larger, and no continuous nanowires are formed. In the case of 8.4 ML, the coverage is too high to avoid the stripes merging. Consequently, in some areas where the stripes are connected by crossing steps and the cross-step diffusion cannot be avoided, many interconnected nanowires more than 20 ML thick are formed after the annealing. At the same time, the surface covered by the wetting layer is also observed in some other areas. If the annealing time is long enough, both elongated islands and interconnected nanowires evolve into big flat-top islands similar to that shown in Fig. 1(d) to reduce step energy and interface strain energy.

Figure 3 shows the schematic diagram that illustrates how Pb nanowires are formed based on our experimental observation and the discussion above. It consists of four steps.

(a) During the deposition at the low substrate temperature of 200 K and the appropriate high flux rate of 1.2 ML/min, Pb adatoms are confined within and diffuse only on the same terrace. As a result of the magic stability induced by QSE, elongated islands of 5 ML thick are formed above the wetting layer.

(b) After 6.4 ML Pb is deposited, Pb stripes of 5 ML thick cover almost the entire $\text{Si}(111)$ substrate except for steps. The system is thermodynamically unfavorable due to the strong interstripe repulsive interaction and thermal stress.

(c) During the room-temperature annealing, Pb atoms move upward and climb up to the upper terrace driven by the strong interstripe repulsion, so that the stripes become narrower and higher.

(d) After the room temperature annealing for 3 h, the array of uniform Pb nanowires with the magic thickness of 9 ML is obtained. The width ratio of the nanowires to the

Si(111) substrate terraces is 0.54 ± 0.02 , which indicates that the system reaches to a metastable configuration as required by the lateral elastic interaction.

IV. CONCLUSIONS

The array of uniform Pb nanowires with the magic thickness of 9 ML was obtained at a critical coverage of 6.4 ML when Pb was deposited with the flux rate of 1.2 ML/min on Si(111) at 200 K and then annealed for 3 h at room temperature. The width ratio of the nanowires to the Si(111) substrate

terraces is almost a constant value of 0.54. We show that the unique morphology is a result of the cooperative effects between kinetics, electronic QSE, and strain induced elastic interaction. The array of uniform nanowires provides an ideal system for the study of 1D superconductivity, a subject of fundamentally important in solid state physics.

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