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Controllable Modulation to Quantum Well States on β-Sn Islands

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We investigate the surface structure and electronic properties of β-Sn islands deposited on a graphitized 6H-SiC (0001) substrate via low temperature scanning tunneling microscopy and spectroscopy. Owing to the confinement of the island geometry, quantum well states (QWSs) are formed, manifesting as equidistant peaks in the tunneling spectra. Furthermore, a distinct strip feature appears on the surfaces of odd-layer Sn islands, ranging from 15–19 layers, which is not present on the surfaces of even-layer Sn islands. The spatial distribution of strips can be modified by applying a bias pulse, using an STM tip. Furthermore, the strip-like structure shows significant impacts on the QWS. An energy splitting of the lowest unoccupied QWSs is observed in strip regions; this may be ascribed to caused the phase shift of the wave functions of the QWSs on the top surface, due to surface distortions created by the aforementioned strips.

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Understanding the physics of nanostructures with decreasing sizes and dimensions is very important in terms of both industrial and scientific interests. Guided by the famous Moore's law,[1] chip processing in the semiconductor industry is now soaring into the quantum age. When the size of samples is comparable to the Fermi wavelength of electrons, the quantum size effect (QSE) due to the confined movements of electrons occurs,[2] resulting in remarkable modifications to the properties of materials, such as superconductivity,[3,4] the local work function,[5] electron-phonon coupling,[6] and thermal stability.[7,8] One typical QSE is the formation of quantum well states (QWS), which are discrete standing-wave eigenstates occurring along confined directions.[9] A previous study has shown that QWSs can be influenced by strains on the surface, as strain relaxation plays an important role in modulating surface chemical potential.[10]

The QWSs have been widely studied in relation to metal films, including Sn,[11] Pb,[12] Cu,[13] Pt,[14] Al,[15] and others.[16,17] In such thin metal film systems, QWSs emerge due to the confinement of electron motion in the direction perpendicular to the film's surface. Many novel properties induced by QWSs, such as bilayer growth,[18,19] the oscillating perpendicular upper critical field,[20] chemical reactivity,[21] selective strip-flow growth, and growth rate modulation,[7] have been intensively studied. Of these, β-Sn islands exhibit peculiar layer-dependent surface strain conditions, which can interact with QWSs to demonstrate novel features. The Sn islands grown on an Sn–induced Si (111)–$(2\sqrt{3}\times 2\sqrt{3})$ R30° surface show an interesting strip structure, which, when it arises from 4 monolayers (MLs), becomes weaker with increasing thickness, disappearing altogether at 11 ML.[11] This structure is caused by strains, relaxed by the thickness of the Sn islands. In addition, the strip structure gives a modulation to QWSs in relation to both energy and intensity.[10] This modulation is caused by spatial-dependent surface chemical potential.

In this Letter, the surface structure and electronic properties of 15–19 ML β-Sn islands, grown on graphene, are studied using low temperature scanning tunneling microscopy and spectroscopy (STM/STS). Our experiments show that the strip features are preserved above 11 ML in this system, but only on the surfaces of odd-layer (OL) islands. Based on structural analysis, we propose a possible formation mechanism for these strips, i.e., surface strain. In addition, the strip regions can be modified by applying a bias-pulse, using an STM tip. Moreover, a novel energy splitting of QWSs on the stripes is observed, which is presumably due to the change of phase shift at the island surface involved in the quantization condition of the QWSs. Our results clearly demonstrate the controllable modulation of QWSs by virtue of tuning surface strain, thereby providing a useful platform

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for studying the interplay between QWSs and their boundary conditions.

Our experiments were conducted in an integrated system, comprising an Unisoku ultra low temperature STM, and a molecular beam epitaxy (MBE) chamber. The base pressures of the system were greater than 2×10^{-10} torr. A high-quality graphene surface was obtained on the 6H-SiC(0001) substrate by means of thermal desorption.[22] The Sn material was then deposited onto the graphene substrate by a Knudsen cell with a deposition rate of 0.15 ML/min, and the substrate was maintained at room temperature. The sample was then transferred to a cooling stage, maintained at 4.2 K, in which electrochemically etched tungsten tips were employed for the STM/STS measurements.

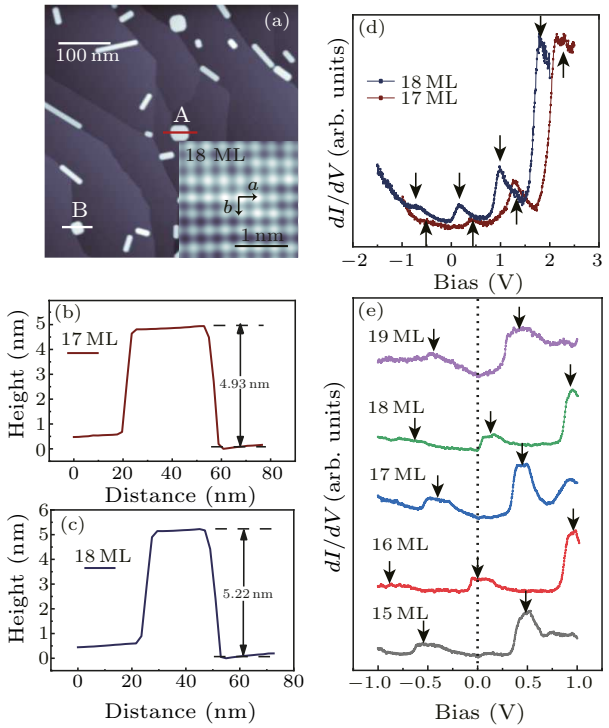

Fig. 1. Morphology and QWSs of β-Sn islands grown on a graphitized 6H-SiC (0001) substrate. (a) Large-scale STM image of Sn islands (bias $V_b = 2$ V, tunneling current $I = 100$ pA) immediately after *in situ* deposition at room temperature. Inset: atomic resolved image on the surface of island B. The in-plane lattices are marked by a and b. (b) and (c) Line profiles along red and blue lines crossing A and B islands, respectively. (d) dI/dV spectra taken from 17 ML and 18 ML Sn islands, marked as A and B in (a), respectively. (e) A sequence of dI/dV spectra taken at different layers of Sn islands. The curves are offset vertically for clarity. The QWS peaks are marked by arrows.

Figure 1(a) shows a large-scale STM image of Sn islands grown on the graphitized 6H-SiC (0001) substrate. The graphene forms some terraces as a result of the heating treatment. Most Sn islands reside at the edge of these graphene terraces, and two shapes of Sn islands are observed: rod-like and square-like. Similar bistability has been reported on Ag islands, which can also be affected by deposition temperature.[23] The atomically resolved STM images of the Sn islands are shown in the inset of Fig. 1(a). The lattice constants of Sn are measured as $a = 3.07$ Å, $b = 3.08$ Å, which agrees well with previous STM results for β-Sn(001).[24] Figures 1(b) and 1(c) show the line profiles cutting along the red and blue lines, respectively, as drawn in Fig. 1(a). The number of layers can be determined according to the monolayer thickness of the β-Sn (100) 2.92 Å,[25] i.e., 4.93 nm = 17 ML for island A, and 5.22 nm = 18 ML for island B. Most of the islands in this sample measure 15–19 ML. There is no evidence to indicate that the shape of the island is related to its height.

Here, STS measurements are also performed to detect the electronic properties of the islands. Vertical confinement leads to the formation of QWSs, observable in dI/dV spectra, as shown in Fig. 1(d). The characteristic peaks marked by arrows have equal intervals in energy terms. This interval represents the well-known energy interval of QWSs. We find that the 18 ML film possesses a QWS near the Fermi surface E_F, which is also observed in other even-layer (EL) films, as shown in Fig. 1(e). We note that the oscillations of the QWSs have a period of 2ML, and that the EL Sn surfaces exhibit a QWS near the E_F. Such oscillations of QWSs have also been studied in relation to Pb films[26] and Sn films.[11]

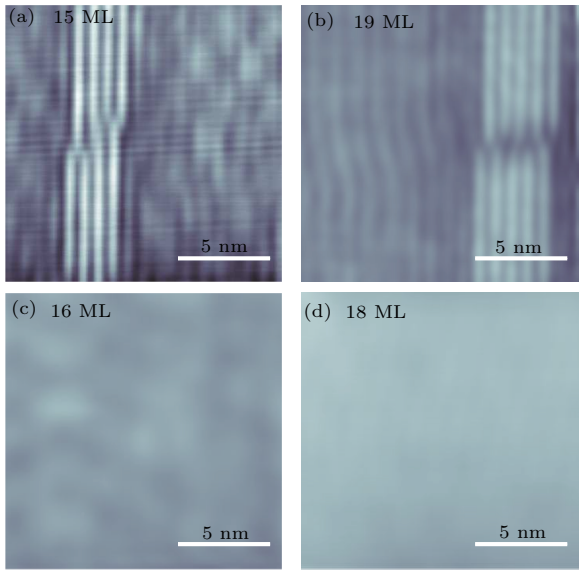

Fig. 2. Surface morphology of OL and EL Sn islands. (a) and (b) Surface topography ($V_b = 100$ mV, $I = 100$ pA) of a 15/19 ML Sn island. Some strip-like features are identified at the surface. (c) and (d) Surface topography ($V_b = 100$ mV, $I = 100$ pA) of a 16/18 ML Sn island.

Next, we conduct an in-depth study on the surface of different islands, comparing the OL and EL Sn islands, as shown in Fig. 2. All the surface topographies are measured at $V_b = 100$ mV and $I = 100$ pA. Strip features are clearly observed at the surface of some Sn islands. The strip features are similar to those described in the literature,[10] which are explained as a form of strain-induced distortion. The difference is

that not all of the islands exhibit this strip feature. In order to understand the seemingly random occurrence of these strip features, both the island height and their shape are considered. Having analyzed a great deal of data, we find that the strips can occur on both square-like and rod-like islands, but are only present on OL islands (15, 17 and 19 ML). On rod-like OL islands, all strips are perpendicular to the long side of the Sn islands, whereas at the surface of EL islands, the surfaces are relatively flat, with no strip features visible. Below, we focus in more detail on the strip regions, attempt to explain possible formation mechanisms, and study their interaction with QWSs.

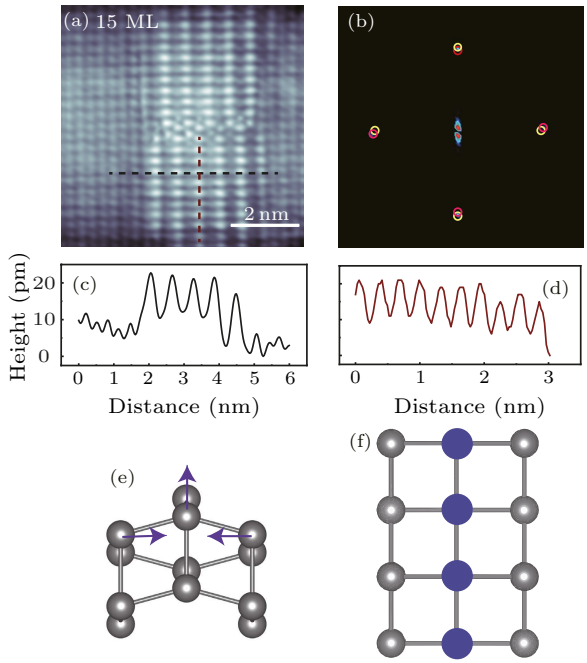

Fig. 3. Structural analysis of strip features. (a) Atomic resolved STM image ($V_b = -20$ mV, $I = 200$ pA) of a 15 ML Sn island. (b) Comparison of FFT of Sn lattice between OL [flat region in (a)] island and EL [see Fig. 1(a)] island. Here, red circles denote OL, and yellow circles represent EL. (c) and (d) Line profiles along the horizontal (black) and vertical (red) dotted lines in (a). Here, (e) and (f) are schematic diagrams illustrating the formation of the strip structure. (e) Side view of β-Sn structure. The directions of displacements of Sn atoms are indicated by arrows. (f) Top view of β-Sn structure. The resulting atomic strip is marked by a blue sphere.

Based on the atomic resolved image, the strips show a significantly raised height [see Fig. 3(a)]. The measured lattice constants of a flat region on OL island are as follows: $a = 3.02$ Å, $b = 3.14$ Å, of which the a (b) value is slightly shorter (longer) than that observed for EL islands. Line profiles perpendicular to the strip and along the strip are shown in Figs. 3(c) and 3(d), respectively. The distance between two strips is 6.02 Å, which is slightly less than for $2a$. The lattice distance along the strip is 3.14 Å, which is the same as for b. Notably, the lattice constants between OL and EL islands show only a little difference. So as to avoid the influence of local distortions and provide an overall comparison, we compare the fast Fourier transforms (FFT) of the atomic images, as shown in Fig. 3(b). The lattice spots in K-space for the EL surface are represented by yellow circles. Compared with the red circles for OL surface, the difference is that the horizontal distance between the yellow circles is shorter than that between the red circles, whereas in relation to the vertical distance, the opposite condition pertains. This means that the atoms on the OL surface experience a general squeeze along a direction. Based on the topographic information and the atomic structure of β-Sn, we propose a possible process for the formation of Sn strips. As shown in Figs. 3(e) and 3(f), the middle Sn atoms rise up due to squeezing from Sn atoms on either side. From the top view, we are able to observe the strip-like features (marked by blue spheres) after squeezing has occurred, which matches well with the experimental topography.

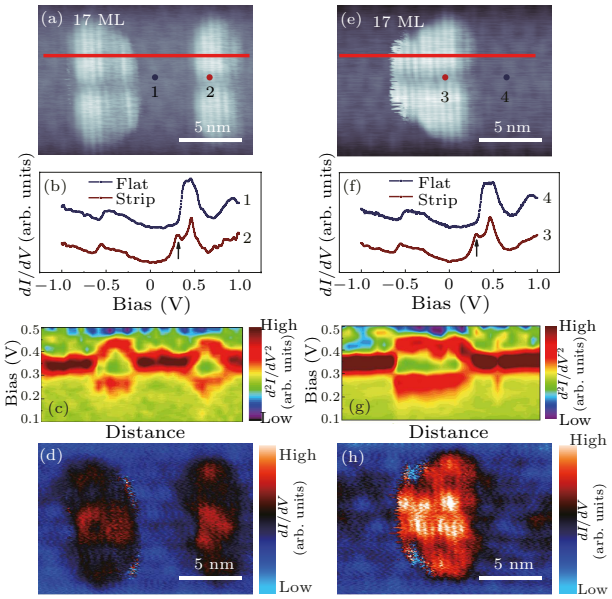

Fig. 4. The effect of strip features on QWSs and changes in strip features. (a) Topography of a strip region ($V_b = 100$ mV, $I = 100$ pA) on a 17 ML island. (b) dI/dV spectra taken at the points labeled by 1 (in flat region) and 2 (in strip region) in (a). (c) Color map of second order differential spectra d^2I/dV^2, taken along the red line in (a). (d) dI/dV mapping, with a bias of 315 mV, of the same area as shown in (a). (e) Surface topography ($V_b = 100$ mV, $I = 100$ pA) of the 17 ML Sn island after a bias pulse of +2 V. (f) dI/dV spectra, taken at the points labeled by 3 and 4 in (e). (g) Color map of second order differential spectra, d^2I/dV^2, taken along the red line shown in (e). (h) dI/dV mapping, with a bias of 315 mV, at the same area as shown in (e).

We further study the effect of strips on electronic states, with particular regard to QWSs. The tunneling spectra taken at flat and strip regions are compared in Fig. 4(b). In the strip region, we observe energy splitting of the lowest unoccupied QWSs, which is marked by an upward-pointing arrow. The original broad energy peak changes into two sharp peaks: one has the same peak position as the original peak, the other shows a lower shift in energy. To confirm

this phenomenon, a series of dI/dV spectra are taken along the red line shown in Fig. 4(a). A color map of second-order differential spectra d^2I/dV^2 is depicted in Fig. 4(c), where the energy splitting on the strips can clearly be observed. We also use dI/dV mapping to study the space distribution of the observed energy splitting. When selecting the energy of the lower peak (315 mV) as the mapping bias, the highlighted areas (with a higher density of states) match well with the distribution of the strips. These results indicate that the surface strips do indeed induce the energy splitting phenomenon observed in the QWSs.

A possible reason for this energy splitting is that the surface distortion changes the phase shift $\delta\Phi_{\rm B}$ of the wave functions of QWSs at the top surface, which is related to the quantization law of QWSs,[27] According to the Bohr–Sommerfeld phase accumulation in Ref. [10], the energy shift of QWSs is expressed as:

$$\delta E(x) = -\frac{\Delta}{2}\left[\frac{\delta\Phi_{\rm B}(x)}{\pi} + \frac{4\delta d}{\lambda_{\rm F}}\right].$$

For the 17 ML Sn islands, the energy interval of the QWSs, i.e., Δ, is 880 meV in the flat region shown in Fig. 4(b). The energy shift between the strip region and the flat region is 315 meV − 442 meV = −127 meV; $\delta d = 0.2$ Å is the height of the strip structure [see Fig. 3(c)], and $\lambda_{\rm F}$ is the Fermi wavelength (3.88 Å for β-Sn crystal). Thus, we obtain $\delta\Phi_{\rm B}(x) = 14.8°$, with x representing the position with respect to the modulated strip. This implies that the surface chemical potentials in the strip and flat regions are different, verifying the difference in morphology. The peak residing at the original position remains because (1) only half of the Sn atoms in strip regions are lifted, and (2) the strip region only covers a small partial of surface of the Sn islands. Thus, the original boundary condition still exists at the top surface. A similar splitting has also been observed in Ag films grown on Si.[28]

An interesting phenomenon is that the strips can be modified by a bias-pulse, provided by an STM tip. Similar STM manipulation has been reported in the study of the growth dynamics of Pb grown on an Si surface.[7] Figure 4(e) shows the same area as Fig. 4(a), but after the application of a bias pulse of +2 V. It is evident that the two strip regions merge together, forming a new strip region at the center. This indicates that the strip structure is metastable, and can be affected by a small disturbance. We then take the same measurements to study the properties of the newly-formed strips. The color map and the mapping image both indicate that the energy splitting areas always follow the strip regions [see Figs. 4(g) and 4(h)]. The newly-established pattern shows no sign of evolution during this measurement, which takes place over a period of about 24 hours. Thus, it is reasonable to assume that the new pattern is stable under 4.2 K. This tip-tunable strip region provides a feasible method for locally modifying QWSs.

In summary, we have investigated the surface structure and electronic properties of β-Sn islands, whose thickness ranges from 15–19 ML deposited on graphitized 6H-SiC (0001) via low temperature STM/STS. The geometry of the β-Sn surfaces and their electronic properties have been determined unambiguously by STM. OL and EL Sn islands are found to be different in terms of surface morphology. The OL Sn islands have a unique strip-like surface structure, while the EL Sn islands have flat surfaces. The spatial distribution of the strips can be modified using an STM tip. At 4.2 K, the strips cause a splitting of QWSs, which is probably induced by the phase shift of the wave function at the top surface due to strip distortions.

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