Dislocation-Induced Local Modulation of the Surface States of Ag(111) Thin Films on Si(111) 7 × 7 Substrates

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Local modulation of the Shockley-type surface state was studied around threading dislocations at the surfaces of ultrathin Ag(111) epitaxial films on Si(111) substrates. Scanning tunneling microscope (STM) observations indicated that the wavelength of the surface state electron was shortened around the dislocations in the electron standing wave pattern. Scanning tunneling spectroscopy (STS) revealed that the bottom of the local surface state (E_0) shifts downward around the dislocation. The shift in E_0 and the lattice displacement Δu_z have a linear relation, which indicates that the shift of the surface state is caused by local relaxation of the misfit strain around the dislocation.

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Shockley-type surface states at the (111) surfaces of normal metals have an ideal two-dimensional free electron gas (2DEG) nature with parabolic dispersion [1,2]. Photoemission spectroscopy (PES) and scanning tunneling microscopy (STM) studies on the dispersion, quantization, and carrier dynamics of the surface state electrons have conduced progress in understanding the nature of 2D electron systems [1,3]. Recently, the dispersion of the (111) surface state 2DEG system was found to be modulated for heteroepitaxially grown ultrathin metal films on semiconductor substrates [4–7]. The strain-induced modulation of 2DEG has been a subject of intense investigation for hetero-semiconductor interface devices. The enhancement of electron mobility realizes high-speed device performance in engineering [8,9]. However, the direct information is still lacking on how the strain modifies the 2DEG electron band, since the buried interfaces are difficult to be addressed experimentally. In contrast, the (111) surface state of metal films on semiconductor substrates can be accessed directly by ARUPS and STM. From this viewpoint, the heteroepitaxially grown ultrathin metal film is a system of great interest to study the misfit strain effect on the electronic structure.

In the previous studies, the strain has been regarded spatially homogeneous at the (111) surface of heteroepitaxial metal films [4–7]. This is because PES provides information that is spatially averaged over the probing light size. A previous STM study [7] was also carried out for the surface electron standing waves from the step edges at flat terraces, which can be safely regarded as being free from local modulation of strain caused by defects. However, the strain is usually not homogeneous in realistic heteroepitaxial systems in which misfit dislocations are easily introduced. The strain is expected to be relaxed significantly around the dislocations and become spatially inhomogeneous [10,11]. Therefore, it is highly desired to investigate the local effect of the misfit dislocations on the modulation of the surface states.

In this Letter, we focus on the surface state near the dislocations at atomically flat, two-step grown Ag(111) films on Si(111) substrates including dislocations [12–14]. Previous PES and STM studies reported that the strain induces a shift of the surface state for the Ag/Si(111) system [6,7]. Our STM and scanning tunneling spectroscopy (STS) study gives the first experimental evidence that the shift of the surface state is modulated locally around the dislocations.

Experiments were carried out in an ultra-high-vacuum (UHV) apparatus [7]. Ag(111) epitaxial films with almost atomically flat morphology were obtained by deposition on Si(111) 7 × 7 substrates at 100 K, with subsequent overnight annealing up to room temperature [13]. The cleanliness of the substrates and the flatness of the Ag films were

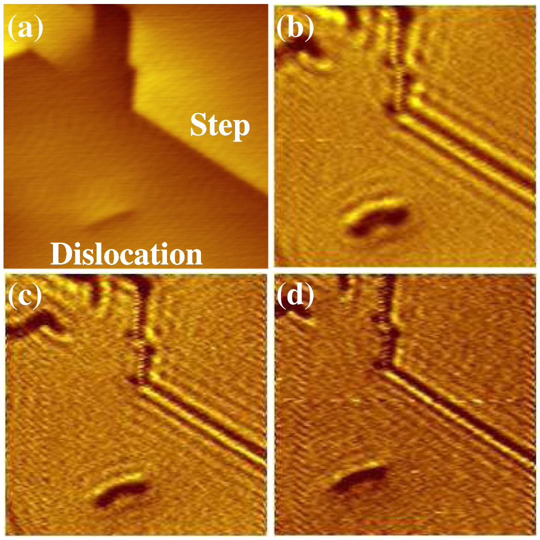

FIG. 1 (color online). (a) STM image and (b)–(d) dI/dV images of a 40 ML Ag(111) film surface. The tunneling current was 0.55 nA. Sample bias voltage was 0.20 V in (a) and (b), 0.30 V in (c), and 0.40 V in (d). Image size is 33.0 nm × 33.0 nm.

confirmed by STM. STM and dI/dV images were simultaneously acquired at 70 K using the conventional lock-in technique by application of a small ac modulation voltage ($V_{p\text{-}p} = 20$ mV, 1.414 kHz) to the sample bias voltage V_s. V_s was varied from 0.1 to 0.5 V for the dI/dV imaging. I-V spectra were obtained by varying V_s from -0.30 to $+0.30$ V at selected points in the STM images. At each point, more than 100 spectra were averaged for an I-V curve. The dI/dV spectra were obtained by numerically differentiating the averaged I-V curve.

Figure 1 depicts STM and dI/dV images of the surface of a 40 monolayer (ML) thick Ag(111) film on a Si(111) substrate. The surface is almost atomically flat, although it includes steps and a dislocation, as indicated in Fig. 1(a). The dislocation makes a 120° angle to the steps that extend along the $[1\bar{1}0]$ direction. Thus, the dislocation is assigned as a Shockley-type extended dislocation, in which the full $\frac{1}{2}[011]$-type dislocation is dissolved into the $\frac{1}{6}[112]$ and $\frac{1}{6}[\bar{1}21]$ partial dislocations at both sides [10].

The corresponding dI/dV images [Figs. 1(b)–1(d)] show the surface electron standing waves originated from the steps and dislocation. Around the steps and the dislocation, the standing waves exhibit a similar V_s dependence. The distance between the peaks in the standing waves corresponds to $\lambda/2$, where λ is the wavelength of the surface state electron [15]. The wavelength becomes shorter with increasing V_s, as expected for the Shockley surface state with a parabolic dispersion.

However, it was found that λ in the standing wave from the dislocation is shorter than that from the step edge, as demonstrated in Fig. 2. The figure depicts the cross section of the surface electron standing waves at $V_s = 0.30$ V from the step (the dotted line) and the dislocation (the solid line) in Fig. 1. The difference in the phase shift (i.e., the relative shift in the position of the first peak) between the two standing waves indicates the difference in the scattering potential for surface electrons at the step and dislocation. Furthermore, it is clear that λ around the dislocation is shorter than that around the step edge from a comparison of the distance between the first and the fourth peaks. The shortening of λ around the dislocations was generally observed at any bias voltage (V_s) for all the Ag(111) films with thicknesses from 10 to 40 ML.

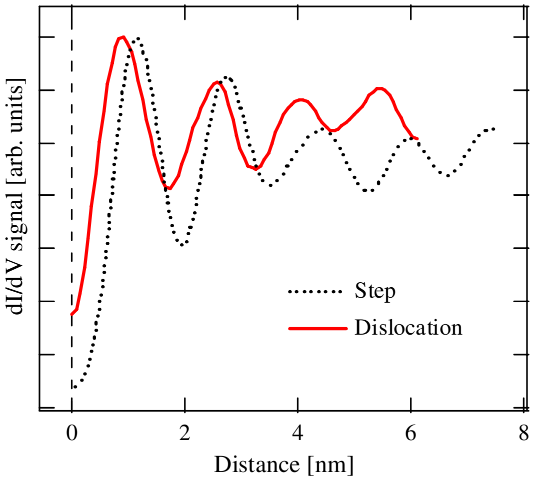

FIG. 2 (color online). Cross sections of the surface electron standing waves from the upper right step and the lower bottom dislocation in the dI/dV image of Fig. 1(c). The bias voltage was 0.30 V.

By plotting the electron energy $E = eV_s$ vs $k = 2\pi/\lambda$ (not shown), we confirmed that the standing wave from the step has parabolic dispersions with an effective mass of $\sim 0.4m_0$. The shortened λ around the dislocation indicates that the surface state dispersion is modulated locally. The substantial shortening of λ indicates that the surface state is shifted downward locally around the dislocations. The downward shift of the parabolic dispersion causes k to be larger at a fixed energy E. k is inversely proportional to λ as $k = 2\pi/\lambda$. Thus, the shortening of λ is induced by the downward shift of the surface state around the dislocations.

However, a highly spatially resolved measurement for the shift in the surface state around the dislocation is not possible from the surface electron standing waves, because the change in λ can only be noticed after comparison of the standing wave patterns over a scale of several half wavelengths. Thus, STS was adopted to investigate the distance-dependent shift in the surface state around the dislocation in more detail. To highlight the effect of the local relaxation of the misfit strain around the dislocation on the shift in the surface state, STS measurements were carried out for a thinner film with a larger accumulated misfit strain. However, the dislocation density becomes too large for extremely thin films [13,14] to regard the effect of a dislocation free from the effect of adjacent dislocations.

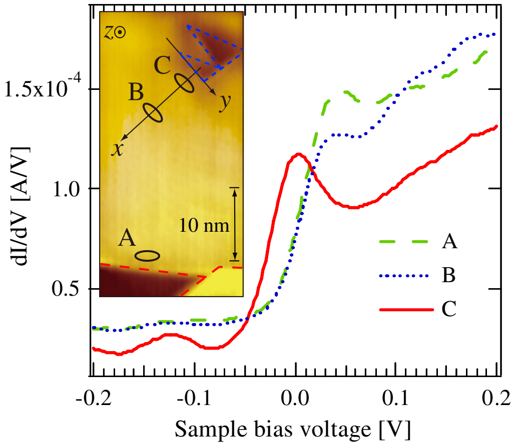

FIG. 3 (color online). dI/dV spectra taken near the step (A), in the midterrace (B), and near the dislocation (C) on a 20 ML thick Ag(111) ultrathin film on a Si(111) substrate. The inset (20 nm × 45 nm) is an STM image of the Ag film surface on which the location for each spectrum is indicated. The step and the joined Lomer-Cottrel type dislocation are located at the bottom side and at the upper right corner in the inset, respectively.

Therefore, we measured the STS spectra of 20 ML thickness Ag films in this study.

Figure 3 shows typical STS (i.e., dI/dV) spectra for a near-step site (A), a midterrace site (B), and a near-dislocation site (C) on a 20 ML thick Ag(111) film on a Si(111) substrate. The locations of the dI/dV spectra are indicated on the STM image in the inset. The step is located at the bottom side, whereas the joined Lomer-Cottrel type double-triangle dislocation is located at the upper right corner in the figure. The double-triangle dislocation unit was fully isolated from the adjacent dislocations and so could be regarded as isolated. At all three sites, the dI/dV spectra exhibit a stepwise increase, as shown in the main panel of Fig. 3. A similar stepwise increase in the dI/dV spectrum was observed at the (111) surface of bulk crystalline Ag, and was attributed to the onset of the Shockley surface state [16,17]. In this respect, the stepwise increases shown in Fig. 3 are interpreted to represent the bottoms of the surface state dispersions on the Ag(111) film. The dI/dV spectra increase substantially around the Fermi level (i.e., 0 V) at the near step (A) and at the midterrace (B) site, whereas it increases at ~ -50 mV near the dislocation (C). This is direct evidence that the band bottom of the surface state (E_0) (the onset of Shockley state) shifts downward locally near the dislocation with respect to that for the near-step and midterrace region.

STS was utilized to investigate the change in E_0 with the distance from the dislocation in the inset of Fig. 3 in more detail. At several points on the x axis, E_0 was deduced as the midpoint of the top and bottom of the stepwise increase in the dI/dV spectrum, as defined in a previous study [17].

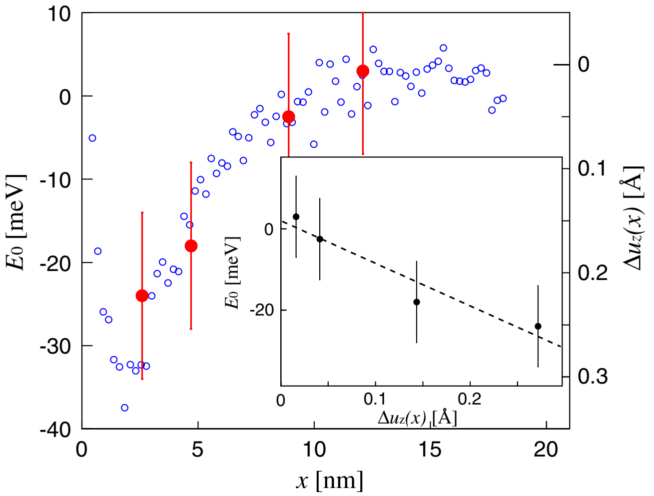

FIG. 4 (color online). Distance-dependent change of the surface state bottom E_0 (filled circles with error bars) and the surface normal displacement Δu_z (small open circles) near the dislocation for a 20 ML thick Ag(111) ultrathin film on a Si(111) substrate. The distance is measured along the x direction in the inset of Fig. 3. The right axis for Δu_z is inverted in the figure to allow for comparison with the x dependence of E_0. The inset depicts the linear relation between E_0 and Δu_z.

The results are depicted by filled circles with error bars in Fig. 4 and show that E_0 is at several ten meV below the Fermi level near the dislocation, but shifts upward gradually with distance x from the dislocation. Finally, E_0 recovered to the midterrace value ($\sim$2 meV) at points 10–15 nm from the dislocation.

We consider that the x-dependent shift in E_0 is caused by local relaxation of the misfit strain in the Ag film around the dislocation. The lattice constant of Ag is shorter than that of Si. Thus, the Ag films are basically under in-plane tensile strain. On the other hand, the bulk band structure of Ag is sensitive to changes in the strain. The strain modifies the band gap at the L point of the bulk Ag crystal [6]. The Shockley surface state at the (111) surface is supported on the *real line* connecting the band gap [18]. Therefore, the strain causes a shift of the surface state through the change in the bulk band structure around the L point band gap.

A simple theory was proposed for the strain-induced modulation of the electronic states around the dislocations by Cottrel *et al.* [19,20]. Their proposal was based on the fact that the Fermi energy generally increases with the compression of lattice. Thus, the Fermi level difference appears at the interface between the compressed and expanded lattice. However, it induces charge transfer and the resulting electric dipole field equalizes the Fermi level on both sides. This dipole field causes the shift in the energy of electronic states. Substantially, the dipole-induced decrease in local work function was observed at the Shockley dislocation-related ridge at Au(111) $22 \times \sqrt{3}$ reconstructed surfaces [21]. In this respect, the shift in the surface state could be considered as a result of the dipole-induced local modulation of the electric potential around the dislocation. However, in heteroepitaxial ultrathin films, the strain is not isotropic and cannot be judged simply as tensile or compressive. The in-plane tensile strain is accompanied by the surface normal compressive strain elastically for ultrathin heteroepitaxial films. Thus, it is difficult to predict the direction of the dipole for the present system in this theory.

A more detailed empirical pseudo potential method (EPM) calculation, in which the anisotropic elastic deformation is fully considered, revealed that the in-plane tensile strain shifts both the lower edge of the band gap and the surface state in the Ag/Si(111) system [6]. The calculation indicated that the change in the in-plane tensile strain is nearly proportional to the shift in the surface state. A 1% increase in the in-plane tensile strain causes a 150 meV upward shift of the surface state in the Ag/Si(111) system [6]. It explains well the downward shift of the surface state around the dislocations. In the present Ag/Si system, the strain relaxation is spatially inhomogeneous, and a considerable part of the in-plane tensile misfit strain is expected to be relaxed locally around the dislocations. In this case, the in-plane tensile strain-induced upward shift is suppressed, and the surface state seems to shift downward locally around the dislocation.

The change in the lattice displacement is directly related to the local strain relaxation and its decay with the distance x around the dislocation. In Fig. 4, the experimentally measured surface normal displacement Δu_z is displayed as a function of the distance x from the dislocation edge at $x = 0$ by small open circles. Δu_z was deduced as the deviation of the local height in respect to that at the midpoint on the upper terrace in the cross section of the STM image. In the figure, the right axis for Δu_z is inverted for comparison with the x-dependent change in E_0. The figure shows that the surface normal lattice displacement u_z is elongated by ~0.3 Å at the edge of the dislocation (i.e., $x = 0$), but gradually decreases with x and becomes zero at $x \sim 10$–20 nm. E_0 showed similar x dependence to that of Δu_z as depicted in the main panel of Fig. 4. The decrease in E_0 is proportional to the increase in Δu_z as shown in the inset of Fig. 4. The increase in Δu_z is elastically equivalent to the decrease in the in-plane tensile strain. Thus, the results in Fig. 4 indicate that the downward shift in the surface state is accompanied by the decrease in the in-plane misfit tensile strain around the dislocation.

Δu_z decreased by 0.3 Å from the midterrace to the edge of the dislocation for the 20 ML thick Ag(111) film. This corresponds to a 0.64% decrease in the in-plane lattice displacement. In the EPM calculation in which the anisotropic elastic deformation was fully considered [6], the 0.64% decrease in the lattice displacement is expected to cause a downward shift in E_0 by 96 meV. This is semiquantitatively consistent with the experimentally observed increase in E_0 of ~40 meV. In addition, E_0 at $x = 0$ is close to that of the surface state for the bulk crystalline Ag(111) surface (−64 meV) [3]. This implies that the misfit strain is almost fully relaxed at the edge of the triangular dislocation.

The triangular dislocation in the inset of Fig. 3 is a Lomer-Cottrel type dislocation, in which a full $\frac{1}{2}\lfloor\bar{1}\,\bar{1}\,0\rfloor$ dislocation in the glide plane dissolves into the $\frac{1}{6}\lfloor\bar{2}\,\bar{1}\,1\rfloor + \frac{1}{6}\lfloor 0\bar{1}1\rfloor + \frac{1}{6}\lfloor\bar{1}\,\bar{1}\,\bar{2}\rfloor$ partial dislocations [22–25]. Here, the surface plane staggers into the upper and lower terraces, but the height difference is not constant and changes from 0 to $\frac{a}{2}\lfloor\bar{1}\,\bar{1}\,0\rfloor$ (a is the lattice constant) at the triangle edge along the y axis. For more quantitative analysis, it is desirable to study the x dependence of E_0 and Δu_z around a simple straight Shockley partial dislocation in which the strain field around the dislocation can be expressed by analytical equations [11]. However, the straight Shockley partial dislocations form small distance arrays [26]. Furthermore, the density of the dislocations increases as the film thickness decreases to reveal the relaxation at the dislocation [13,14]. In this case, the surface state could be modified by the quantum confinement [17,27] in the array of the straight Shockley dislocations. Meanwhile, the misfit strain-induced upward shift in the surface state decreases rapidly at the dislocation-free terrace area as the film thickness increases [7]. Thus, the shift in E_0 and Δu_z was analyzed around the isolated triangular dislocation on the Ag film of moderate thickness (20 ML) in this study.

In summary, the spatial inhomogeneity of the surface state was investigated for epitaxially grown Ag(111) ultrathin films on Si(111) substrates. The surface state electrons are scattered at both the steps and the misfit dislocations, which reveals standing wave patterns at the film surfaces. The wavelength of the surface state electron is shorter around the dislocations than around the steps. The STS spectrum indicates that E_0 shifts downwards locally around the dislocation. The shift in E_0 has the same x dependence as that of $|u_z|$. These results indicate that local strain relaxation is the cause of the downward shift of the parabolic surface state dispersion around the dislocation in the Ag/Si(111) system.

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