Anisotropic Charge Ordering on the Gallium Surface

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Low-temperature scanning tunneling microscopy of atomically flat Ga(001) islands revealed the 2D electronic superlattice composed of stripe domains. Tunnel spectroscopy of these surface electrons indicates the formation of a 2D charge-ordered state of Wigner-crystal type driven by competition of short-range and long-range Coulomb energies. At the boundaries of stripe domains the energy spectra exhibit splitting due to charged excitonic states and shift due to charge doping, altogether indicating the self-assembly of 1D hole stripes. The size distribution of stripe domains is broadened around $4a$.

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In low-dimensional materials the tendency of electrons to minimize their mutual Coulomb repulsion often creates strongly correlated Wigner-crystal-like phases. The interest in correlated electronic phases is greatly stimulated by the synthesis of novel correlated materials, such as complex oxides [1], and by the advances in engineering of artificial low-dimensional nanostructures [2]. Scanning tunneling microscopy (STM) has a special role in the study of strongly correlated electrons because of the ability of this technique to combine structural and spectroscopic analysis at the subnanometer scale. STM revealed charge density waves (CDW) in metallic submonolayers [3,4], anisotropic Mott transition in thin films of polyvalent metals [5,6], and anisotropic charge ordering and charge stripes on surfaces of cuprates [7,8] and manganites [9]. The surfaces studied in STM experiments, often prepared *in situ* using molecular beam epitaxy (MBE), are atomically flat and free of defects [2–6]. Two-dimensional electrons on these surfaces are usually weakly coupled to a reservoir of bulk states which makes them an ideal object for the study of doped Mott-Hubbard insulators and quantum phase transitions [10].

Single crystals of gallium (Ga), whose elementary unit cell is shown in Figs. 1(a) and 1(b), represent very promising candidates for such study. These crystals are characterized by an anisotropic layered structure and are composed of metallic Ga(001) planes separated from each other by covalent Ga-Ga bonds [11–13]. The electrical conductance of these covalent bonds is an order of magnitude less than the in-plane conductance, and the anisotropy increases at low temperatures. The terminating surface layer of Ga(001) crystals represents a unique "free standing" 2D system whose physical properties are different from the properties of bulk. Assuming that the covalent bonds in the terminating layer remain intact, one comes to the conclusion that the surface conductance in this material occurs through a single monolayer of Ga atoms rather than through bilayers as it happens in bulk. Indeed, according to room-temperature STM study of Ga(001) [14], the arrangement of atoms on this surface coincides with the model construction in Fig. 1(b). At low temperatures, below $T_0 = 220$ K, Ga(001) exhibits the 2D surface phase transition accompanied by doubling of the 2D unit cell. In low-energy electron diffraction this transition is manifested through $(\pm\frac{1}{2}, \pm\frac{1}{2})$ superlattice satellites accompanied by fractional $(\frac{1}{4})$ fine structure [15]. The intrinsic instability of Ga(001) surface towards 2D electronic phase transitions was also debated in theory [12], where such an instability was attributed to the half-filled nature of this 2D system.

In this Letter we report the first low-temperature STM study of a Ga(001) surface. Our study revealed the 2D charge-ordered state of Wigner-crystal-type arising from the competition of long-range and short-range Coulomb interactions. At the boundaries of antiphase domains our

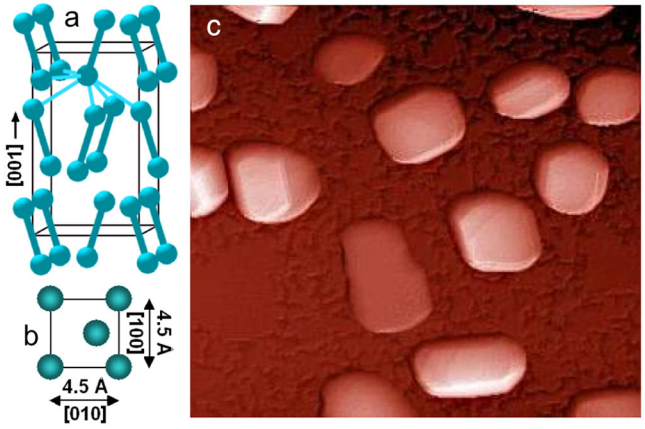

FIG. 1 (color online). (a) The elementary unit cell of Ga is composed of dimer molecules kept by covalent bonds (shown as thick rods) and additionally interconnected to each other through 2D network of metallic bonds (shown as thin rods). (b) Top view of Ga unit cell: $a \times a = 4.5 \times 4.5$ Å^2. (c) STM image of flattop Ga(001) islands epitaxially grown on Si(100) surface. The image sizes are 400×400 nm^2. The image was obtained at tunneling current $I = 0.2$ nA and tip voltage $V_{\text{tip}} = -500$ mV.

measurements revealed self-assembled 1D hole stripes. Our results demonstrate a completely new method of detection and analysis of local charge doping in low-dimensional electronic systems.

Thin films of gallium were prepared by thermal evaporation in ultrahigh vacuum (UHV) on clean and atomically ordered Si(111) and Si(100) substrates. During deposition of Ga the substrates were kept at room temperature. The room-temperature MBE growth of Ga films on Si(111) and Si(100) substrates consists of (a) formation of continuous 2D metallic wetting layer and (b) nucleation of Ga(001) islands on top of this layer. The top surface of these islands is atomically flat. The quality and the chemical composition of our samples (before and after deposition) were monitored using Auger spectroscopy and electron diffraction. After deposition the samples were transferred *in situ* into the low-temperature UHV STM operating at 77 K. In Fig. 1(c) we show the 400×400 nm^2 STM image of top-flat Ga(001) islands epitaxially grown on Si(100) surface. The lateral dimensions of gallium islands vary from 500 to 1000 Å, while their heights change from 20 to 50 Å. A very similar distribution of lateral dimensions and heights of gallium islands was achieved when using Si(111) as a substrate. The unusual surface electronic phenomena, reported in this Letter, were discovered using STM on top of these epitaxial islands.

A typical STM image obtained at 77 K on top of an epitaxial Ga(001) island on Si(100) is shown in Fig. 2. The thickness of the island was 23 Å, and the image sizes are 155×120 Å^2. As can be seen, the surface of Ga(001) is composed of 1D stripe domains superimposed with the 2D square superlattice. The period of this superlattice $d = 9.0$ Å is twice as large as the size of Ga(001) unit cell $a = 4.5$ Å. For convenience, some of the domain boundaries in Fig. 2 are highlighted by dashed lines. The most frequently observed size of stripe domains is $4a$, although $6a$ and $8a$ domains can also be found in Fig. 2.

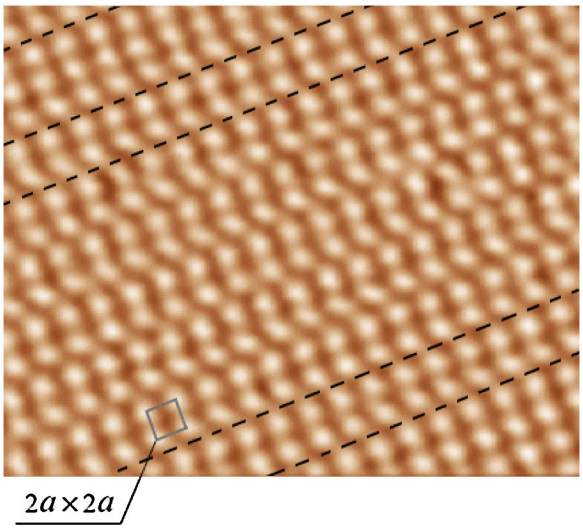

FIG. 2 (color online). STM image obtained at 77 K on top of Ga(001) island on Si(100). The image sizes are 155×120 Å^2. The electronic superlattice, whose periodicity is 9.0×9.0 Å^2, is composed of unidirectional stripe domains. Some of the domain boundaries are indicated by dashed lines. The image was obtained at $I = 0.2$ nA, $V_{\text{tip}} = -500$ mV.

In order to understand the electronic properties of a striped superlattice on a Ga(001) surface, measurements of the tunneling density of states (DOS) were performed. The two different types of spectra were found, as shown in Fig. 3. In the central portion of the stripe domains we observed single-gap spectra (a) where occupied and unoccupied narrow bands are symmetrically aligned with respect to the Fermi level. At the domain boundaries we observed double-gap spectra (b) where electronic bands are split into the two sets. Such spectra are usually considered a signature of the fractionally filled Hubbard system, where the separation between occupied and unoccupied electronic bands is determined by the on site (U) Coulomb repulsion. The band splitting at the domain boundaries, as we will discuss in more detail in the next paragraph, can be attributed to the nearest-neighbor Coulomb repulsion energy (V) [16] frequently used in the extended Hubbard model to describe the long-range Coulomb interaction. According to the extended Hubbard model [10,16–18], a low-dimensional electronic system may undergo two basic

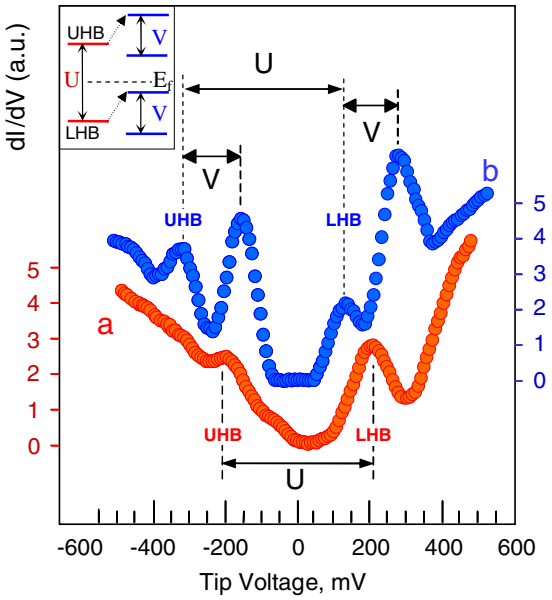

FIG. 3 (color online). Tunnel spectra of Ga(001) at 77 K reveal fractionally filled surface Hubbard bands: (a) single-gap spectra in the central portion of domains, (b) double-gap spectra at the domain boundaries. Because of hole doping of domain boundaries, the upper and the lower Hubbard bands (labeled as UHB and LHB) are shifted towards higher energies. Simultaneously, two spectral satellites with relative energy of $-V$ develop below these bands. The inset shows the schematics of energy levels.

types of Mott-Hubbard transition: (a) spin density waves transition which occurs when $nV < U$, and (b) CDW transition taking place when $nV > U$. The latter is frequently referred to as charge-ordered state or "electronic" CDW. The coordination number of lattice n depends on the dimensionality of the system, and for 2D square lattice $n = 4$. According to our data $V = 150$ meV and $U = 420$ meV. Since the ratio of $V/U = 0.36 > \frac{1}{4}$ the on site Coulomb repulsion (U) becomes less than the overall Coulomb repulsion from neighbors (nV). As a consequence, the system undergoes a quantum phase transition and lowers its total potential energy by creating a superlattice of localized electron pairs. Thus, the analysis of tunnel spectra indicates that the 2D square superlattice observed by STM on Ga(001) is the 2D CDW induced by long-range Coulomb interaction.

Experimental observation of two different, split and nonsplit, energy spectra indicates that a competition of short-range and long-range Coulomb energies, predicted in the extended Hubbard model, indeed takes place. The most direct evidence of such competing Coulomb interactions comes from the ability to "turn off" one of them (V) and to observe how a double-gap spectrum collapses into a single-gap spectrum, as in Fig. 3. As shown by theory [16], observation of nearest-neighbor Coulomb energy (V) through electron addition and removal processes, such as electron tunneling, is facilitated by charged excitonic states arising from hole doping. It is due to these states $U \pm V$ energy gaps can be observed in tunnel spectra. In the absence of hole doping the excitonic states become chargeless and observation of V in tunnel spectra is not possible. It seems natural that charged excitonic states develop at the boundaries of stripe domains ("defected" regions of CDW), i.e., exactly where double-gap energy spectra are being observed. Because of local hole doping of domain boundaries, the upper and the lower Hubbard bands (UHB and LHB in Fig. 3) shift towards higher energies. Simultaneously, two spectral satellites with relative energy of $-V$ develop below these bands, in agreement with Hubbard theory [16]. Such satellites are known to be the manifestation of charged excitonic states. For the 2D Hubbard system the spectral weight of these satellites can be quite significant and comparable to the spectral weight of Hubbard bands already at moderate doping [16]. An additional argument in favor of our model is that the transition between two types of observed energy spectra spatially develops on a length scale of Mott-Hubbard exciton ($\sim a$). The broadening of Hubbard bands in Fig. 3 is most likely caused by coupling between surface and bulk electronic states. Thus, detailed analysis of tunnel spectra suggests that the boundaries of stripe CDW domains on the Ga(001) surface are doped by holes and these holes are most likely supplied from bulk of Ga islands. The simultaneous observation of spectral shift and spectral splitting in local DOS spectra represents a powerful experimental tool for detection of local charge doping in low-dimensional electronic systems.

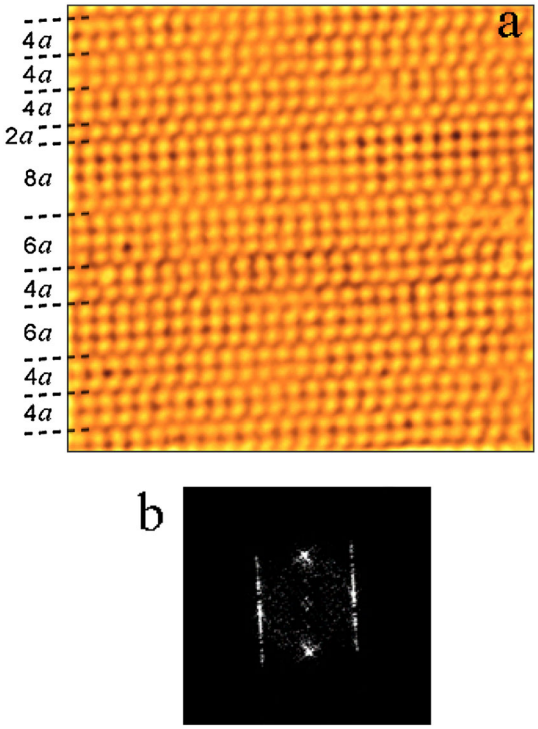

FIG. 4 (color online). (a) STM image obtained at 77 K on top of Ga(001) island on Si(111). The image sizes are 215×200 Å^2. The domain boundaries are indicated by dashed lines. The image was obtained at $I = 0.2$ nA and $V_{\text{tip}} = -500$ mV. (b) The Fourier transform of STM image in (a).

Another example of striped CDW superlattice is shown in Fig. 4(a). The film thickness here was 45 Å, and the image sizes are 215×200 Å^2. Unlike the STM image shown in Fig. 2, this measurement was made on top of the Ga(001) island grown on a Si(111) surface. The stripe domains in this STM image are almost horizontal, and their width varies from $2a$ to $8a$. Again, $4a$ is the most frequently observed domain size. For all studied Ga islands the phase shift between neighboring domains is found to always be π, which corresponds to lateral displacement equal to one unit cell ($a = 4.5$ Å). Indeed, since CDW are pinned on the atomic lattice, the phase shift at domain boundaries must be commensurate with unit-cell size. As a consequence, the 1D modulation of charge density, with period of a rather than $2a$, develops at these boundaries. In principle, such a twofold increase of the modulation wave vector indicates the "annihilation" of the insulating state and the recovery of the metallic state (1D metal).

In Fig. 4(b) we show the 2D Fourier transform of the STM image in Fig. 4(a), i.e., the reciprocal space visualization of the low-temperature phase of Ga(001). The Fourier transform of STM, as it was shown earlier [7,19–21], represents an extremely powerful method for analysis of 2D Fermi surfaces and charge disorder at nanometer

scale. Two of the superlattice peaks in Fig. 4(b) are strongly broadened along the vertical axis and form a pair of straight lines. These lines, oriented perpendicular to domain boundaries, arise from nonuniform size distribution of stripe domains. The most frequently observed size of stripe domain $4a$ corresponds to doubling of CDW periodicity. Our observation remarkably coincides with theoretical predictions [22,23] of $4a$-separated self-assembled charge stripes, whose existence in layered cuprates [7,8], manganites [9,24], and nickelates [25] was earlier confirmed experimentally. The hypothesis of atomic-scale phase separation in doped Mott-Hubbard insulators, resulting in self-assembly of 1D charge stripes, was initially proposed in conjunction with high-temperature superconductivity in layered cuprates. According to this idea, doping holes segregate into parallel 1D atomic channels (''virtual'' wires) separated from each other by undoped regions of Mott-Hubbard insulator. All of this surprisingly resembles our conclusions based on the analysis of local tunnel spectra of a Ga(001) surface. The most unique features of the 2D layered system studied in our experiments are (a) unlike in oxides, the physical mechanism of doping involves a charge transfer between surface and bulk (self-doping), and (b) self-assembly of 1D charge stripes on top of metallic islands. We believe that due to bulk Coulomb screening of surface charges, the equidistantly ordered system of 1D stripes ''melts'' and the size distribution of domains broadens around $4a$. This happens because of significantly reduced Coulomb energy associated with individual charge stripe and significantly reduced Coulomb interaction between charge stripes, altogether making their order more vulnerable to thermal fluctuations. Moreover, for the same reason the ground state of charge stripes on a Ga(001) surface is likely to be metallic (1D metal) rather than insulating, which was earlier found in layered oxides [7–9,24,25].

In conclusion, the possibility of direct spectroscopic observation and direct comparison of short-range and long-range Coulomb energies in strongly correlated Hubbard systems represents a significant step in understanding the driving mechanisms of charge ordering. It is due to the combination of structural and spectroscopic analysis, which is possible only with *in situ* STM, the results of our study verified for the first time a basic microscopic prediction of Hubbard model: a quantum phase transition at a critical value of V.

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