Artificial two-dimensional Mott insulating superstructures with a large Mott gap

Authors

*Affiliations*

**Abstract**

Mott insulators, with a large Mott gap such as the transition metal oxides, are significant to study the interplay to high-Tc superconductivity and quantum spin liquid etc. However, most of the currently discovered Mott insulators host a much smaller gap than the transition metal oxides. Here, we report a method to realize the two-dimensional (2D) Mott insulating structures with a large Mott gap of a few electron volts. Instead of the transition metals with d orbital electrons, we adopted only the Sn atoms with s and p orbital electrons to construct new artificial 2D atomic structures on the base template of Sn/Si(111)-. In this way, the electron orbitals are hybridized, and meanwhile the hopping is effectively tuned, leading to the large Mott gaps ranging from 2.5 eV to 3.1 eV, as corroborated by the Mott-Hubbard model based theory. Our study offers a new possible platform for further study of strong correlation physics.

**Introduction**

Mott insulators are originated from the strong electron correlation, and may give rise to other exotic states, such as unconventional high-Tc superconductivity (SC) and quantum spin liquid state (QSL), through spin frustration or electron doping [1](#_ENREF_1), [2](#_ENREF_2). The fundamental Mott physics can be well captured by the Hubbard model [3](#_ENREF_3). When the on-site repulsive Coulomb interaction (U) dominates over the kinetic energy (proportional to hopping integral, t), the electrons are prevented from doubly occupying a site and thus prefer to be singly localized at each site. There exists an energy separation of U between the electron that occupies an empty site and a site already taken by another electron. As a result, the band is split into the lower Hubbard band (LHB) and upper Hubbard band (UHB) and thus a Mott-Hubbard gap opens for the half-filling [4](#_ENREF_4). Driven by the interests on understanding the mechanism of unconventional superconductivity and searching for the candidate materials of QSL states, a number of Mott insulators have been discovered and extensively explored in the past few decades, including transition metal oxides (e.g., cuprates[5-7](#_ENREF_5) and Ir oxides[8](#_ENREF_8), [9](#_ENREF_9)), transition metal dichalcogenides (e.g., 1T-TaS2 and 1T-TaSe2[10-13](#_ENREF_10)), organic compounds[14-16](#_ENREF_14), C603- fulleride family[17](#_ENREF_17) and stacked graphene[18-20](#_ENREF_18).

Owing to the strong on-site Coulomb interactions (large U) of the 3d electrons[21](#_ENREF_21), [22](#_ENREF_22), the transition metal oxides host a prominently large Mott gap of a few electron volts (eV), and are valuable in the study of strong correlation physics. However, for the materials with a moderate U that is not strong enough to directly open a Mott gap, e.g., 1T-TaS2, C603- fulleride family and stacked graphene, the expected distinct narrow bands (small t) at half-filling around EF is mainly responsible for the Mott transition, but with a much smaller Mott gap of tens to hundreds of meV [19](#_ENREF_19), [23](#_ENREF_23), [24](#_ENREF_24). Efforts have been made to tune the Mott insulating states, such as applying pressure[25-29](#_ENREF_25), electrical field[20](#_ENREF_20) or chemical doping[30](#_ENREF_30). It turns out that to obtain a large-gapped Mott insulator is challenging.

The size of Mott gap is generally determined by the ratio of *U*/*t*. To artificially tune the lattice parameters, such as the crystal symmetry or interatomic spacing [31](#_ENREF_31), can modulate the on-site Coulomb interaction, the hopping integrals and thus effectively the crucial parameter of U/t [refs]. It has been reported that the superstructure of metal atoms adsorbed on the semiconductor surface, e.g., the triangular lattice of K/Si(111)[32](#_ENREF_32) and Sn/Si(111)[33-35](#_ENREF_33), results in the formation of two-dimensional (2D) Mott insulating ground state. The Mott gap was estimated to be ~40 mV on Sn/Si(111)-[36](#_ENREF_36), [37](#_ENREF_37).

Here, we demonstrate a new scenario to form 2D Mott insulators with prominently large Mott gap through the construction of artificial lattices on the base template of Sn/Si(111)-. New superstructures with large lattice periodicities were subsequently obtained, namely , and , respectively. *In-situ* spectroscopic measurements confirm the large Mott gaps ranging from ~2.5 eV to ~3.1 eV, nearly one and half orders of magnitude larger than that of Sn/Si(111)-. Moreover, the size of the measured Mott gaps exhibits a spatial uniformity within the whole unit cell, in good consistence with the theory proposed based on the Mott-Hubbard model. [Shun-Li, 这里加一句话？澄清一下用以区别band insulator和Mott insulator?] This study offers a new platform for the further exploration of strong correlation physics.

**Results and discussions**

Figure 1a illustrates the construction of a R3 triangular Mott insulating lattices of metal adatoms adsorbed on semiconducting substrate, such as K/Si(111) and Sn/Si(111), etc. In the Sn/Si(111)-, an Mott transition was discovered at low temperature. The moderate U and narrow half-filled surface state band collaboratively result in a Mott gap of ~ 40 meV [35-37](#_ENREF_35). Based on such a triangular R3 template, to rearrange or add the metal atoms to construct new superstructures with a larger lattice periodicity might allow to effectively tune the U/t. As illustrated in Fig.1b, clustering the metal atoms can make the electron orbitals more hybridized and localized [refs], [therefore the t or U can be effectively tuned and how?][large periodicity是否有啥作用？]. Consequently, a larger Mott gap is expected to form on such a new reconstructed surface.

Following this scenario, we intend to experimentally develop such new artificial superstructures on the base template of Sn/Si(111)-. As shown in Fig. 1a-c, by adjusting the Sn coverage and growth temperature, three well-ordered superstructures are formed, which are hitherto undiscovered. The three new structures all host the large lattice periodicity, and and , as named as phase I (the honeycomb-like), phase II (the stripe-like) and phase III (the vortex-like) in the following for simplicity. For instance, the honeycomb-like superstructure is identified as with a = b = 3.0 nm. Similarly, the stripe-like phase II superstructure is determined to be with a = ~4.41 nm and b = ~2.42 nm, and the phase III with a = b = ~5 nm. The detailed information about the growth method can be found in Supplementary Fig. S1. Figure 2d-f display the corresponding atomically-resolved STM images, which show the accurate atomic positions in the three phases. The according structural models are thus proposed based on the direct imaging of atomic positions, as shown in Fig. 2g-i.

Selective visualization of the atomic orbitals at certain tunneling conditions was viewed on the surface, as shown in the sequence of bias-dependent STM images (supplementary Fig. S2). At negative biases, the STM contrast does not show significant changes. However, the empty-state images obviously depend on the bias voltage with the pattern varied. The similar experimental results have also been observed on the other two superstructure, and . [这段没有论述]

STS measurements were *in-situ* performed to reveal the electronic properties of the three superstructures. As shown in Fig. 3a, the dI/dV spectra, reflect the local density of states (LDOS), demonstrate the insulating nature with large energy gap of ~2.5 eV, ~3.1 eV and ~2.95 eV for , and respectively. As seen from the spatially resolved dI/dV spectra taken on the surface (Fig. 3b,c) and the extracted spectra at each different atomic positions in a unit cell (Fig. S5), the insulating gap size is almost constant. The homogeneous insulating gap on surfaces of the other two superstructures, and , are also demonstrated (as presented in Fig. S6).

Theoretical calculations were carried out to reveal the nature of the insulating state. Based on the experimental proposal shown in Fig.2g-i, simplified structural models were established for the LDOS calculations. For the surface, the structural model adopt for calculations is displayed in Fig. 4a. The 20 atomic sites in a unit cell are labeled as 0 to 19 with the three atoms located at the center of each honeycomb (labeled as 20 to 22 in Fig. S5) are neglected. When Hubbard U is not considered, as shown in supplementary Fig. S7a-b, the calculated band structure and the total DOS indicate the insulating nature with an energy gap of ~2 eV. The LDOS was also calculated and displayed in supplementary Fig. S7c. We found that the gap size varies from atom to atom. For instance, the energy gap at the atom labeled as “0” is ~2.5 eV, and yet that at the atom “1” is smaller than 1 eV, as displayed in Fig. 4b-c. This inhomogeneous LDOS is obviously contradictory to the experimental uniform insulating gap (Fig. 4c and supplementary Fig. S5). In consideration of the non-negligible in-site Coulomb repulsion in this system, we focus on the calculation results with Hubbard U. As shown in the evolution of total DOS with U (Fig. 4d), the average insulating gap becomes gradually decreased when taking into account of Hubbard U and a transition from band insulator to metal is identified at U= ~ 3 eV. As the applied U further increases to ~ 4 eV, an energy gap near EF reappears, indicating a metal-insulator transition. The including of U= 6 eV leads to an experimentally comparable large energy gap of ~ 2.31 eV. We further explored the corresponding LDOS and found that the insulating gap is uniform at each atomic sites from 0 to 19 (Fig. 4e-f and Fig. S8), in consistent with the experimentally observed homogeneous dI/dV spectra. The agreement between the experimental observation and theoretical calculation with Hubbard U indicates the Mott origin of the large insulating gap of ~ 2.5 eV for surface.

For and surfaces, we similarly constructed the simplified models for theoretical calculations, as shown in Fig. 5a and d respectively. For both of them, the band structure and the calculated total DOS without Hubbard-U (U= 0) indicate their metallic state with non-vanishing DOS near EF. The calculation considering Hubbard-U was further carried out and a transition of metal-insulator happens at U= ~2 eV, as seen in supplementary Fig. S9 and S11. The calculated DOS with U= 6 eV for and are respectively displayed in Fig. 5b and 5e. Both of them exist a band gap of ~3.2 eV, comparable to the experimental result of ~ 3.1 eV, revealing their Mott insulating nature. Due to the fact that the actual atomic arrangements are slightly deviated from the proposed models, we introduce the random variables on the hopping integral t (, is the distance between the atomic sites of i and j) to study the influence of deviations on the calculation results. The evolution of the calculated DOS with Hubbard-U is in line with the results without considering random variables, as shown in Fig. S10 and Fig. S12. When the random variable ranged from 0.7 to 1.3 is introduced, the energy gap for surface at U= 6 eV is calculated to host a fluctuation of only 8% (Fig. 5c), which implies that the tiny influence of the deviation on the DOS. Similar result is also found on surface, as displayed in Fig. 5f. In addition, the theoretical calculations of the LDOS with U= 6 eV at different atomic sites show the constant energy gap, same as the uniform dI/dV spectra observed experimentally, as seen in supplementary Fig. S9d and Fig. S11d for and respectively. The good agreements further confirm these two superstructures are also large-gap Mott insulators.

**Conclusion**

In summary, we realized three superstructures on Sn/Si(111) system that is undiscovered heretofore, namely , and . Large Mott gaps ranging from 2.5 eV to 3.1 eV were observed on them, different from the and surfaces whose metallic and semiconducting nature are demonstrated. Such large gapped Mott insulators provide a more suitable platform to study the related exotic quantum states, such as spin density wave, quantum spin liquid states and unconventional superconductivity.

**Methods**

**MBE growth of Sn/Si(111) sub-monolayers.** The Si(111)-(7×7) reconstruction surface was chosen to be substrate for the growth. It was obtained by the following standard procedures: degassing overnight at ~600 ℃ and then repeatedly flashing at ~1200 ℃ for several cycles in ultrahigh vacuum. Before deposition, the prepared substrates with well-ordered reconstruction surfaces were roughly checked with STM. The evaporated Sn atoms were then deposited on Si(111) -(7×7) surfaces at a flux of 1/3 ML per minute. The substrate was kept at RT. A sequence of thermal annealing were carried out and the superstructures of , and were subsequently obtained at 230 ℃, 350℃ and 400℃, respectively. By further annealing at 550℃ and 700℃ respectively, the and surfaces finally formed.

**STM characterization.** A commercial low-temperature STM (UNISOKU) was used for low-temperature measurements at 78 K. The base pressure is 1×10-10 Torr. Mechanically cut Pt-Ir tips were used and checked on silver islands before the measurements. The dI/dV signals were acquired by a lock-in amplifier with the modulation of 45 mV and frequency of 879 Hz.

**Theoretical calculation.**

**Figure caption**

Fig. 1. Schematic illustration of inducing a large Mott gap in an artificial 2D system. (a) A 2D triangular lattice with the red rhombus marking the unit cell. (b) A large-period superstructure transformed from the structure in (a). The red rhombus marks the new surface unit cell. (c, d) The corresponding schematic pictures for the band structures of the 2D lattices in (a, b) respectively.

Fig. 2. STM characterization of three new superstructures of Sn sub-monolayers on Si(111). (a-c) Large-scale STM images (size: 100×100 nm2) taken on , and surfaces. They are taken at *U*= +3.5 V, *U*= -2 V, *U*= -2 V (*I*t= 100 pA) respectively. (d-f) The atomically resolved STM images of them taken at *U*= -2 V, *I*t= 200 pA. The surface unit cells of them are marked in black. (g-i) The corresponding proposed atomic structural models. The marked surface unit cells in (g-i) are same as that in (d-f).

Fig. 3. The observation of energy gaps on the three new superstructures. (a) The typical dI/dV spectra taken on , and surfaces (*U*= -2 V, *I*t= 200 pA, modulation: 45 mV). The green triangles mark the conduction band minimum (CBM) and valence band maximum (VBM). (b) topographic image taken on surface (*U*= -2 V, *I*t= 100 pA, 40×40 nm2). (c) Spatial-resolved dI/dV spectra taken along the white allowed line in (b) （*U*= -1.7 V, *I*t= 200 pA, modulation: 45 mV).

Fig. 4. TBA and LDA+U calculated LDOS for surface. (a) Theoretically constructed atomic structural model for calculation. The 20 atomic sites in each surface unit cell are labeled as 0 to 19. (b-c) The calculated LDOS without considering Hubbard U at two different atomic sites, 0 and 1. The red dashed lines correspond to the chemical potentials. (d) The evolution of the calculated average DOS with Hubbard U from U= 0 eV to U= 6 eV. (e-f) The calculated LDOS with U= 6 eV at the two different atomic sites, 0 and 1. The red dashed lines correspond to the chemical potentials.

Fig. 5. LDA+U calculation of and surfaces based on the simplified models. (a, d) The proposed simplified models for and superstructures respectively. (b, e) The calculated average DOS with U= 6 eV for and superstructures respectively**.** The green dashed lines correspond to the chemical potentials. (c) The calculated average DOS for superstructure at U= 6 eV with the random hopping introduced. The random hopping is defined as where the random variable ranges from 0.7 to 1.3. (f) The calculated average DOS for superstructure at U= 6 eV with the random hopping introduced. the random variable ranges from 0.95 to 1.05.

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