Hidden phase in a two-dimensional Sn layer stabilized by modulation hole doping

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Semiconductor surfaces and ultrathin interfaces exhibit an interesting variety of two-dimensional quantum matter phases, such as charge density waves, spin density waves and superconducting condensates. Yet, the electronic properties of these broken symmetry phases are extremely difficult to control due to the inherent difficulty of doping a strictly two-dimensional material without introducing chemical disorder. Here we successfully exploit a modulation doping scheme to uncover, in conjunction with a scanning tunnelling microscope tip-assist, a hidden equilibrium phase in a hole-doped bilayer of Sn on Si(111). This new phase is intrinsically phase separated into insulating domains with polar and nonpolar symmetries. Its formation involves a spontaneous symmetry breaking process that appears to be electronically driven, notwithstanding the lack of metallicty in this system. This modulation doping approach allows access to novel phases of matter, promising new avenues for exploring competing quantum matter phases on a silicon platform.

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Some of the conceptually most interesting materials in condensed matter research feature interacting quasiparticles that are associated with their charge, spin and lattice degrees of freedom. The many-body nature of these interactions often produces ‘quantum matter’ condensates characterized by macroscopic quantum coherence, new order-parameter symmetries and alluring physical properties. Prominent examples include charge- or spin-density wave condensates, magnetism and superconductivity. The deliberate introduction of excess charge carriers in a parent material through chemical doping has been a key strategy to access these phases and tailor their properties. A particularly appealing scheme is modulation doping, in which chemical impurities are placed in the electronically inactive regions of a solid-state heterostructure while donating their valence charge to the active regions. Because the dopants and free carrier regions are spatially separated, carrier doping can be accomplished without significantly modifying the potential landscape of the material of interest. Indeed, modulation doping has been a key strategy in the search for novel quantum matter phases such as fractional quantum Hall states in semiconductor heterostructures and unconventional superconductivity in layered perovskites.

Crystal surfaces are inherently two dimensional (2D), and there is an increasing body of evidence that simple monatomic adsorbate layers on semiconductor surfaces exhibit hallmarks of quantum matter, such as long-range quantum coherence and spontaneous symmetry breaking. These systems are of particular interest because electronically they are strictly 2D. Attempts to dope these surface systems via deposition of, for example, alkali metal atoms have had mixed success. Low doses of alkali adsorbates can shift the transition temperature of a Peierls-like surface instability, but it remains difficult to attribute the temperature shift exclusively to charge doping as the adsorbate atoms introduce many defects. Higher alkali coverages amount to overall chemical modification and, hence, property tuning of the parent material is very limited. In fact, no new phases have emerged from this approach. Clearly, a modulation doping scheme for surfaces and interfaces would be highly desirable in the search for novel 2D quantum materials.

Here, we successfully control the n-type and p-type carrier density of the Si(111)/(2√3 × 2√3)R30°-Sn surface reconstruction by changing the chemical potential in the bulk substrate while leaving the chemical composition and structural integrity of the surface intact. The (2√3 × 2√3)R30° surface reconstruction retains its translational symmetry upon electron doping, but the hole-doped reconstruction phase-separates into insulating (2√3 × 2√3)R30° and (4√3 × 2√3)R30° domains. The formation mechanism of this novel (4√3 × 2√3)R30° phase involves a rare displacive transition, assisted by proximity coupling to the tip of a scanning tunnelling microscope (STM). This successful demonstration of the modulation doping scheme, and particularly its ability to unveil a hitherto inaccessible hidden state of matter, may pave the way for the discovery of other emergent phases on crystal surfaces, possibly including superconductivity.

Results

Modulation doping of the surface reconstruction. The n-type Si(111)/(2√3 × 2√3)R30°-Sn reconstruction was prepared by depositing approximately one monolayer (ML) of Sn on the 7 × 7 reconstructed surface of a heavily doped n-type Si(111) wafer (see Methods). Likewise, hole doping is accomplished by growing an identical (2√3 × 2√3)R30° Sn layer on boron-doped substrates with either a 7 × 7 or a B-induced (2√3 × 2√3)R30°-B surface reconstruction. As discussed in Supplementary Note 1, any change in the bulk chemical will lead to a readjustment of the chemical potential in the surface layer. This readjustment involves charge transfer between the surface states and the bulk, and generally implies doping by the excess charges or ‘dopant charges’ in the surface states. The resulting band alignments for the n- and p-type systems are shown in Supplementary Fig. 1.

Figure 1b shows a schematic atomic model of the B-2√3Sn structure, similar to an earlier proposed model but taking into account the presence of boron at the Si lattice location. In this model, boron dopants are separated from the Sn atoms by at least 1 ML. A side view of the Sn/$(2√3 × 2√3)R30°$ interface on the Tornevick model is shown in Fig. 1a. If these boron atoms are all ionized, the hole concentration would amount to ~0.3 hole per Sn atom. From here on, we label the $(2√3 × 2√3)R30°$-Sn layers on the n-type and p-type 7 × 7 substrates as n-2√3Sn and p-2√3Sn, respectively. Those on the $(3√3 × √3)R30°$-B substrate are labelled B-2√3Sn.

The (2√3 × 2√3)R30° Sn layer grown on the $(2√3 × 2√3)R30°$-B surface reconstruction corresponds to the highest hole-doping level where boron atoms have segregated towards the surface, populating the $S_b$ lattice locations below the Si adatoms, see Fig. 1a. If these boron atoms are all ionized, the hole concentration would amount to ~0.3 hole per Sn atom. From here on, we label the $(2√3 × 2√3)R30°$-Sn layers on the n-type and p-type 7 × 7 substrates as n-2√3Sn and p-2√3Sn, respectively. Those on the $(3√3 × √3)R30°$-B substrate are labelled B-2√3Sn.

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two bond distances. There are four boron atoms per (2√3 × 2√3)R30° unit cell. The Sn layer is composed of 14 Sn atoms per unit cell with 4 Sn atoms adopting an outward relaxed double-dimer configuration. The presence of these tetramers gives the structure a double-layer appearance (see Supplementary Note 2). Room-temperature STM images in Fig. 2a,b reveal identical structures for the n-2√3Sn and B-2√3Sn interfaces. High-resolution insets reveal the characteristic double-dimer structure for both n-2√3Sn and B-2√3Sn. The two dimers are symmetric but differ in height, consistent with previous results. The close similarity between the n-2√3Sn and B-2√3Sn structures is corroborated by the nearly identical I(V) spectra in low-energy electron diffraction as well as their identical melting temperature (see Supplementary Notes 3 and 4). Evidently, the subsurface boron-dopant layer does not affect the structure of the Sn overlayer in a significant way.

**Spontaneous symmetry breaking via hole doping.** Upon cooling to 4.4 K, the electron-doped n-2√3Sn surface remains intact (Fig. 2c). In contrast, the hole-doped B-2√3Sn surface gradually transforms into a new (4√3 × 2√3/R30° phase (henceforth B-4√3Sn) below ~100 K (Fig. 2d). Here, the bright dimers are rotated 45°, forming a staggered zigzag pattern (Fig. 2e). The formation of this structure appears to be ‘tip assisted’. In particular, the freshly prepared surface is fully covered by the B-2√3Sn phase, even at 4.4 K, provided that images are recorded with negative sample bias. While changing the tunnelling conditions to positive bias, the majority of the surface transforms into the (4√3 × 2√3/R30° phase for the p-type (B-2√3Sn) interface in b.d. No such transition is observed for the n-type interface (a.c). Scale bars in (a-d) are 5 nm; scale bar in e is 1 nm. Scanning parameters (Vt and It) are 2 V, 0.2 nA (a), 1 V, 0.2 nA (a inset), 2 V, 0.5 nA (b), 2 V 0.3 nA (b inset), −2.3 V, 0.5 nA (c), +1.5 V, 0.02 nA (d) and +1.2 V, 0.15 nA (e). (e) Zoomed-in image of the surface area marked in d. Dashed lines mark the primitive (2√3 × 2√3/R30° and (4√3 × 2√3/R30° unit cells of the B-2√3Sn and B-4√3Sn phase, respectively, while solid lines mark the corresponding centred-rectangular and rectangular unit cells. Up-dimers are marked by ovals. (f) Area fractions of the B-4√3Sn (solid squares) and p-4√3Sn (solid triangles) surface phases as a function of temperature. To determine the change in transition temperature, the p-4√3Sn data were rigidly shifted and superposed with the B-4√3Sn data (hollow triangles). Each data point is obtained from a surface area that is at least 14,000 nm² in size, and is fully converged as a function of image size. Areas close to step edges and domain boundaries were excluded from the statistics.

The formation of this structure appears to be ‘tip assisted’. In particular, the freshly prepared surface is fully covered by the B-2√3Sn phase, even at 4.4 K, provided that images are recorded with negative sample bias. By switching the tunnelling conditions to positive bias, the majority of the surface transforms into the new B-4√3Sn structure. In contrast to observations on Si(100), the tip-assisted formation of this hidden phase is mostly irreversible with respect to the tunnelling conditions at 4.4 K (see Supplementary Note 5).

The area fractions of the coexisting 2√3Sn and 4√3Sn structures were determined as a function of temperature by scanning the same image repeatedly in dual bias mode until the domain ratios are fully stabilized (Fig. 2f, see Supplementary Note 5). These ratios are fully reproducible and reversible with temperature (within the errors of margin indicated below), and are independent of the phase-change history of the surface. This suggests that they represent an equilibrium configuration of the system. Interestingly, the area fraction or ‘order parameter’ of the B-4√3Sn phase no longer changes below 40 K and saturates at 0.75 ± 0.07. Very similar behaviour is observed for p-2√3Sn (Supplementary Note 6), except that the order-parameter curve has shifted to lower temperature by ~17 K (Fig. 2f), consistent with the nominally lower hole content for this interface (Supplementary Notes 1 and 6).

It should be noted that the concentration of the near-surface B dopants differs significantly for the p-2√3Sn and B-2√3Sn surfaces, as the latter contains 1/3 ML of boron at the Sb lattice location. Yet, the B-4√3Sn area fractions at 4 K are nearly identical. It is therefore unlikely that the formation of the 4√3Sn structure should be attributed to direct chemical interaction between boron and tin. Furthermore, there is no indication of striped inhomogeneity, either structurally or electronically, in the p-type 2√3Sn systems that could trigger the formation of the striped 4√3Sn domains. Such subsurface inhomogeneity would readily be evident in the dI/dV maps of the 2√3 structure (Supplementary Note 7). This then leaves hole doping as the only plausible mechanism for the formation of the 4√3 domains. Interestingly, the exponential domain width distribution indicates

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**Figure 2** | **STM images of the (2√3 × 2√3)R30° Sn structures on n-type and p-type Si(T11)1.** Notice the transition from the (2√3 × 2√3)R30° to (4√3 × 2√3)R30° phase for the p-type (B-2√3Sn) interface in b.d. No such transition is observed for the n-type interface (a.c). Scale bars in (a-d) are 5 nm; scale bar in e is 1 nm. Scanning parameters (Vt and It) are 2 V, 0.2 nA (a), 1 V, 0.2 nA (a inset), 2 V, 0.5 nA (b), 2 V 0.3 nA (b inset), −2.3 V, 0.5 nA (c), +1.5 V, 0.02 nA (d) and +1.2 V, 0.15 nA (e). (e) Zoomed-in image of the surface area marked in d. Dashed lines mark the primitive (2√3 × 2√3)R30° and (4√3 × 2√3)R30° unit cells of the B-2√3Sn and B-4√3Sn phase, respectively, while solid lines mark the corresponding centred-rectangular and rectangular unit cells. Up-dimers are marked by ovals. (f) Area fractions of the B-4√3Sn (solid squares) and p-4√3Sn (solid triangles) surface phases as a function of temperature. To determine the change in transition temperature, the p-4√3Sn data were rigidly shifted and superposed with the B-4√3Sn data (hollow triangles). Each data point is obtained from a surface area that is at least 14,000 nm² in size, and is fully converged as a function of image size. Areas close to step edges and domain boundaries were excluded from the statistics.
that neither elastic nor electrostatic long-range interactions play a significant role in stabilizing the unusual coexistence of the $2\sqrt{3}$ and $4\sqrt{3}$ structures (Supplementary Note 8).

Figure 3 presents a high-resolution STM image of the B-$4\sqrt{3}$Sn phase, along with a remnant patch of the B-$2\sqrt{3}$Sn phase, recorded at 4.4 K. The tetramer subunits of the B-$4\sqrt{3}$Sn phase acquire (approximate) twofold rotational symmetry, whereas the tetramers of the B-$2\sqrt{3}$Sn phase exhibit mirror plane symmetry. As indicated in the right panel of Fig. 3, the high-temperature $2\sqrt{3}$ phase has a rhombic space group symmetry (cm, 2D space group no. 5), characterized by the existence of both mirror ($m_m'$) and glide plane ($g, g'$) symmetry. The $4\sqrt{3}$ image in Fig. 3 has a rectangular space group symmetry ($p2gg$, space group no. 8), but because the underlying substrate lacks twofold rotational symmetry, the overall symmetry of the $4\sqrt{3}$ structure must be $pg$ (space group no. 4; the weak breaking of $p2gg$ symmetry can be observed under different tunnelling conditions, as shown in Supplementary Note 9). The structural transition is characterized by a loss of mirror plane symmetry, as well as a loss of centring translation if one adopts a centred rectangular unit cell for the $2\sqrt{3}$ phase (Figs 3 and 2e). Most importantly, the high-temperature phase cannot be obtained via superposition of low-temperature domains or by thermal averaging of the up-down positions of the adatoms of the low-temperature phase. Thus, the $2\sqrt{3}$ to $4\sqrt{3}$ transition appears to be displacive in nature, which is highly unusual as most other continuous surface structural transitions are of the order–disorder type as a result of dynamical fluctuations of the adatom heights or diffusive motion of the Sn adatoms. Note that the $2\sqrt{3}$ phase has polar symmetry, meaning that it could support a macroscopic electrical polarization parallel to the mirror plane. The $4\sqrt{3}$ phase is approximately nonpolar. This could affect the relative stability of the $2\sqrt{3}$ phase in the presence of an external electric field and, consequently, the activation barrier for the tip-assisted phase transformation. A more detailed discussion is provided in the Supplementary Note 5.

**Band alignment and chemical potential.** The electronic structure and structural transition are further characterized by scanning tunnelling spectroscopy at 77 and 4.4 K (Fig. 4). The normalized differential tunnelling conductance ($dI/dV(I/V)$) is approximately proportional to the local density of states at the surface. The $dI/dV(I/V)$ curves for the n-$2\sqrt{3}$Sn, p-$2\sqrt{3}$Sn and B-$2\sqrt{3}$Sn systems indicate an energy band gap of $\sim 0.45$ eV. In Supplementary Note 1, we find that the Fermi level is located 0.03 eV above the bottom of the empty surface state band for the n-$2\sqrt{3}$Sn surface and $\sim 0.12$ eV above the top of the filled surface state band for the p-$2\sqrt{3}$Sn surface (77 K). Accordingly, the maximum shift in the surface chemical potential achievable via bulk doping amounts to 0.36 eV. Indeed, when shifting the p-$2\sqrt{3}$Sn spectrum 0.36 eV to the left, as indicated by the dashed line in Fig. 4a, we see that the spectral features of the n- and p-type surfaces line up quite nicely. The B-$2\sqrt{3}$Sn and p-$2\sqrt{3}$Sn spectra are very similar. The structural similarity between the p- and n-type $2\sqrt{3}$Sn surfaces and the negligible role of boron chemistry in the formation of the $4\sqrt{3}$Sn structure for the p-type substrates strongly indicates that the stability of the mixed phase

![Figure 3](image-url) High-resolution STM image of the B-$4\sqrt{3}$Sn phase at 4.4 K. The green shaded area marks a narrow patch of the B-$2\sqrt{3}$Sn phase. The Sn tetramers of the $2\sqrt{3}$Sn and $4\sqrt{3}$Sn structures are highlighted by circles. Large circles mark the outward-relaxed atomic protrusions and smaller circles the inward-relaxed atomic features. Scanning parameters are $V_c = 1 V, I_t = 0.2$ nA. The scale bar is 1 nm. Mirror plane and glide plane symmetries are indicated on the right.

![Figure 4](image-url) Scanning tunnelling spectroscopy (STS) measurements. (a) $dI/dV(I/V)$ spectra of the B-$2\sqrt{3}$Sn, p-$2\sqrt{3}$Sn and n-$2\sqrt{3}$Sn surfaces obtained at 77 K. The spectra for p-$2\sqrt{3}$Sn and B-$2\sqrt{3}$Sn are shifted vertically for clarity. The Fermi level is located at 0 V. By shifting the p-$2\sqrt{3}$Sn spectrum 0.36 eV toward lower energy (dashed line), and superposing it with n-$2\sqrt{3}$Sn spectrum, it is seen that the low-energy spectral features line-up almost perfectly. Triangles below each curve mark the highest occupied surface state (left) and lowest unoccupied surface state (right), while a solid bar indicates the estimated location of the VBM (left) and CBM (right) of the bulk Si bands near the surface with the bar length representing the error range (see Supplementary Note 1). (b) $dI/dV(I/V)$ spectra of the B-$2\sqrt{3}$Sn and B-$4\sqrt{3}$Sn interfaces obtained at 4.4 K, showing a slightly larger band gap for the B-$4\sqrt{3}$Sn phase. All STS spectra were measured on top of the bright dimers (STS at other locations within a unit cell are showing similar features). Each $dI/dV(I/V)$ spectrum is obtained by dividing the $dI/dV$ curve by its smoothed $I(V)$ curve.
is related to the location of the chemical potential at the surface. To further corroborate this point, we compensated the hole concentration by depositing 0.005 ML of K or Cs on the B-2√3Sn surface (see Supplementary Note 10 and Supplementary Fig. 12). This results in an upward shift of the chemical potential, consistent with the injection of n-type charge carriers from the alkali atoms, and an almost complete reversal of the 2√3Sn to 4√3Sn phase transformation at 60 K. This then conclusively shows that this phase transformation originates from modulation hole doping. The modulation doping approach works because Fermi-level pinning is weak, presumably due to the low density of defect states27. This allows for a rather wide sweep of the Fermi level location at the surface with relatively low carrier concentrations and provides access to different parts of the phase diagram.

The dI/dV spectra of the p-type B-2√3Sn and B-4√3Sn phases (Fig. 4b) reveal some important differences as well, such as the peaks at +1.2 and −0.5 eV and the wider band gap of ~0.7 eV for the B-4√3Sn structure. The latter seems consistent with the fact that the B-4√3Sn structure is favoured at low temperature.

Discussion

The formation of the mixed phase clearly requires nonthermal activation through a negatively biased STM tip. As such, it represents a hidden state of matter, although one that is long-lived and stabilized in the presence of hole doping. Whether or not the mixed phase represents a global minimum cannot be decided from the current investigation, though it is natural to assume that the broken symmetry state represents the total energy minimum. Nonetheless, exceptions to this rule exist18.

The presence of a displacive insulator-to-insulator transition on a semiconductor surface is also highly unusual. While a continuous cm→pg phase transition would be symmetry allowed29, the persistent coexistence of the 2√3Sn and 4√3Sn phases and crossover behaviour at high temperature are both indicative of a preempted first-order mechanism30, one that requires activation by the STM tip. The latter may be needed to access a transitional and possibly symmetric tetramer configuration via local excitation. The subsequent vertical relaxation of the tetramer atoms and the doubling of the lattice periodicity would involve one or several soft lattice modes. Such a phonon instability and associated charge fluctuation is likely affected by the presence of screening charges at the interface with presumably opposite effects for the depletion layer and hole reservoir present on the n- and p-type Si substrates, respectively.

Finally, we note that surface defects do not play a significant role in the nucleation and pinning of the surface domains. All the evidence seems to indicate that the hidden phase is intrinsically phase separated, suggesting the presence of multiple minima in the thermodynamic potential as a function of carrier doping. This is reminiscent of the electronic phase separation in some complex oxides31. An important distinction here is that the two surface phases are both nonmetallic and that the domains are easily visualized.

In summary, a modulation doping approach, which introduces charge only but avoids chemical perturbation to the surface, allows access to novel surface phases and hidden symmetries. It is achieved by adjusting the bulk chemical potential and the concentration of subsurface B dopants. This method is expected to be applicable to other well-ordered semiconductor surface reconstructions as long as the corresponding surface states are located inside the bulk band gap, and as long as the substrate material can be doped both n- and p-type over a considerably wide range of doping levels. The same idea can be applied to complex oxide heterostructures.

It should therefore be possible to map out electronic phase diagrams in a variety of other surface systems. A most intriguing possibility would be the existence of a superconducting instability or quantum critical point in a surface layer15. Besides this conceptual appeal, we have also shown that cooperative phenomena can be realized and tuned in relatively simple sp-bonded 2D materials systems on a Si platform. This notion may ultimately bring the rich physics of complexity closer to the realm of technological innovation.

Methods

Preparation of the substrates. Four types of Si(111) wafers were used: heavily As-doped n-type Si with room-temperature resistivity of 0.002 Ω cm, and three different B-doped p-type Si wafers with room temperature resistivities of ~0.004, ~0.009 and ~0.032 Ω cm. The heavily doped Si substrates give rise to finite conductivity at low temperatures, which is essential for the STM/scanning tunnelling spectroscopy measurements. Samples cut from these wafers were ultrasonically cleaned with acetone and alcohol, and then processed following standard procedures in ultrahigh vacuum: degassing at 600 °C overnight, flashing at ~1,250 °C and 900 °C to room temperature over the course of several minutes. A Si(111) (7×7) reconstruction surface is obtained for the n-type and ~0.032 Ω cm p-type Si wafers. A (√3 × √3)R30°-B reconstructed surface is prepared on the most heavily B-doped (0.009 Ω cm) material by using a longer annealing time, for example, 5 h at 1,150 °C, followed by slow cooling, 5 h at 1,150 °C, followed by slow cooling, 7 h at room temperature over the course of several hours to facilitate the segregation of ~1/5 ML of B to the s, below the surface13. A reduced annealing time for this heavily doped material produces a highly defective (√3 × √3)R30°-B surface with reduced boron content. The slightly more resistive 0.009 Ω cm wafer exhibits a mixed defective (√3 × √3)R30°-B and 7 x 7 surface33.

Sample preparation and measurements. The substrates were thoroughly characterized with STM to ensure that well-ordered reconstructed surfaces were present before the Sn deposition. The (√3 × √3)R30°-B surface contains a small number of Sn defects where Si atoms populate some of the Si, lattice sites18. For studies of the B-2√3Sn phase, we kept the concentration of Sn5 defects below ~15 defects per 2,500 nm2. The Si(111) (√3 × √3)R30°-Sn surface reconstructions were prepared on the four different substrates by thermally depositing ~1 ML of Sn at a substrate temperature of ~550 °C. The sample was post annealed at this temperature for several minutes and cooled to room temperature.

For room-temperature and low-temperature measurements, we used a commercial low-temperature STM (Omicron). Chemically etched tungsten tips were used and checked on gold films before the measurements. This system is also equipped with potassium and caesium dispensers from SAES. The potassium or caesium atoms are deposited onto the surfaces held at ~100 K to reduce the diffusion of the adsorbed atoms. The dI/dV signal was acquired by a lock-in amplifier using a typical frequency of 831 Hz and modulation amplitude between 1 and 10 mV. Low-energy electron diffraction (for structural characterization) and X-ray photoelectron spectroscopy (XPS) studies (for band bending measurements) were conducted in a separate UHV system. This system was also equipped with a Sn effusion cell and a variable-temperature STM so that the surface preparation and atomic-scale characterization could be reproduced. The low-energy electron diffraction and X-ray photoelectron spectroscopy measurements are described in Supplementary Notes 1, 3 and 4.

Data availability. Original data will be made available upon request (hamo@utk.edu).

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**Author contributions**

F.M., D.M., W.T. and T.S.S. did the experiments; P.V. provided technical support for the experiments; Y.-T.H. and R.D.D. analysed the low-energy electron diffraction (V) data; P.C.S. and H.H.W. led the project; P.C.S., H.H.W., F.M. and T.S.S. analysed other data and wrote the manuscript; and all authors were involved in discussion.

**Additional information**

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