

When defects are not defects

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2D MATERIALS

When defects are not defects

Line defects in two-dimensional borophene can self-assemble into new crystalline phases, blurring the distinctions between perfect and defective crystal.

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An impurity atom in a crystal is normally referred to as a defect, which locally breaks the periodic structure of the crystalline lattice. When the concentration of impurities increases, the material is not considered to be defective, but regarded as an alloy, which can be ordered or disordered depending on the spatial arrangements of the host and impurity atoms. Likewise, when many vacancies are present, one can think about the material alloying with vacancies. The behavior of vacancies in solids is more complicated, though – they frequently agglomerate and form extended defects, e.g. dislocation loops in irradiated metals, or even voids, as in monocrystalline silicon, and in case of compounds can give rise to the formation of new phases with different stoichiometries, with a good example being tin sulfide crystals with different chalcogen content (SnS_2 , Sn_2S_3 , and SnS).

All of the above is relevant to two-dimensional (2D) materials [1] like widely studied graphene and hexagonal boron nitride, or recently synthesized borophenes [2, 3], 2D polymorphs of boron. The reduced dimensionality, however, affects the topology of defects in these systems: for example, it is evident that edge dislocations in two-dimensions are not line but point defects, making the studies on defects particularly interesting. Moreover, vacancy lines can easily be transferred to dislocations, contrary to bulk systems. The influences of those imperfections on material properties become more prominent in systems with reduced dimensionalities. In the mean time, 2D materials, made up of entirely their surface, are ideal systems for studying defect behaviors by using, for example, scanning tunneling microscopy (STM), a technique which has the capability not only to directly ‘see’ each atom and hence each defect in the crystal lattice [4], but also to probe the electronic structure at the atomic scale. Now writing in *Nature Materials*, Xiaolong Liu and colleagues [5] report a very peculiar behavior of line defects in borophene, where the line defects intermix and self-assemble into periodic domains, restoring the translational symmetry of the crystal and blurring the traditional distinction between perfect and defective crystals, generating new phases of borophene, and modulating their properties.

In contrast to semiconducting bulk boron, borophene is an anisotropic metal with charge carriers behaving as massless Dirac fermions, making it a promising platform for developing novel high-speed low-dissipation electronic devices [6]. In addition to a corrugated sheet composed of boron atoms on a triangular lattice [2], many borophene polymorphs with periodic ‘missing atoms’ forming hexagonal vacancies (hollow hexagons, HHs) have been predicted to exist [7,8], which could be regarded as an ordered alloy of vacancies and boron atoms. They have close cohesive energies but different arrangements and concentrations of such vacancies in an otherwise triangular lattice. Given the synthetic nature of borophene, the intrinsic defects in borophene remain largely unexplored. Such defects can be defined as deviations from the perfectly periodic structure, for example as perturbations in the ordered array of vacancies. Linear defects have now been identified and investigated [5] by Liu and

colleagues using a combination of ultra-high vacuum STM and density functional theory (DFT) calculations. A co-existence of line defects and their self-assembly into new phases have been demonstrated. As evident from the STM image in Fig. 1a, borophene sheets synthesized on Ag(111) thin films under certain conditions contain a large amount of line defects. Interestingly, vacancy lines do not disappear, as in, e.g., graphene by forming a short edge dislocation, but are thermodynamically stable. Two borophene phases correspond to different concentrations (ν) of HHs, $\nu = 1/6$ and $1/5$. Interestingly, line defects in each phase are identified to adopt the unit structure of the other phase, intermixing these two borophene phases.

The perfect lattice match and rotational registry with Ag (111) along the HH rows at phase boundaries gives rise to negligible interface energy, indicating that the $\nu_{1/6}$ and $\nu_{1/5}$ rows can become building blocks being assembled into new borophene phases with intricate periodic arrangement of the rows. An example is presented in Fig. 1e, where two new borophene phases corresponding to $\nu_{4/21}$ and $\nu_{7/36}$ sheets are observed with different mixing ratios of the two rows. As the system remains metallic, interesting electronic effects, for example, the development of charge-density waves can be expected, as hinted by experimental measurements and DFT calculations.

From a practical standpoint, borophene sheets with different arrangements of line defects could be used for producing new phases with highly anisotropic and tunable electronic and thermal properties, which may find applications in plasmonic devices. If borophene sheets could be rolled up into seamless cylinders, as graphene into nanotubes, this would make it possible to further manipulate the electronic properties of the system, as one can expect from theoretical calculations performed for phosphorene [9]. Future work will reveal the full potential of this material, but at the moment we have a fascinating example demonstrating self-assembly of intrinsic defects in a 2D material and defect-mediated engineering of material structure and properties, as recently shown also for 2D transition metal dichalcogenides where periodic dislocation arrays can induce the formation of coherent MoS₂ 1D channels embedded in WSe₂ constituting a 2D superlattice [10].

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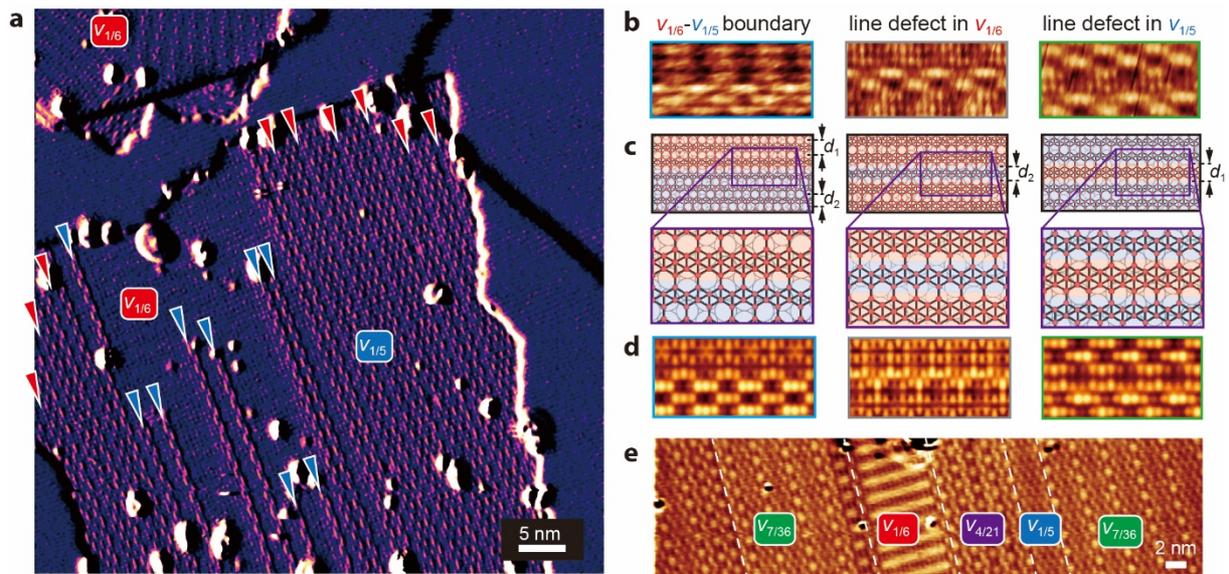


Figure 1. Borophene line defects and their self-assembly into new phases. (a) Derivative image of a typical STM topography of mixed-phase borophene. The presence of parallel line defects is evident. Line defects in the $v_{1/6}$ and $v_{1/5}$ phases are indicated by the blue and red arrow heads. (b) STM images of regions corresponding to the $v_{1/6}$ and $v_{1/5}$ phase boundary, line defect in $v_{1/6}$, and line defect in $v_{1/5}$, respectively. (c) DFT-optimized structure models. Note different inter-row spacing d_1 and d_2 of the line defects in the $v_{1/6}$ and $v_{1/5}$ phases. (d) Simulated STM images corresponding to the three regions in (b). (e) A borophene sheet containing domains with different periodic assemblies of $v_{1/6}$ and $v_{1/5}$ rows, including two new phases of borophene ($v_{7/36}$ and $v_{4/21}$ sheets). Adapted from ref. [5] Macmillan Publishers Ltd.