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Regular Arrangement of Two-Dimensional Clusters of Blue Phosphorene on Ag(111)

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Two-dimensional (2D) blue phosphorene with a honeycomb structure is the phosphorus analog of graphene, and is regarded as a promising 2D material with a large tunable band gap and high charge-carrier mobility. Here, using the molecular beam epitaxy method, we synthesize monolayer blue phosphorene on the Ag(111) surface. Combined with first-principles calculations, scanning tunneling microscopy measurements reveal that the blue phosphorene on the Ag(111) surface consists of 2D clusters with a buckling 1×1 lattice, arranged regularly on the Ag(111). The formation of these phosphorus clusters stems from the strain modulation induced by the lattice mismatch between blue phosphorene and the Ag(111) substrate. Moreover, x-ray photoelectron spectroscopy measurements are performed to study the instability of the blue phosphorene clusters in air. The realization of regular nanoclusters of blue phosphorene with unique sizes and morphology provides an ideal platform for the exploration of the quantum physical properties and applications of blue phosphorene.

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The discovery of graphene and its remarkable properties have inspired the development of a new class of materials known as "two-dimensional (2D) materials".[1−4] In the past decade, intensive research efforts have been devoted to monoelemental 2D materials beyond graphene (X-enes), such as silicene,[5−9] germanene,[10−14] stanene,[15−17] and borophene,[18−24] due to their unique properties and wide range of potential applications. Recently, phosphorene, which is the 2D form of phosphorus, has attracted considerable attention as an emerging 2D material with promising electronic and optoelectronic properties.[25] As the most abundant pnictogen in the Earth, elemental phosphorus has various allotropes, known as white, red, black, violet, and yellow phosphorus.[26] Of these allotropes, black phosphorus is the most stable form, possessing a layered structure in which the phosphorus atoms resemble a puckered honeycomb structure, characterized by armchair ridges in the side view of the layer [see Fig. 1(a)].[27] Single- and few-layer phosphorene films obtained by exfoliation from bulk black phosphorus have been shown to possess a thickness-dependent direct band gap and high charge carrier mobility, both of which are highly desirable for potential use in e.g., next-generation optoelectronic devices.[28−31]

The existence of blue phosphorus was first predicted by DFT calculations,[32] and was predicted to have a layered honeycomb structure and to be as stable as black phosphorus. In contrast to black phosphorus, the atoms within a single layer of blue phosphorus are arranged in a buckled honeycomb lattice, closer in appearance to silicene, as illustrated in Fig. 1(b). The unit cell of an isolated blue phosphorus monolayer (known as blue phosphorene) has a lattice constant of 0.328 nm. The buckling, which is defined as the vertical distance between the two neighboring P atoms, has been calculated as 0.13 nm.[32−35] Unlike the black phosphorus monolayer or black phosphorene, with its intrinsic direct band gap of ∼1 eV, blue phosphorene has an indirect band gap of ∼2 eV, which makes blue phosphorene a promising candidate for use in high-performance electronic nanodevices of the future.

Unlike black phosphorene, 2D blue phosphorene is absent in nature, and cannot be directly fabricated by mechanical exfoliation.[36] Recently, single layer blue phosphorene has been successfully synthesized on the Au(111) surface by molecular beam epitaxy (MBE). The synthesized phosphorene exhibits a 5×5 superstructure with respect to Au(111), commensurate with the 4×4 blue phosphorene lattice.[37−39] However, the atomic structure of the phosphorus thin film on Au(111) is still the subject of controversy. Recently, Tian *et al.* provided a reliable model of a 2D porous gold-phosphorus network, whereby blue phosphorene subunits are linked by gold atoms.[40] Since the morphology and structures of elemental 2D materials depend strongly on interfacial interactions,[5−9,18−24]

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and the properties of the 2D materials are likely to change when these materials are grown on different substrates, the choice of a suitable substrate and the investigation of their nucleation mechanism and growth behavior may be of great importance in terms of obtaining blue phosphorene with a reliable configuration and morphology.[41,42]

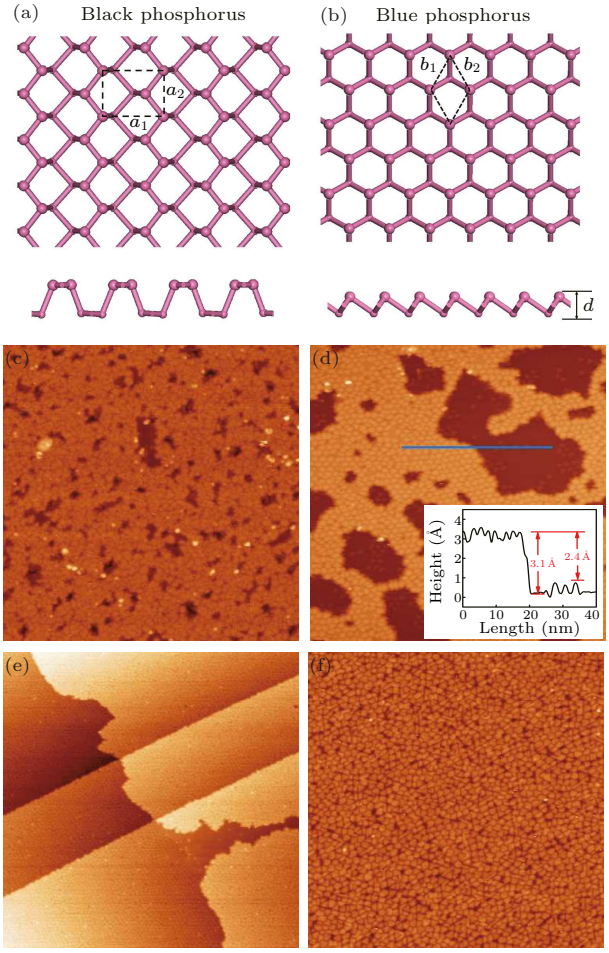

Fig. 1. [(a), (b)] Top view (upper) and side view (lower) of atomic models of black phosphorus and blue phosphorus. The unit cells are highlighted by a black rectangle and a black rhombus, respectively; a_1 and a_2 are the armchair edge and zigzag edge of black phosphorus, and $a_1 = 4.37$ Å and $a_2 = 3.31$ Å; b_1 and b_2 are the zigzag edges of blue phosphorus, where $b_1 = b_2 = 3.28$ Å; d is the distance between the buckled blue phosphorus atomic layers, and $d = 0.13$ nm. [(c), (d)] STM images (80 nm × 80 nm) of a phosphorus film grown on Ag(111) surface at room temperature (c) and subsequently annealed at 370 K (d). Inset: line profile along the blue line. (e) STM image (160 nm × 160 nm) of phosphorus film grown on Ag(111) surface at a substrate temperature of 420 K. (f) Zoom-in STM image (40 nm × 40 nm) of (e). The scanning parameters are: (c) sample bias = −3 V, $I_t = 0.06$ nA, (d) sample bias = −2 V, $I_t = 0.04$ nA, (e) sample bias = −3 V, $I_t = 0.03$ nA, (f) sample bias = −2 V, $I_t = 0.03$ nA.

The Ag(111) surface is an important substrate that has already been used to realize several monoelemental two-dimensional materials, such as silicene,[6] germanene,[14] stanene,[17] and borophene.[22] In this study, we chose the Ag(111) surface as the substrate for growing a phosphorus film. Scanning tunneling microscopy (STM) measurements reveal that the obtained phosphorus monolayer consists of regular 2D clusters of blue phosphorene with a buckled 1×1 lattice. Combined with first-principle calculations, we provide a structural model to illustrate the regular arrangement of 2D nanoclusters on the Ag(111) surface, finding that the formation of 2D clusters of blue phosphorene is due to the strain induced by the lattice mismatch between the blue phosphorene and the Ag(111) substrate. In addition, x-ray photoemission spectroscopy (XPS) experiments have been conducted to analyze the stability of blue phosphorene in air.

The experiments were carried out in an ultrahigh vacuum (UHV) system (Omicron VT STM) with a base pressure below 1×10^{-10} mbar. A single crystal Ag(111) substrate was cleaned via cycles of argon ion sputtering (1.5 kV, 2×10^{-5} mbar), and subsequent annealing at 800 K. The phosphorus was evaporated at 480 K from a crucible containing high-purity bulk red phosphorus (99.999%) onto the substrate. The deposition rate of the phosphorus was maintained at 0.07–0.1 ML/min, as calibrated by the adsorption of phosphorus on an Si(111) substrate. The topography of the film was measured using an *in situ* STM at room temperature (∼300 K) in constant current mode. An electrochemically etched tungsten tip was used for the STM experiments. The chemical composition of the phosphorus films was analyzed by *ex situ* XPS measurements [the excitation source used for the XPS measurement was Al K_α ($h\nu = 1350.1$ eV), and the energy resolution was approximately 450 meV] at room temperature in the UHV chamber.

Firstly, phosphorus atoms were thermally evaporated onto the Ag(111) surface, maintained at room temperature. Figure 1(c) shows the obtained phosphorus film, with a coverage of less than one monolayer. This consists of irregularly arranged small domains, and some small areas of bare Ag(111) surface. Annealing such a sample at 370 K results in regular arrangements of nanodomains, and the generation of additional uncovered substrate areas [see Fig. 1(d)]. The line profile along the line across the phosphorus island in Fig. 1(d) is shown in the inset, indicating that the height of the phosphorus island is 3.1 Å. On the Ag(111) surface uncovered by phosphorus after annealing, many similar small domains with heights of 0.7 Å, which is equal to the value obtained by subtracting 2.4 Å from 3.1 Å, are observed [see Fig. 1(d)]. Considering that the step height of Ag(111) is 2.4 Å, we conclude that the small domains of lower height are blue phosphorene on the lower step of the substrate. That is to say, after annealing, some Ag atoms on the surface layer are removed, and the phosphorus atoms adsorb on the exposed Ag step, resulting in the presence of blue phosphorene on different steps of the Ag(111). When the substrate temperature is increased to 480 K, the phosphorus atoms are desorbed from the substrate completely, generating a clean Ag(111) surface.

To eliminate defects and improve the quality of the phosphorus films, phosphorus atoms were then de-

posited on Ag(111) surface at a higher substrate temperature (420 K). The STM image shown in Fig. 1(e) indicates that the phosphorus film obtained in this manner covers the entire Ag(111) surface. A magnified view of the STM image presented in Fig. 1(f) shows that the phosphorus film consists of fascinating uniform nanodomains that tessellate the Ag surface so as to completely cover it.

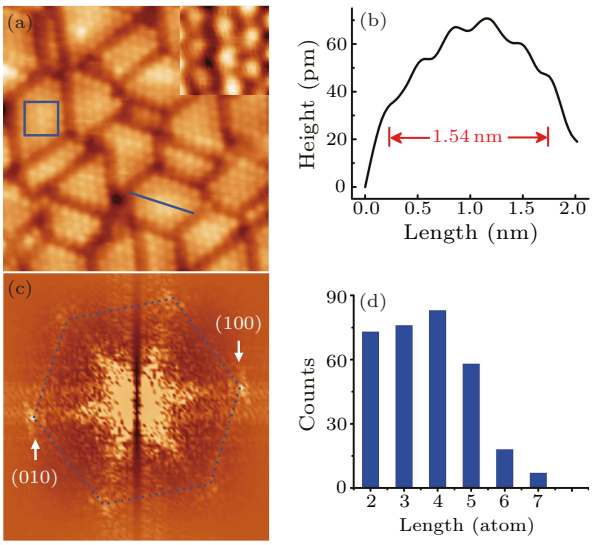

Fig. 2. (a) High-resolution STM image (8 nm×8 nm, sample bias = −1 V, I_t = 0.1 nA) of monolayer blue phosphorene on Ag(111) reveals the structure of the nanodomains. Inset: magnified view of the STM image (1 nm × 1 nm, sample bias = −1 V, I_t = 0.1 nA) of the area marked by the blue square. (b) Line profile along the blue line in (a). (c) Result of the FFT of the image shown in (a), with low frequencies partially cut off so as to highlight the six spots. (d) Statistics of the edge length of nanodomains. The x-coordinate represents the number of bright spots in the phosphorene clusters.

To confirm the formation of blue phosphorene, it is necessary to determine the atomic structure of the phosphorus film and the arrangement of the nanodomains. The high-resolution STM topographic image shown in Fig. 2(a) reveals that the phosphorus domains with well-defined geometries are predominantly hexagonal and trapezoid-shaped. The number of triangular-shaped phosphorus domains is slightly lower compared to the trapezoid-shaped and hexagonal-shaped domains. All of the domains consist of hcp bright spots, and the edges of the domains are oriented along the highest symmetric crystallographic orientations of the Ag(111) substrate. The fast Fourier transformation of the STM image [Fig. 2(c)] shows one set of six spots with C_6 symmetry, indicating that all of the domains have a common 1×1 lattice, in contrast to the 5×5 superstructure of phosphorus on Au(111) found in Ref. [37]. The line profile along the line across one domain [Fig. 2(b)] shows that the average lattice constant can be determined as 3.08 Å. This is considerably smaller than the theoretical lattice constant for free-standing blue phosphorene (3.28 Å), and is incommensurate with the lattice of Ag(111) (2.88 Å).[31] Considering these results, together with the observation that the spots in the center of the domains are brighter than those at the edges, we conclude that the as-grown phosphorus domains are distorted blue phosphorene clusters, compressively strained by as much as 6.4% due to the large lattice mismatch with the Ag(111) substrate. As a result, the blue phosphorene cannot spread over the entire surface, but can only survive over the distance of several lattice constants. We performed statistical analysis on the edge length of the phosphorus domains, and the result is shown in Fig. 2(d), in which the edge with four spots are the most favored. Thus, our preliminary conclusion is that a phosphorus film, consisting of distorted clusters of blue phosphorene 1×1 lattice, forms on the Ag(111) surface.

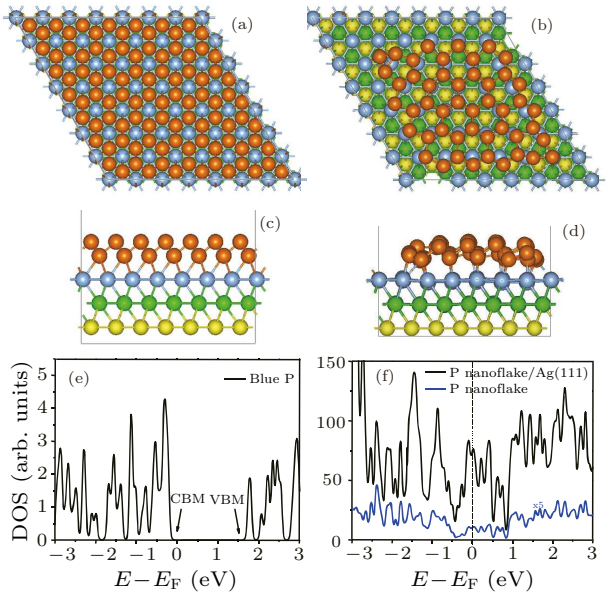

Fig. 3. [(a), (c)] Top and side views of infinite blue phosphorene monolayer stacked on Ag(111) optimized by DFT: lower-buckled phosphorus atoms are located at the fcc sites of Ag(111). [(b), (d)] Top and side views of optimized structures of a 4 × 4 blue phosphorene domain, adsorbed on Ag(111). Color codes: red sphere, phosphorus atoms; blue sphere, Ag atoms in the first layer; green spheres, Ag atoms in the second layer; yellow spheres, Ag atoms in the third layer. (e) Calculated PDOS of free-standing infinite blue phosphorene monolayer. (f) Calculated PDOS of blue phosphorene nanoflakes stacked on Ag(111).

In the theoretically predicted model of blue phosphorene, phosphorus atoms are arranged in a buckled honeycomb structure, in which each unit cell contains two inequivalent atoms.[33] Once blue phosphorene is adsorbed on the substrate, the interaction between the unsaturated P atoms and the Ag substrate should influence the stacking configuration of the phosphorene adlayer on the Ag(111). Therefore, we performed first-principles calculations based on this system. The calculations were performed using the Vienna *ab initio* simulation package (VASP) on the framework of density functional theory (DFT).[43–46] The Ag and P were described via projector augmented wave (PAW) potentials.[47] The exchange-correlation interactions of electrons were described via the PBE function.[48] The plane-wave cut-off energy was set to 260 eV. The energy convergence criterion was 10^{-5} eV, and the con-

vergence criterion of force was 0.05 eV/Å for each ion. A 7×7 slab model was used to simulate the Ag(111) surface, consisting of three atomic layers with 147 Ag atoms. A 4×4 nanoflake of blue phosphorus was then set onto the surface for the purpose of geometric optimization. As this was a large cell ($a = b = 20.22$ Å, $c = 20$ Å), only the Γ point was sampled in all calculations to reduce the computational cost. For an infinite blue phosphorene monolayer adsorbed on Ag(111), the calculation results indicate that the lower-buckled phosphorus atoms are located at the fcc sites of the Ag(111) [see Figs. 3(a) and 3(c)]. Since the statistical analysis of the edge length of blue phosphorene domains gives $4a$ (where a is the lattice constant of blue phosphorene) as the most probable domain width, we investigated the relaxation process of a 4×4 blue phosphorene cluster with one atomic layer. Subsequent to relaxation, the lattice of blue phosphorene is largely distorted along the edges of this blue phosphorene domain, while the inner part can effectively maintain the unreconstructed honeycomb structure, as shown in Figs. 3(b) and 3(d). The distances between the P atoms and the Ag surface are in a range from 2.10 Å to 3.85 Å. To estimate the stability of the distorted blue phosphorene nanoflake on Ag(111), we calculated the average binding energy $E_{\rm b}$, defined as follows:

$$E_{\rm b} = (E_{\rm tot} - E_{\rm sub} - nE_{\rm BP})/n,$$

where $E_{\rm tot}$ denotes the total energy of the adsorption model, $E_{\rm sub}$ is the energy of Ag(111) substrate, $E_{\rm BP}$ is the energy of a phosphorus atom in free standing blue phosphorene, and n is the number of P atoms in the adsorption model. Under such definitions, $E_{\rm b}$ is -0.12 eV (negative for exothermic) for a phosphorus atom in the nanoflake on Ag(111), while it is $+0.42$ eV (positive for endothermic) for a phosphorus atom in compressive blue phosphorene on Ag(111) to match the lattice constant. This indicates that the two-dimensional blue phosphorene layer requires some degree of distortion to release the compressive strain, e.g., breaking some P–P bonds and forming P–Ag bonds. This result agrees well with the experimental observation that the inner blue phosphorene domains are brighter than those on the edges in the STM image. Thus, according to DFT calculations, the strain induced by the large lattice mismatch results in the formation of small blue phosphorene 1×1 clusters on the Ag(111) surface.

It has been reported that a bandgap can be engineered via a substrate-induced superlattice of phosphorene on the Au(111) surface.[49] Strain effects have also been reported to play an important role in the superconductivity of black phosphorene.[50] The blue phosphorene clusters on the Ag (111) substrate can also be regarded as quantum dots, forming natural mixed-dimensional heterostructures. Modulating the interfacial electron transfer by controlling the size of the quantum dots is anticipated to reveal exceptional properties.[51] Based on the data from the Bader analysis, 1.24 electrons are transferred from the Ag(111) to the phosphorus nanoflake. The PDOS also shows that the nanoflake has continuous states around the fermi level [see Fig. 3(f)], in contrast to the free-standing blue phosphorene with a gap [Fig. 3(e)]. It is expected that the unique size distribution of the clusters will provide a novel method for modulating the electronic structure of blue phosphorene.

Although Ag(111) has the same lattice constant as the Au(111) surface (both 2.88 Å), the adsorbed phosphorus atoms on the Au(111) surface prefer to form a 5×5 superstructure commensurate with that of the 4×4 blue phosphorene lattice.[37–39] The most likely reason for this difference between the Au(111) and Ag(111) substrate is that the stronger interactions between phosphorus and the Ag(111) surface drive the P atoms' registry with the Ag lattice. The lower buckled P atoms are strongly bonded with the three Ag atoms in the hollow sites of the substrate, leading to the formation of blue phosphorene clusters on the Ag(111) surface. On the other hand, due to the strong interactions between the P atoms and the Ag substrate atoms, a high-quality phosphorus film, consisting of 2D blue phosphorene clusters can be formed on the Ag(111) substrate.

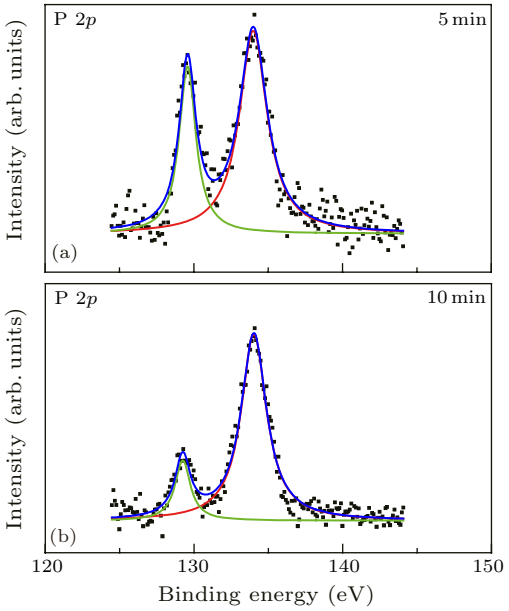

Fig. 4. XPS results for monolayer phosphorus film on Ag(111) on exposure to air. P $2p$ core level spectra of the phosphorus film on Ag(111) surface exposed to air for 5 min (a) and 10 min (b). Blue curves correspond to original data. The peak in the P $2p$ spectra splits into two peaks of 129.5 eV and 134 eV, indicated by the green and red fitting lines, respectively.

XPS measurements were performed to analyze the chemical composition of the phosphorus film on exposure to air. Figures 4(a) and 4(b) show the phosphorus $2p$ core level spectra of the phosphorus film exposed to air for 5 min and 10 min, respectively. The peak in the phosphorus $2p$ spectra splits into two peaks of 129.5 eV and 134 eV that are indicated by the green and red fitting lines in Fig. 4, respectively. The peak at 129.5 eV is redshifted by 0.4 eV compared to the pristine phosphorus $2p$ peak of the clean bulk black

phosphorus (129.9 eV),[39] and can be considered as the pristine spectrum of the blue phosphorene clusters on the Ag(111) surface, while the peak at 134 eV is assigned to the signal of oxidized phosphorus. The relative intensity of the latter peak clearly increases with the extension of the exposure time from 5 min to 10 min, indicating that the phosphorus films are easily oxidized upon exposure to air. However, the oxidation is not very rapid. As a result, the 2D clusters can be capped with a buffer layer for further investigations in the ambient environment.

In summary, a monolayer phosphorus film has been successfully grown via MBE on an Ag(111) surface. The film consists of regularly arranged clusters of blue phosphorene with buckled 1×1 lattice, which is quite different from that grown on an Au(111) surface. The lattice mismatch and relatively strong interactions between phosphorus and the Ag(111) surface, which cannot be overcome by the thermo-dynamical effect, induce the formation of the cluster-structural 2D blue phosphorene. A more detailed investigation of the growth behavior of phosphorus on Ag(111) surface may provide guidance to finding appropriate substrates for the realization of desired phosphorus nanostructures. The XPS measurements verify the air instability of phosphorene clusters, providing useful guidance for further study. Due to the combination of the exotic electronic properties of blue phosphorene and clusters with tunable size and morphology, this system may prove to be an interesting platform for investigations of novel quantum effects in blue phosphorene.

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