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► To cite this version:

Wei Zhang, Hanna Enriquez, Andrew Mayne, Azzedine Bendounan, Ari Seitsonen, et al.. First steps of blue phosphorene growth on Au(1 1 1). Materials Today: Proceedings, 2021, 39, pp.1153-1156. 10.1016/j.matpr.2020.07.197 . hal-03329226

HAL Id: hal-03329226

<https://hal.science/hal-03329226>

Submitted on 10 Mar 2023

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First steps of blue phosphorene growth on Au(111)

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Abstract

Blue phosphorene (blue-P) has attracted considerable attention due to its potential applications in optical and electronic devices. However, its synthesis has remained a challenge. Here, we report an experimental investigation of the first steps of blue-P growth on Au(111) surface by molecular-beam epitaxy. The structure was characterized by *in situ* low temperature scanning tunneling microscopy, low-energy electron diffraction, combined with density functional theory calculations. We reveal two-dimensional (2D) phosphorus clusters (P-clusters) formed on surface at 150°C, where the most prevalent structure of P-clusters is composed of triangles with six protrusions. We also demonstrate the transformation of these P-clusters into a single layer of blue-P after post-annealing at 260°C. Our observation of the growth process is a necessary step for exploring the growth mechanisms further.

Keywords: phosphorene; two-dimensional materials; low temperature scanning tunneling microscopy; molecular beam epitaxy

1. Introduction

After the successful production of graphene [1,2], an extensive research effort has been put into investigating other two-dimensional (2D) materials, notably silicene [3-5], germanene [6,7], borophene [8,9], transition metal dichalcogenides [10-12] and phosphorene [13-16]. Phosphorene can be viewed as a single layer of black phosphorus, has a tunable gap ranging from 0.3 eV [17-19] in the bulk to 1.5 eV [20] in a monolayer. Since black phosphorus layers are held together by the weak van der Waals interaction, much like graphene, black phosphorene (black-P) could be obtained by mechanical exfoliation and liquid exfoliation methods [21,22]. Based on its suitable band gap, few-layer black-P transistors have been demonstrated with a high hole mobility of 1000 cm² V⁻¹ s⁻¹ and drain current modulation on the order of 10⁵ [23]. These results indicate that phosphorene is a promising candidate for next-generation electronic devices.

Recently, a previously unknown phase of phosphorus has been predicted by *ab initio* density functional theory calculations [24], named blue phosphorus, which is nearly as stable as black phosphorus. Unlike black phosphorus, which exhibits a strongly puckered structure, blue phosphorus arranges in a more flat honeycomb structure. The benefit of blue phosphorus is its wide bandgap. The single layer of blue phosphorus, called blue phosphorene (blue-P), should be easily obtained through the exfoliation of a 3D crystal, due to the weak interlayer interaction, however, bulk blue phosphorus does not exist in nature. Therefore, developing methods for blue-P growth is a necessary step for further exploring its unique properties and potential applications. The blue-P on Au(111) substrate has been successfully synthesized using molecular-beam epitaxy (MBE) methods [25-30]. However, there are many issues that still remain to be clarified for blue phosphorene on Au(111) surface.

Here, we report on the first stages of phosphorene growth on Au(111), through the combination of *in situ* low temperature scanning tunneling microscopy (LT-STM), low-energy electron diffraction (LEED), and density

functional theory (DFT) calculations. We reveal well-defined 2D P-clusters formed on surface at 150°C, where the most prevalent structure of the P-clusters is composed of triangles with six protrusions, which then transform into a single layer of blue-P with the (5×5) periodicity at 260°C.

2. Experimental

2.1. Epitaxial growth of blue phosphorene on Au(111)

The Au(111) surface was prepared by several cycles of Ar⁺ sputtering. The beam energy was 650 eV at 1.3×10^{-5} mbar, followed by post-annealing at a temperature of 500°C for 40 minutes. The sample was prepared in an ultrahigh-vacuum chamber with a base pressure better than 3.0×10^{-10} mbar, in which phosphorus was evaporated on Au(111) surface from an alumina crucible loaded with bulk black phosphorus. The Au(111) substrate was held at 150°C during the deposition.

2.2. Characterization

During the phosphorus deposition, the surface structure and the chemical composition were systematically monitored by *in-situ* Auger electron spectroscopy (AES) and LEED, which were performed at room temperature. The STM experiments were carried out in an Omicron LT-STM for surface characterization, operated at 78 K. The base pressure was better than 3.0×10^{-11} mbar. All the images were obtained under constant current mode. Tungsten tips were made by electrochemical etching.

2.3. Computational method

The density functional theory (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) using version 5.4.1 [31-33], which implements the projector augmented wave (PAW) method [34,35], and the GGA-PBE functional [36]. We used a plane-wave energy cutoff of 255 eV, and the Brillouin zone was sampled using a $4 \times 4 \times 1$ k-point mesh. The model is composed of 5 layers of gold atoms forming the Au(111) structure, and a 15-17 Å of vacuum space placed vertically between slabs. The structure was relaxed until the force criterion was 0.01 eV/Å.

3. Results and discussion

Fig. 1 shows filled state STM images of the initial stage of epitaxial growth of phosphorus on Au(111) at 150°C with phosphorus coverage of ~ 0.5 ML. Fig. 1a shows the triangular-shaped P-clusters predominantly formed on Au(111), meanwhile irregular-shaped P-clusters are also observed in a few small areas. Fig. 1b displays a high-resolution STM image where the different sized of P-clusters are highlighted by the black circles. After careful inspection of Fig. 1b, it was found that the most prevalent structure of P-clusters on Au(111) is composed of triangles with six protrusions. A similar structure has been reported [25].

In Fig. 2a, the deposition of phosphorene yields a (5×5) superstructure with respect to the Au(111) surface after post-annealing at 260°C, which is consistent with previous reports [25-29]. Fig. 2b depicts the topography of the (5×5) phosphorene formed on Au(111) surface, revealing a flower-like shape with a long-range ordered structure. Compared with the growth at 150°C (Fig. 1b), we observe that each triangle is composed of bright trimers after post-annealing the phosphorus layer on Au(111) at 260°C. Fig. 2c shows the line profile along the blue line in Fig. 2b, indicating a periodicity of bright trimers of 1.44 nm, which is equal to five times the lattice constant of the Au(111) surface ($5 \times 0.288 \text{ nm} = 1.44 \text{ nm}$), in good agreement with the diffraction result. To understand these experimental findings, we performed DFT calculations. A structural model of phosphorene on Au(111) surface was proposed, based on the LEED and STM measurements. We can know that the Au (5×5) lattice parameter matches with the (4×4) unit cell of phosphorene, resulting in the formation of a stretched blue phosphorene sheet on Au(111) surface with a buckled honeycomb arrangement. In addition, our experimental STM observations show that 3 extra P atoms per triangle need to be added on top. Fig. 2d shows the details of the (5×5) blue phosphorene superstructure. The unit cell (the blue rhombus) consists in 38 phosphorus atoms situated in different position on Au(111) surface, where three atoms are adsorbed on top of the triangle, which is remarkably consistent with the

STM observations. This shows the system prefers to form clusters rather than a contiguous 2D sheet under these conditions.

4. Conclusion

We have reported on an early stages of blue-P growth on Au(111) surface using the MBE methods. As demonstrated by the combined *in situ* STM, LEED and DFT calculations, we found a 2D P-clusters formed on surface at 150°C, where the most prevalent structure of P-clusters is composed of triangles with six protrusions. After post-annealing the phosphorus layer on Au(111) at 260°C the blue-P are mainly composed of triangles with three protrusions in good agreement with the DFT calculation. Our results help us to understand the mechanism of epitaxial growth of blue-P.

Acknowledgements

W. Zhang would like to thank the China Scholarship Council (CSC) for the Ph.D. financial support (scholarship).

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Figure Captions

Fig. 1. Filled state STM images corresponding to P-clusters on Au(111). (a) Large-scale image of P-clusters on Au(111) ($U = -1.6$ V, $I = 1.0$ nA). (b) High-resolution STM image of P-clusters on Au(111), revealing different size P-clusters highlighted in black circles ($U = -1.5$ V, $I = 1.0$ nA).

Fig. 2. (a) LEED pattern recorded at 57 eV for blue-P on Au(111) after post-annealing at 260°C. The (1×1) spots of Au(111) substrate and (4×4) blue-P are highlighted by black and red circles, respectively. (b) STM topography of phosphorene on Au(111) after post-annealing at 260°C ($U = -250$ mV, $I = 1.34$ nA). (c) Profile taken along the blue line in (b), revealing the distance between two phosphorus trimers of 1.44 nm. (d) The DFT model systems with atomic resolution image of blue-P on the (5×5) Au(111) ($U = -100$ mV, $I = 2.60$ nA). Unit cell of (5×5) phosphorene includes two trimers of phosphorus atoms, which is labeled by the blue rhombus.



