

Morphology Evolution of Flat Blue Phosphorene on Cu(111) with Increasing Phosphorus Coverage

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Blue phosphorene (Blue P) is a phosphorous allotrope with buckled honeycomb lattice, and it is predicted to possess excellent electronic properties. The synthesis of Blue P, however, has been a challenging task. Here, we report the growth of macroscopically continuous Blue P monolayer on Cu(111) substrate, and a rich surface morphological evolution with increasing P exposure and sample temperature, as observed with *in situ* scanning tunneling microscopy and spectroscopy (STM/STS). Nearly straight stripes along $[11\bar{2}]$ and equivalent directions (with a $12\times\sqrt{3}$ rectangular supercell) are formed first, followed with a $(\sqrt{3}(111)\times\sqrt{3}(111))R25.3^\circ$ spiral hexagonal superstructure when the sample is held at ~ 470 K during P exposure. With further P exposure at higher sample temperatures, non-spiral hexagonal superlattices of smaller periods were observed. These observed patterns can be explained as a tensile-stressed flat Blue P honeycomb layer bound strongly with a compressed Cu atomic layer formed on Cu(111), with the flat Blue P honeycomb lattice matching with the $(\sqrt{3}\times\sqrt{3})R30^\circ$ of the compressed Cu atomic layer. Besides the intrinsic tendency similar to the herringbone reconstruction on Au(111) surface, the formation of the compressed Cu surface layer is facilitated by the compressive stress applied by the flat Blue P layer, as well as electron transfer from Cu to the Blue P. With these driving forces, the areal atomic density in the compressed Cu layer increases from the bulk value by a factor of $\sim 8\%$ in the stripe phase to more than 15% in the non-spiral hexagonal phase. As the P-P bond length approaches its optimal value, however, the binding strength between the Blue P and Cu layers weakens, which reduces the compressive stress on the Cu surface. Subsequently, certain amount of Cu atoms are released from the compressed layer, which may form small islands on the surface, as observed in some regions of the sample.