Graphene Growth on Palladium (111)

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Abstract:

Growth of graphene films on a palladium (111) (Pd(111)) surface has been achieved by surface segregation of carbon. The resulting films were characterized by Auger electron spectroscopy (AES), atomic force microscopy (AFM), and scanning tunneling microscopy (STM). A growth procedure was found that results in the formation of large-scale (> 1 mm^2), single layer graphene on the Pd(111) surface. Graphene islands were found to follow the Stranski-Krastanov growth mode. In most cases, graphene islands imaged with a scanning tunneling microscope (SEM) exhibit a Moiré pattern with a periodicity of 2.3 ± 0.1 nm, consistent with the [$2\bar{1}\bar{1}0$] direction in graphene being aligned with the [$1\bar{1}0$] direction of the Pd(111) surface.

Introduction:

Graphene, a two-dimensional crystalline sheet of sp^2-bonded carbon atoms arranged in a honeycomb lattice, has garnered the interest of many researchers in recent years due to its remarkable structure and electronic properties [1]. These unique properties have sparked interest in the practical applications of graphene, from its use in electric batteries to graphene-based electronics [1]. For many of these applications, the fabrication of large-area, high-quality, single-layer graphene films is essential to their success.

Several methods of fabrication that aim to satisfy these requirements exist, each with advantages and disadvantages. The results reported below are based on a graphene fabrication method that operates by the segregation and precipitation of carbon from the bulk of a metal to the metal surface [2]. The objective of the work presented here was to determine a growth procedure capable of producing large-scale, single layer graphene on a Pd(111) surface.

The precipitation of carbon on carbon-doped metal surfaces has been studied by Hamilton and Blakely [3]. Figure 1 shows their qualitative findings of carbon coverage versus the temperature to which the metal sample was heated. This figure shows that there is an intermediate temperature range in which single-layer graphene is formed on the metal surface.

Experimental Procedures:

Graphene films were grown by a surface segregation and precipitation process on a carbon-doped Pd(111) surface. The Pd sample was 2 mm thick and had a 10 × 3 mm area available for graphene growth. The substrate was doped to 0.5 at % carbon by a solid-state diffusion method in which the metal surface was covered in high-purity graphite powder and annealed at 800°C for 200 hours under ultra-high vacuum (UHV) conditions.

To produce a graphene layer on the Pd(111) surface, the carbon-doped metal sample was heated by electron back-bombardment under UHV conditions. The temperature and duration of the heating was varied depending on the desired growth conditions. The sample temperature was monitored with an optical pyrometer. After characterization, the Pd(111) surface was cleaned by argon ion sputtering, followed by heating to 900°C to dissolve all remaining surface carbon into the bulk. The cleaned sample was then ready to undergo another growth procedure.

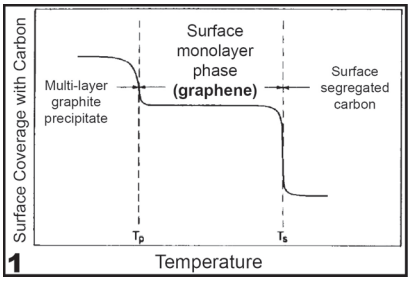

Figure 1, left: Qualitative dependence of carbon coverage on growth temperature as determined by Hamilton and Blakely [3].

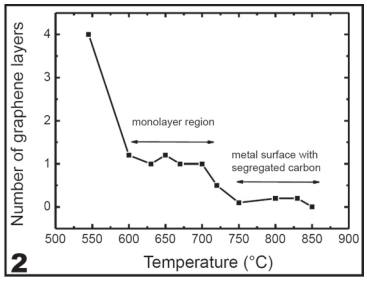

Figure 2, right: Dependence of carbon coverage on growth temperature.

Resulting graphene films were characterized with a scanning Auger microscope (ULVAC-PHI model SAM650) and a STM at room temperature in UHV conditions. Films were also examined with an AFM (SPA300 AFM) at ambient conditions.

Results and Conclusions:

Using AES, the growth of graphene on the Pd(111) surface was characterized over a range of growth temperatures. Figure 2 illustrates the dependence of the thickness of the graphene film on the growth temperature. This result clearly resembles the results of Hamilton and Blakely [3] from Figure 1.

In addition to this characterization, a growth procedure was found that resulted in large-area, single layer graphene films. This procedure involved heating the sample to 720°C for 10 minutes. Also, before growth, the sample was heated to 900°C to dissolve surface carbon. Unlike the typical growth procedure, argon ion sputtering was not used to clean the surface before growth. The resulting graphene film was determined to be a single layer by AES and covered almost the entire Pd(111) surface.

For growth temperatures at and below 600°C, the formation of three-dimensional, multi-layer graphene islands was observed. These islands formed on top of a single graphene layer, providing evidence that this mechanism of graphene growth follows the Stranski-Krastanov growth mode.

STM images of graphene islands revealed a clear superstructure with six-fold symmetry and a periodicity of 2.3 ± 0.1 nm (see Figure 3). This superstructure has been interpreted as a Moiré pattern resulting from the superposition of the graphene lattice on the palladium surface [4], and the value of the pattern's periodicity indicates that the $[2\bar{1}\bar{1}0]$ direction in graphene is parallel to the $[1\bar{1}0]$ direction of the Pd(111) surface [4]. This orientation implies that the growth of graphene on the Pd(111) surface is nearly epitaxial.

All graphene islands examined with STM and AFM were located adjacent to or spanning a step edge of the palladium surface (see Figure 4), suggesting that graphene islands preferentially nucleate at step edges.

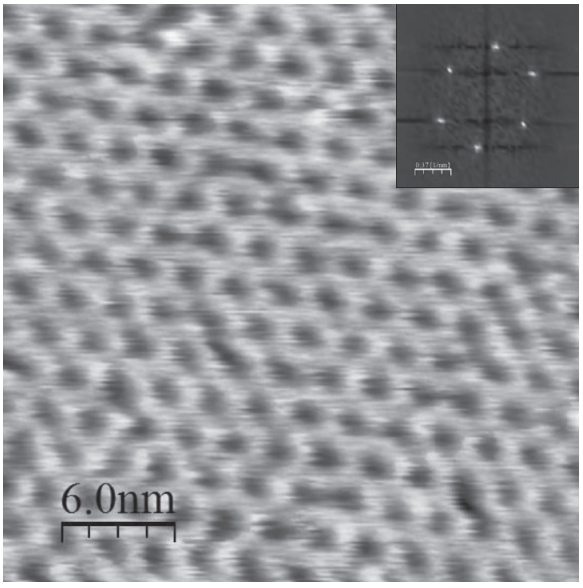

Figure 3: An STM image of a graphene island formed from heating the sample to 700°C for 10 minutes (Inset: Fourier transform of the image).

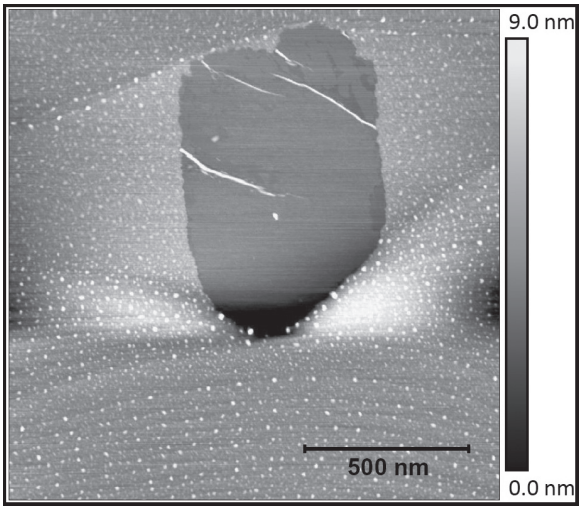

Figure 4: An AFM image of a small graphene island that is adjacent to a step in the Pd(111) surface. Carbon nanowires can be seen on the graphene surface.

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