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ARTICLE

Growth Behavior Evolution of Al_2O_3 Deposited on HOPG by Atomic Layer Deposition

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Abstract: Al_2O_3 dielectrics were fabricated on highly ordered pyrolytic graphite (HOPG) by atomic layer deposition (ALD) and the effects of growth temperatures and number of ALD cycles on growth behaviors were studied. It is found that Al_2O_3 preferentially grows along the step edges which promote the formation of Al_2O_3 nanowires at the initial stage. Al_2O_3 nanowires can exist after 100 ALD cycles at 50, 150, and 200 °C, but discontinuous Al_2O_3 thin films rather than nanowires are evidenced at 100 °C. Moreover, the Al_2O_3 layers evolve into continuous thin films with increasing number of ALD cycles. It suggests the growth behavior undergoes a transition from three-dimensional mode to quasi two-dimensional mode with increasing number of ALD cycles. The rates of transition and lateral growth are dependent on growth temperatures. Raman spectra indicate that HOPG maintains undamaged and greatly reserves its original properties after the deposition of Al_2O_3. The results are of great significance to the fabrication of high-quality dielectric layers on graphene as well as the related devices.

Key words: Al_2O_3; HOPG; atomic layer deposition; growth behavior

With the incredible shrinking of the transistor dimensions described by Moore's law, the scaling of planar Si transistors is close to the limit, and transistors with sub-10 nm channel lengths are coming within the next few years[1]. Owing to the short-channel effects, the electrical properties of transistors with sub-10 nm channel lengths become unstable[2]. Therefore, lots of researches have been conducted into the subject. Recently, graphene as the nano-electronics has attracted significant attentions because of its extraordinary electrical and physical properties, and great efforts have been made for the applications of top-gated graphene field effect transistors (GFETs)[3-5]. High-*k* dielectric layer, e.g., Al_2O_3, HfO_2, and ZrO_2, plays an important role in the GFETs[6,7], and therefore, the implementation of high-*k* dielectrics on graphene needs to be solved urgently.

Highly-oriented pyrolytic graphite (HOPG) possesses a layered hexagonal carbon net structure stacked periodically along the *c*-axis by weak π-π bonded interaction between neighbour layers[6,8]. Each graphene layer maintains an atomically flat surface with sharp step edges, and the fresh surfaces can be used to imitate the ideal graphene surfaces. Atomic layer deposition (ALD) is regarded as an excellent technique to acquire thin films with good conformality and controllable film thickness owing to the self-limiting growth mechanism[9-11]. In fact, ALD has already been chosen for the fabrication of gate oxides in the microelectronic industry[8]. However, these oxides on pristine graphene by ALD are hindered due to the lack of dangling bonds in the graphene plane[6-8,12]. Lots of effective studies, including covalent and noncovalent functionalization of graphene, have been conducted[13-17]. It is well known that the nucleation of high-*k* oxides always occurs at the defects or dangling bands. However, the evolution of growth mechanism for ALD high-*k* dielectrics on the graphene is rarely reported.

In this paper, Al_2O_3 with different numbers of ALD cycles were deposited on HOPG substrates. The effects of

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growth temperatures and number of ALD cycles on growth behaviors were discussed. A schematic model based on the lateral growth was put forward to understand the evolution of Al_2O_3 growth behavior on HOPG.

1 Experiment

HOPG samples, grade A, were prepared by peeling off several top layers of graphite using scotch tape. After freshly cleaved, the samples were transferred into a horizontal flow-type hot-wall ALD system immediately, and then preheated for 20 min at 250 °C to remove the moisture and other impurities on the surface. Trimethylaluminum (TMA) and the H_2O_2 solution (40%) were used as the metal precursor and the oxidant, respectively. Nitrogen (99.9995%) with a local pressure of 33.3 Pa was used as the carrier and purging gas. The deposition temperatures were set at 50, 100, 150, and 200 °C. Each ALD reaction cycle was set as one dose of TMA (1 s) with a 30 s purge and one dose of H_2O_2 (0.2 s) with another 60 s purge. 100, 200, and 300 ALD cycles Al_2O_3 were prepared at each temperature.

The surface morphologies were characterized by atomic force microscopy (AFM, Bruker Dimension Icon) in tapping mode. The morphologies of Al_2O_3 on HOPG was investigated by the field emission scanning electron microscope (SEM, FEI Quanta 600 FEG) operated at 5 kV. Raman spectroscopies were obtained by the Horiba HR 800 spectrometer with an excitation wavelength of 633 nm.

2 Results and Discussion

2.1 Effect of growth temperature on morphologies of ALD-Al_2O_3 on HOPG

Fig.1 shows topographic AFM images of the freshly exfoliated HOPG surface with scanning areas of 1 μm×1 μm and 10 μm×10 μm. As shown in Fig.1a, the exfoliated HOPG possesses atomically smooth planes with sharp step edges. The step height is equivalent to few monolayers of graphene. Each plane has an elongated structure with two straight edges, and few defects can be detected, shown in Fig.1b. As previously reported[8, 18], the dangling bands are generated along the edges after the mechanical exfoliation, in which the chemical activities are richer than that in the inert planes.

Fig.2 shows SEM images of 100 ALD cycles Al_2O_3 deposited on HOPG at different temperatures. As shown in Fig.2a, Al_2O_3 nanowires are formed with a width of 24~40 nm (shown in Fig.3a) at 200 °C. Generally, the dangling bonds at the step edges provide the nucleation sites for the initial ALD growth. Therefore, Al_2O_3 grows preferentially along the step edges rather than on the inert planes. As a result, the nanowires appear gradually[6,8]. In addition, numerous protrusions appear around the nanowires duo to the initial lateral growth. Further, the multi-branched nanowires are achieved at 150 °C (Fig.2b), and the width of nanowires slightly decreases to 8~24 nm (Fig.3b). The

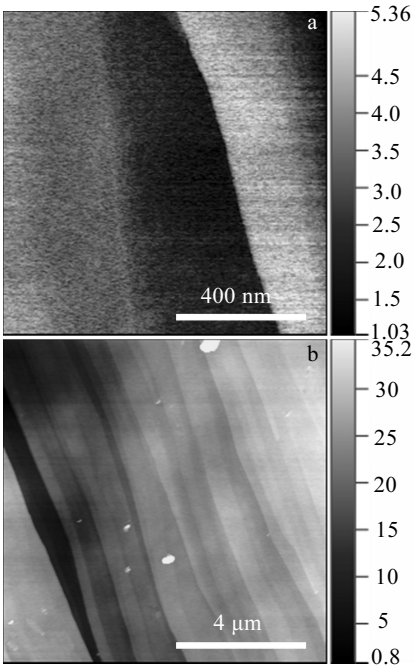

Fig.1 AFM images of fresh HOPG with scanning area of 1 μm × 1 μm (a) and 10 μm × 10 μm (b)

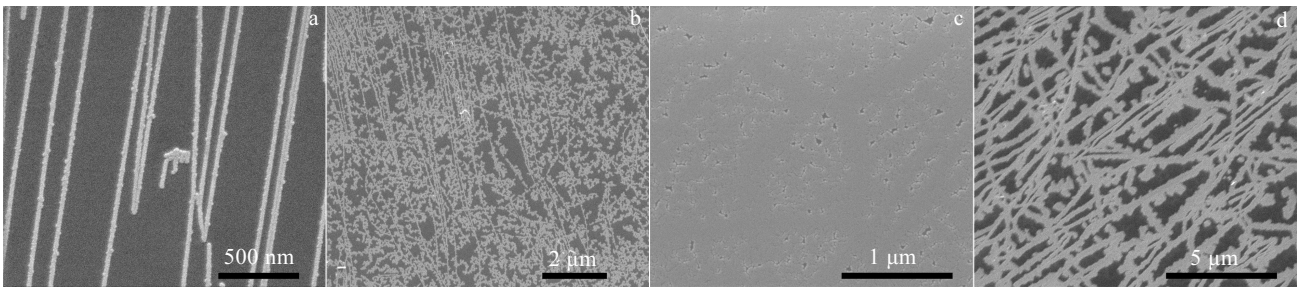

Fig.2 SEM images of 100 ALD cycles Al_2O_3 deposited on HOPG at 200 °C (a), 150 °C (b), 100 °C (c), and 50 °C (d)

multi-branched structure may be attributed to the increasing lateral growth rate duo to the decreasing desorption of the precursors at 150 °C[19]. Moreover, Al_2O_3 grows into a discontinuous film at 100 °C (Fig.2c), indicating that the growth behavior undergoes a transition from three-dimensional (3D) mode to quasi two-dimensional (2D) mode. Because of the decreasing reaction rate of the precursors with growth temperature, the nanowires reappear and interlace each other at 50 °C (Fig.2d), and the width of the nanowires increases to 125~325 nm (Fig.3c), indicating the growth behavior transforms from quasi 2D mode to 3D mode with decreasing temperature from 100 to 50 °C.

Fig.4 shows the width distribution of steps on fresh HOPG, and the spacing of Al_2O_3 nanowires. They exhibit a similar distribution pattern with varying widths of 100~400 nm, which indirectly confirms that Al_2O_3 nanowires preferential grow at the step edges. It also illustrates that step edges with a higher chemical reactivity are conducive to the nucleation in the initial ALD growth[6].

2.2 Effect of ALD cycles on morphologies of ALD-Al_2O_3 on HOPG

Fig.5 shows SEM images of 200 and 300 ALD cycles Al_2O_3 deposited at 200 and 100 °C. Al_2O_3 nanowires are formed along the step edges for 100 ALD cycles at 200 °C declines (Fig.2a), but the number of Al_2O_3 nanowires sharply declines and a discontinuous film appears for 200 ALD cycles (Fig.5a). The porosity factor is approximately 19.4%. The film gradually tends to be continuous with the porosity factor decreasing to 8.6% for 300 ALD cycles (Fig.5b). However, a discontinuous film without nanowires is formed only for 100 ALD cycles at 100 °C (Fig.2c), and the porosity factor is as low as 4.7%, indicating that the growth behavior is highly affected by growth temperatures. When the number of ALD cycles is elevated to 200, it slightly decreases to 3.7% (Fig.5c). Particularly, the Al_2O_3 turns into a continuous film for 300 ALD cycles (Fig.5d). It suggests that the growth behavior undergoes a transition from 3D mode to quasi 2D mode with increasing number of ALD cycles.

A schematic model was put forward to describe the evolution of growth behavior as shown in Fig.6. At the initial growth stage, Al_2O_3 preferentially grows along the

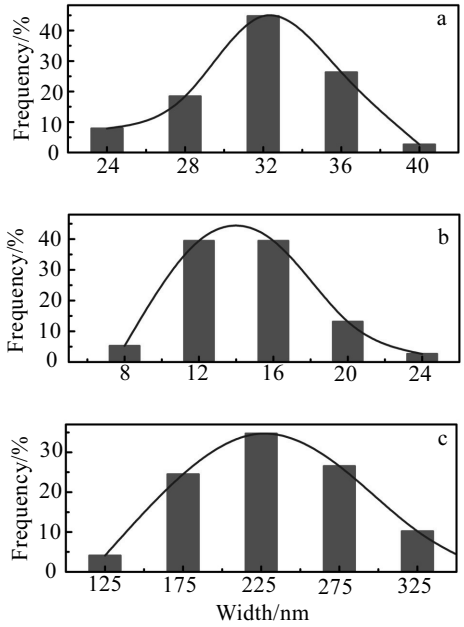

Fig.3 Width distribution of Al_2O_3 nanowires: (a), (b) and (c) corresponding to Fig.2a, 2b and 2d, respectively

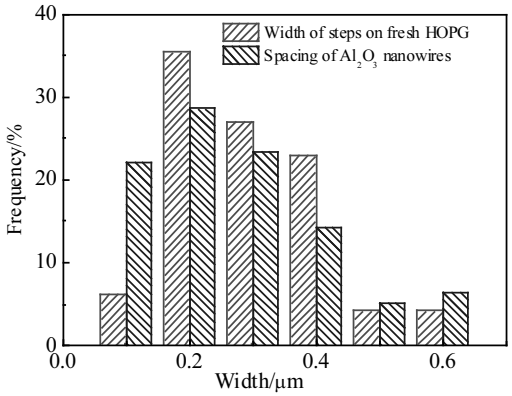

Fig.4 Width distribution of steps on fresh HOPG and the spacing of Al_2O_3 nanowires in Fig.2a

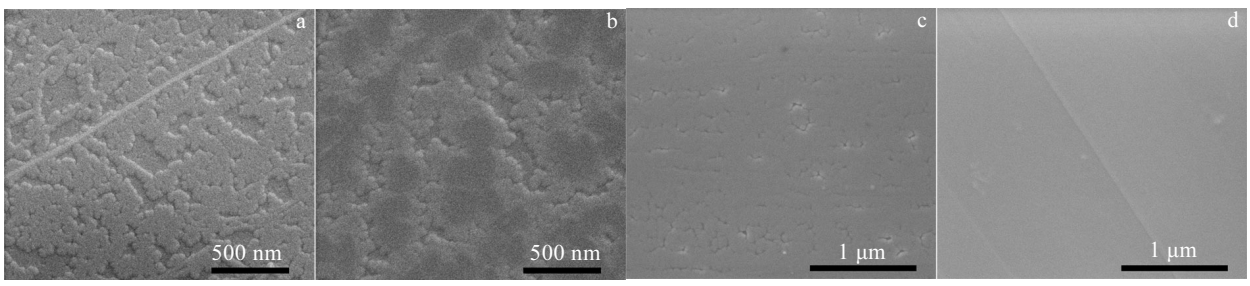

Fig.5 SEM images of Al_2O_3 deposited on HOPG with 200 and 300 ALD cycles at 200 °C (a, b), and at 100 °C, (c, d), respectively

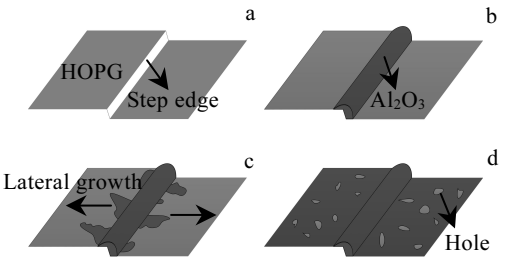

Fig.6 Schematic model of the evolution of Al_2O_3 growth behavior deposited on HOPG: (a) grows along the stap edge, (b) nanowires appear, (c) multi-branched structures emerge and (d) form a continuous film with increasing number of ALD cycles

step edges, and then the nanowires appear (Fig.6b). Owing to the lateral growth, the multi-branched structures emerge around the nanowires (Fig.6c), and then they coalesce to form a continuous film with increasing number of ALD cycles (Fig.6d). On the other hand, as previously reported by Xuan et al.[8], the vertical growth rate generally remains constant, and thereby the surface of Al_2O_3 films can be quite smooth.

2.3 Effect of Al_2O_3 on the structure of HOPG

Raman spectra of HOPG before and after the deposition of Al_2O_3 with 100, 200, and 300 ALD cycles at 200 °C are obtained, as shown in Fig.7. Two main peaks of G and 2D located at 1605 and 2708 cm^{-1} are observed[20]. The intensities of peaks become weaker after the deposition of Al_2O_3, which is in agreement with the previous reports[21]. In addition, D band at 1350 cm^{-1} corresponding to the defects or disorder does not appear either before or after the deposition of Al_2O_3[17], and the positions of the G and 2D band remain unchanged. This indicates that the graphene plane is almost undamaged and greatly reserves its original properties after the deposition of Al_2O_3.

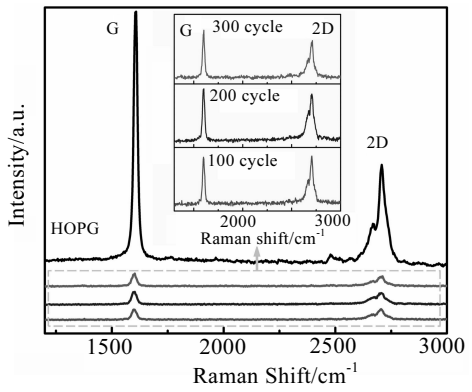

Fig.7 Raman spectra of HOPG before and after the deposition of Al_2O_3 with 100, 200, and 300 ALD cycles

3 Conclusions

1) Al_2O_3 preferentially grows along the step edges which promote the formation of Al_2O_3 nanowires at the initial stage. Al_2O_3 layers can evolve into continuous thin films with increasing number of ALD cycles.

2) The growth behavior undergoes a transition from 3D mode to quasi 2D mode with increasing number of ALD cycles. The rates of transition and lateral growth are dependent on growth temperatures.

3) Raman spectra indicate that HOPG maintains undamaged and greatly reserves its original properties after the deposition of Al_2O_3. The results are of great significance to the fabrication of high-quality dielectric layers on graphene as well as the related devices.

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HOPG 上 ALD 沉积 Al_2O_3 介电薄膜的生长行为研究

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摘　要：采用原子层沉积（ALD）的方法，选择三甲基铝（TMA）和H_2O_2作为反应前驱体，在高定向热解石墨（HOPG）基体上沉积Al_2O_3。系统研究了反应温度和生长周次对Al_2O_3生长行为的影响。研究表明：受HOPG表面饱和成键的影响，Al_2O_3在衬底表面处形核困难，在生长初期主要表现为台阶处择优生长，其形态为线状结构。当沉积100周次Al_2O_3时，其中在沉积温度为50 °C、150 °C和200 °C时呈现为纳米线状结构，而在100 °C时呈现为非连续薄膜。随着生长周次的增加，不同温度下沉积态Al_2O_3都趋于形成连续薄膜，表明其生长行为发生了由三维岛状生长模式向二维平面生长模式的转变。分析认为，生长模式的转变是由纳米线状结构横向生长造成的；横向生长速率主要受生长温度影响。拉曼结果表明：沉积后的石墨烯层结构未受影响，可保留其原有的优越性能。

关键词：Al_2O_3；HOPG；原子层沉积；生长行为

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