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Graphene is a hexagonally bonded sheet of carbon atoms that exhibits superior transport properties with a velocity of 10^8 cm/s and a room-temperature mobility of $>15\,000$ cm^2/V s. How to grow gate dielectrics on graphene with low defect states is a challenge for graphene-based nanoelectronics. Here, we present the growth behavior of Al_2O_3 and HfO_2 films on highly ordered pyrolytic graphite (HOPG) by atomic layer deposition (ALD). To our surprise, large numbers of Al_2O_3 and HfO_2 nanoribbons, with dimensions of 5–200 nm in width and >50 μm in length, are observed on HOPG surfaces at growth temperature between 200 and 250 °C. This is due to the large numbers of step edges of graphene on HOPG surfaces, which serve as nucleation sites for the ALD process. These Al_2O_3 and HfO_2 nanoribbons can be used as hard masks to generate graphene nanoribbons or as top-gate dielectrics for graphene devices. This methodology could be extended to synthesize insulating, semiconducting, and metallic nanostructures and their combinations. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828338]

Recently, the discovery of superior transport properties in mechanically exfoliated graphene sheets or epitaxial graphene grown on SiC substrate has generated enormous interests in academy and industry.[1–4] Graphene is a hexagonal network of carbon atoms connected by strong covalent σ-σ bonds that exhibits nondispersive transport characteristics. The electron velocity in graphene is $\sim 10^8$ cm/s and the mobility is $>15\,000$ cm^2/V s at room temperature, which is much higher than those from most of semiconductor materials. These properties make a possible new class of carbon-based transistors and integrated circuits with performance superior to silicon, germanium, and III-V compound semiconductors. While the prospect of controlling the band gap in graphene by forming nanoribbons using nanolithography is an important step toward graphene devices,[5,6] one remaining challenge for graphene-based transistors is the formation of high-quality, ultrathin dielectrics with low interface trap density.

Atomic layer deposition (ALD) is a thin-film growth technique for depositing uniform and conformal films with atomic precision. ALD is a special modification of the chemical vapor deposition (CVD) method with the distinctive feature of alternate and cyclic supply of each gaseous precursors to the reactor chamber at relatively low temperature (<350 °C). The alternate pulses of the precursors are chemisorbed on the exposed substrate surface and the excesses are removed by a purge step. The key feature of the ALD methods is the saturation of all the reaction and purging steps, which makes film growth self-limiting on the surface. The precision achieved with ALD allows processing of nanometer scale films in a controlled manner. ALD methods and applications have developed rapidly over the last few years, in particular, for high-*k* gate oxides.[7] ALD high-*k* Hf-based oxide has become a manufacturing process to replace SiO_2 in 45 nm node Si complementary metal-oxide-semiconductor (CMOS) digital integrated circuits starting in the second half of 2007.[8] It is natural to investigate oxide growth on graphene using ALD, the state-of-the-art CMOS technology. But ALD process on graphene, similar to suspended single-walled carbon nanotubes (SWCNTs), is expected to be very different from the deposition on conventional semiconductors or oxides, because the perfect graphite basal surface is chemically inert.[9,10] However, it is of great interest to study the growth mechanism of ALD high-*k* dielectrics on this novel electronic channel material. In this letter, we study the growth behavior of ALD Al_2O_3 and HfO_2 films on highly ordered pyrolytic graphite (HOPG) substrate at different growth temperatures. Field emission scanning electron microscope (FESEM) and atomic force microscope (AFM) are used for characterization.

HOPG is a periodic stack of two-dimensional graphene layers along the *c* axis. Each graphene layer is weakly π-π bonded to its neighbors leading to graphene layers that can easily be cleaved or peeled off, providing an atomically smooth fresh surface with step edges. Fresh HOPG surfaces could be used to reasonably mimic ideal graphene surfaces. After freshly cleaved, HOPG (grade ZYH) surfaces were prepared by peeling off several top layers of graphite with scotch tape, the samples were immediately transferred into an ASM F-120 ALD reactor. It took about 1 h to ramp up to the growth temperature from room temperature at the pressure of 2–6 Torr of N_2 purging. 1–35 nm ALD Al_2O_3 films were deposited at growth temperatures of 200–300 °C by alternating pulses of trimethyl aluminum (TMA) and water (H_2O) as precursors. The pulse length and N_2 purge time are 0.8 s and 2.0 s for TMA, and 1.0 s and 2.0 s for H_2O, respectively. For HfO_2 ALD growth, hafnium chloride ($HfCl_4$) and H_2O were used as Hf source and oxidant, respectively. The pulse length and N_2 purge time are 1.4 s and 2.0 s for $HfCl_4$, and 1.0 s and 2.0 s for H_2O, respectively. The films were characterized by Hitachi S-4800 FESEM and Veeco Dimension 3100 AFM.

Figure 1(a) shows the AFM topography image and line profile of fresh HOPG surface with an atomically smooth (rms=0.04 nm) carbon surface and atomically sharp step

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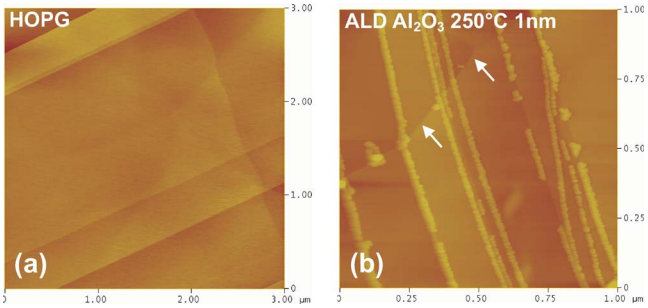

FIG. 1. (Color online) (a) AFM images of HOPG surface with graphene terraces and (b) similar surface after 1 nm thick ALD Al_2O_3 growth.

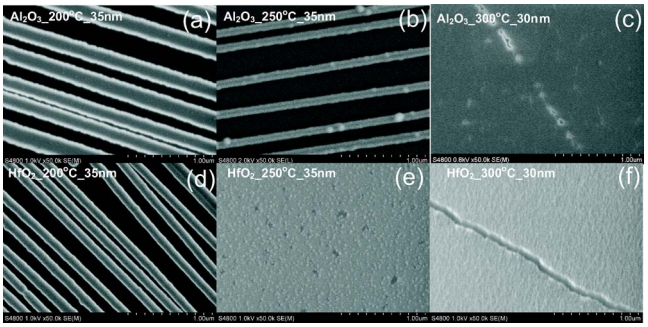

FIG. 2. (Color online) High-quality nanoribbons are formed in the conditions of (a), (b), and (d) on HOPG surface, while very rough and discontinuous films are formed out of ALD process window, as shown in (c), (e), and (f).

edges created by broken graphene layers. From the line profile, the step height is measured to be 0.3–0.4 nm, confirming that it is generated by a single graphene layer. Figure 1(b) shows the AFM image and line profile of a similar area after 10 cycles, i.e., 1 nm of ALD Al_2O_3 process at 250 °C growth temperature. From the line profile, the graphene surface remains bare and atomically smooth with a rms roughness of 0.04 nm, indicating that no Al_2O_3 films are grown on graphene surface. This demonstrates that conventional H_2O-based ALD process cannot grow two-dimensional, continuous, and isotropic oxide films directly on graphene surfaces. On the other hand, Al_2O_3 nanoribbons with ~1.5 nm height and several nanometers wide were clearly observed at step edges, indicating that ALD Al_2O_3 films only grow along the step edges. These results are also supported by the fact that H_2O-based ALD films cannot grow on SWCNTs, oppose to NO_2 and TMA based ALD technique, where strong absorption of NO_2 and TMA on chemically inert SWCNTs surface results in the nucleation of ALD precursors.[11] The results indicate that ALD could also be used as a decoration method for nanoscale features, in particular, when a low-temperature process is required.

Interestingly enough, atomically sharp step edges on graphene provides one-dimensional (1D) broken carbon bonds along the terraces, which serves as 1D nucleation center for the initial ALD process. It provides a perfect material system with 1D dangling bonds by nature. Graphene sheets are comprised of a hexagonal lattice of carbon bonded by a strong σ bonding in the *a-b* plane. When cutting through an infinite graphene sheet, two semi-infinite graphene sheets with 1D edge are obtained. Therefore, two types of edges (armchair or zigzag) exist depending on the cutting direction. Because of the dangling bonds, these edges have much higher chemical or catalytic reactivity than inert basal graphene planes.[9] Theoretical calculation or experimental results show that small molecules, such as X_2 (X=F, Cl, and Br),[10] H_2,[12] O_2,[13] SO_2,[14] and NO (Ref. 15) gases, are chemically adsorbed on the armchair and zigzag edges at room temperature, but only a weak physical adsorption takes place on the basal planes. H_2O is also preferentially adsorbed at these edges resulting in nucleated ALD films at edges. Similar results are widely reported in physical vapor deposited metals,[16,17] CVD SiO_2 (Ref. 18) and Pt,[19] and electrochemical deposited Mo (Ref. 20) and Bi_2Te_3 (Ref. 21) systems, sometimes called as "step edge decoration." Since the building blocks for future graphene-based transistors are a few nanometers wide graphene ribbons, the electronic transport properties are mainly determined by the edge states of these graphene nanoribbons.[22] Surface chemistry study on these 1D dangling bonds is of great importance to passivate or functionalize these edges. Due to the possible different bonding energy of C-dangling bonds from armchair or zigzag edges, the chemical reaction of ALD could be selective with these two types of edges. This selectivity could be within a narrow process window. Nevertheless, some indications of this selectivity are observed, i.e., as highlighted by arrows in Fig. 1(b). The step edges in certain directions do not serve as nucleation centers for ALD process in certain process conditions. More studies on the selectivity based on edge orientations are ongoing.

Figure 2 shows the SEM images of ALD Al_2O_3 and HfO_2 nanoribbons grown on HOPG at different growth temperatures. Al_2O_3 and HfO_2 nanoribbons with dimensions of 5–200 nm in width and >50 μm in length are obtained in a controlled fashion at growth temperatures of 200–250 °C, as illustrated in Figs. 2(a), 2(b), and 2(d). For growth temperatures above 250 °C, rough and discontinuous films are formed, as shown in Figs. 2(c), 2(e), and 2(f). This experiment demonstrates an approach to generate relatively regular nanoribbons on HOPG using well-controlled gas-phase ALD if the growth temperature is within the right ALD process window. This approach is not limited to oxide or insulator nanoribbons. The work could be expanded easily to create semiconductor nanoribbons or metallic nanoribbons or their combinations, since ALD processes of semiconductors (i.e., ZnS and GaP) and metals (i.e., Ru, Pd, Ir, and Pt) are well-established.[23] These semiconductor or metallic nanoribbons can be transferred to other substrates for further device fabrication. Meanwhile, the insulating nanoribbons could be used as a hard mask for dry etching to create graphene nanoribbons underneath. For example, high mobility epitaxial graphene can be formed on SiC surface with regular, dense, and atomic sharp step edges.[4,24] The combination of insulating nanoribbons and graphene nanoribbons is the ideal building block for top-gate graphene transistors.

The lateral size of ribbons has an almost linear dependence on ALD cycles with a constant lateral growth rate, as shown in Fig. 3(a). The lateral growth rate is temperature dependent. For example, the lateral growth rate at 200 °C for ALD Al_2O_3 is about 50% larger than that at 250 °C. Within the ALD process window, the higher the growth temperature is, the more dynamic the TMA molecules are with less chance to be susceptible on clean graphene surface, and the lower the lateral growth rate is. The vertical growth rate is a perfect ALD growth of ~0.1 nm/cycle independent on growth temperature, as shown in Fig. 3(b). The observed

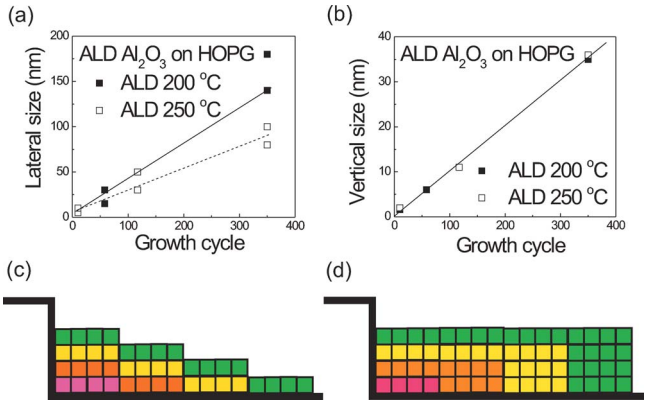

FIG. 3. (Color online) (a) Lateral growth rate of ALD Al_2O_3 on HOPG. (b) Vertical growth rate of ALD Al_2O_3 on HOPG. (c) The expected ALD growth mode nucleated at the step edges of graphene. (d) The possible growth mode for these ALD nanoribbons, which is not a typical ALD growth. Each square refers to one molecule such as Al_2O_3 or HfO_2. The pink, orange, yellow, and green squares refer to the molecules synthesized by the first, second, third, and fourth ALD cycles.

larger lateral growth rate versus vertical growth rate is quite common in metal-organic CVD growth of other materials. It should also depend on chemical properties of precursors and detailed ALD process, such as $HfCl_4$ versus tetakis(ethylmethylamido)hafnium. Figures 3(c) and 3(d) illustrate the possible two chemical processes of how ALD Al_2O_3 and HfO_2 nanostructures are formed at the graphene step edges. Wedge shape structures are expected for a typical ALD process, as shown in Fig. 3(c). But the SEM and AFM studies confirm that the ALD process grows nanoribbons on graphene surfaces, as illustrated in Fig. 3(d), instead of nanowedges. It is not very clear at this moment how the 1D-type ALD growth mode should be.

In summary, we have discovered an ALD method for synthesizing oxide nanoribbons on HOPG surface with the control of nanoribbon dimensions. This methodology could be extended to synthesize any insulating, semiconducting, and metallic nanostructures or combinations thereof since a wide variety of materials can be grown by ALD. Two-dimensional homogenous ALD gate dielectrics could be formed on graphene by the implementation of NO or NO_2 and TMA as noncovalent functionalization layers on graphene before the ALD process.[25,26]

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