In-situ studies of high- κ dielectrics for graphene-based devices

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The discovery and experimental isolation of graphene, a single layer of carbon atoms in a hexagonal lattice, has spurred a tremendous amount of research in recent years due to its unique transport and physical properties (1). These novel characteristics suggest that graphene is a viable candidate material for nanoelectronic switches beyond the end of the Si-CMOS roadmap. All such proposed devices will require the integration of a scalable high-κ dielectric. Engineering of chemical interactions and bonding at the dielectric-graphene interface will be crucial to the performance and reliability of any device. However, the inert nature of the basal plane of graphene presents challenges to the deposition of thin dielectrics.

We present *in-situ* studies of high-κ dielectric formation by electron beam evaporation of metals and subsequent controlled oxidation. The work was performed using an *in-situ* UHV cluster system with analytical and deposition modules, including monochromatic x-ray photoelectron spectroscopy (XPS), electron beam evaporation, oxidation and annealing as described elsewhere (2).

In an effort to overcome the inert nature of the graphene surface, metals were deposited by e-beam evaporation on the surface of natural graphite and subsequently oxidized to form a thin dielectric. Two metals, Al and Hf, were studied in this work as a model system to establish the interfaces associated with Al_2O_3 and HfO_2 on graphene. The metals were deposited on exfoliated and annealed graphite surfaces. The metals were oxidized using high-purity O_2, UV O_3 and RF-generated O_3 at several temperatures ranging from 25°C to 300°C.

We observed that the Al films were fully oxidized for the exfoliated graphite surfaces, but not for the annealed graphite surfaces as determined from the metallic states in the Al 2*p* XPS spectrum shown in Fig. 1. The metallic state of the Al 2*p* XPS peak is clearly detected for the cleaned surface but not in the unannealed case. A calculation of thickness based upon C *1s* attenuation indicates that the thickness of the deposited metal layer is 8.3Å, assuming the overlayer is uniform.

In order to better understand the interface chemistry at the graphite/metal(oxide) interface we also evaluated the interface between graphite and Hf, which has a larger electronegativity difference with C than Al. The formation of HfC bonds was observed immediately after deposition of Hf at a substrate temperature of 25°C. Oxidation in an O_3 environment at 200°C converted the HfC to HfO_2. Furthermore, a significant difference is observed in the C 1*s* peak of oxidized Al and oxidized Hf. The high binding energy side of the C1*s* for the HfO_2 shows a larger asymmetry than that from the original graphite surface in comparison to Al_2O_3 formation (not shown). This data suggests that C-C bonds are broken at the graphene/Hf interface during the oxidation process.

A companion sample with single- and few-layer graphene flakes on SiO_2 processed simultaneously with the graphite sample shows complete consumption of the graphene layer as a result of HfC to HfO_2 conversion. The consumption of graphene was confirmed by optical microscope images and Raman spectroscopy before and after *in-situ* processing, supporting the fact that graphene is damaged during deposition and oxidation of Hf on C. This also supports utilizing large area graphite as a reasonable surface with which to investigate graphene interfacial chemistry.

The effect of the chamber background pressure during metal deposition was also investigated. Deposition at 4×10^{-10} mbar pressure led to reduced HfC formation, below the detection limit of XPS as shown in Fig. 2

The effect of carbide bond formation and damage to graphene layers during oxidation will have a major effect on the selection of metals and processes for both metal contact deposition and gate dielectric integration.

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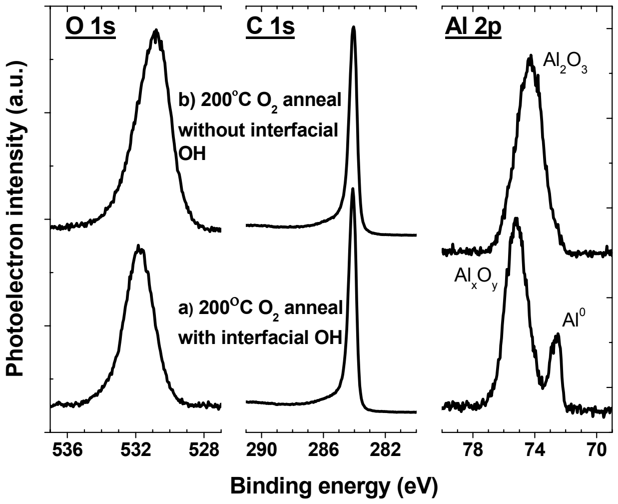

Figure 1: Oxidized Al showing (a) partial oxidation on exfoliated and annealed graphite, (b) complete oxidation on exfoliated graphite.

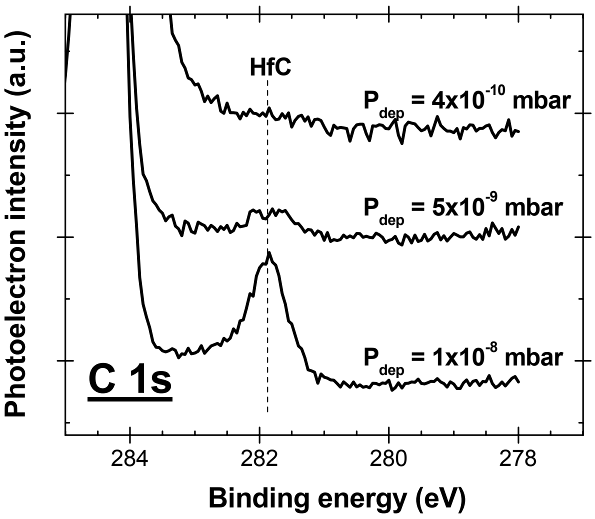

Figure 2: High-resolution C 1s XPS spectrum showing correlation of HfC bonding with background pressure in e-beam deposition chamber.