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Inside Look into Catalytic Condenser for Programmable Solid Acids using STEM

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The application of ultrathin catalytic film provides prospects of breakthroughs in precise control of electron density at catalyst active sites [1]. Specifically, we have applied an ultrathin amorphous alumina (am-Al_2O_3) film with graphene as the active layer in a catalytic condenser device [2]. It enabled modulated electron depletion from the alumina active layer with different applied voltages, providing gate-tunable chemical reaction rate. Despite its novel multi-state-controlled charge transport behavior, the conductance of the alumina film and the charge accumulation between the alumina/graphene interface largely depend on the thickness and structure of the functional layers. Towards this end, we have applied advanced scanning electron microscopy (SEM) and analytical transmission electron microscopy (TEM) techniques to study the microstructure of this catalytic device and compositional information of the interfaces.

The catalytic functional layers were consisted of am-Al_2O_3, graphene and HfO_2 dielectric on the top of p-type Si substrate (Figure 1a). The HfO_2 dielectric layer was deposited to Si substrate by atomic layer deposition (ALD) method, followed by a transferred graphene layer and a 4 nm am-Al_2O_3 by ALD. To investigate the morphology of the am-Al_2O_3-graphene layers, SEM was used to obtain the top-view image of the device. To further understand the interfaces between am-Al_2O_3/graphene and graphene/HfO_2, we performed TEM study of cross-sectional samples. In addition to the structural characterization, complementary scanning TEM (STEM) energy dispersive X-ray (EDX) maps verified the existence of the graphene layer and composition of the am-Al_2O_3 layer (Figure 1d). STEM images and STEM-EDX elemental maps were obtained using Thermo Fisher Talos F200X G2 S-TEM equipped with Super-X EDX spectrometer.

The top-view SEM images and SEM-EDX elemental maps revealed a uniform am-Al_2O_3 film on top of a graphene layer with wrinkles and hexagon-shaped second layers (Figure 1b, Figure 2). This supports our hypothesis that the use of H_2O in ALD created OH-sites on the graphene surface at low deposition temperatures, thus contributing to the successful formation of the uniform alumina film [3, 4]. Besides the uniformity of the am-Al_2O_3 film, the cross-sectional TEM images showed presence of a ~ 6 Å graphene layer and a ~ 4 nm ultrathin am-Al_2O_3 layer (Figure 1c), ensuring that the accumulated charge is accessible to reactive fluids on the top surface [2]. The uniform and ultrathin features as well as amorphous structure of the alumina film are essential for charge accumulation and tunable hole density on the am-Al_2O_3/graphene interface. In addition to the am-Al_2O_3 layer, a high-quality HfO_2 layer ensures uniform distribution of charges along the graphene-catalyst layer, thus crucial for the efficiency of the catalytic reactions. We have observed ~10 nm thick polycrystalline feature at the top of the HfO_2 layer (Figure 1c), which can increase surface roughness, introduce pinholes, and affect the electronic properties compared to amorphous HfO_2 [5]. These results indicate that it is essential to control the temperature during device fabrication to avoid crystallization of HfO_2 and optimize the device performance [6].

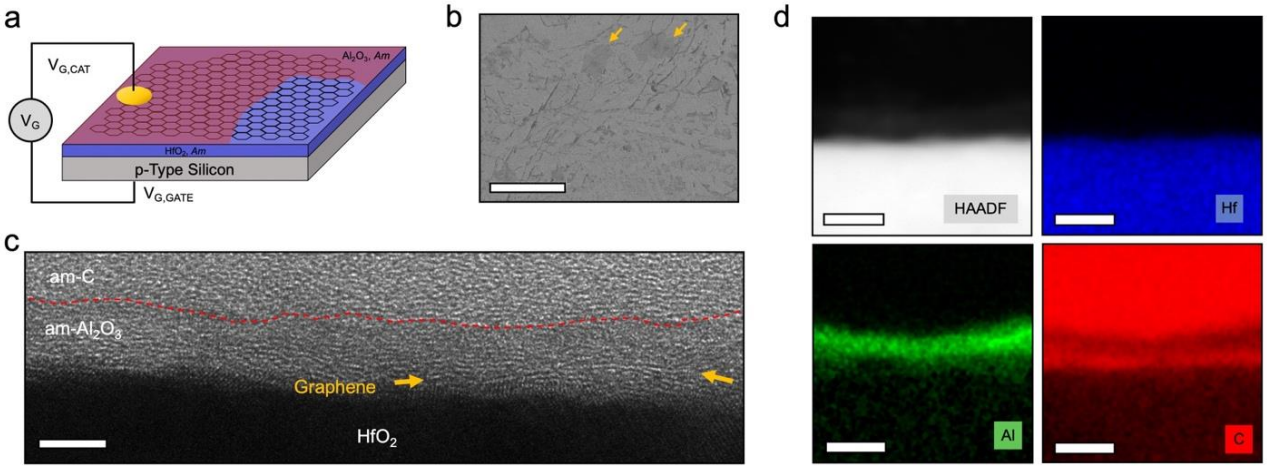

Figure 1. (a) The schematic model of the device. Layers from bottom to top are p-type silicon substrate, HfO_2, graphene, and am-Al_2O_3 respectively. (b) Top-view SEM image of the device. The cracks visible in the image are from the graphene. Yellow arrows indicate the hexagons regions of the second graphene layer. Scale bar is 50 mm. (c) Cross-sectional bright-field TEM image of the device showing all the functional layers in stack. Scale bar is 5 nm. (d) HAADF-STEM image and the complimentary EDX elemental maps of the device in cross-section. The C signal beneath the Al shows where the graphene is, while the C signal above Al shows the amorphous C protection layer. Scale bar is 10 nm.

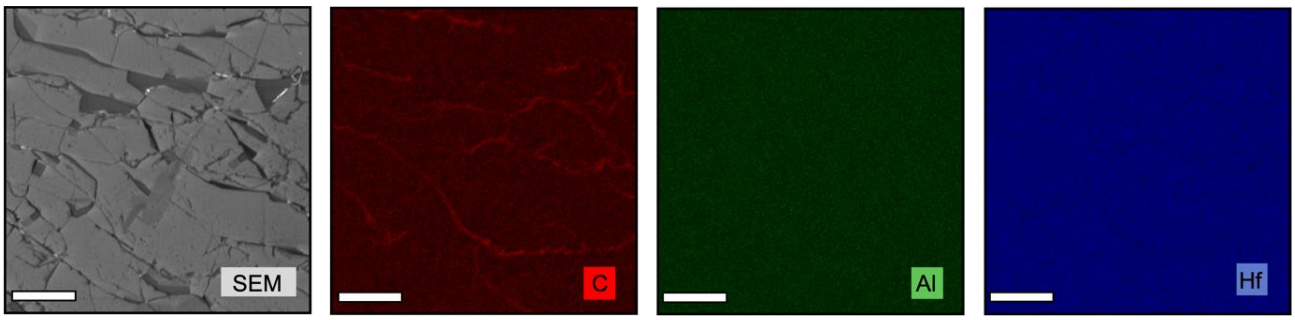

Figure 2. SEM top-view image with complementary EDX maps of the device on Si substrate. It includes HfO_2, graphene and am-Al_2O_3. Graphene folds and wrinkles are observed. Scale bar is 10 mm.

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