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Epitaxial Growth of ZnO Monolayer on Graphene: The Thinnest Metal Oxide Semiconductor

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Heteroepitaxial growth of metal oxide semiconductors on two-dimensional layered nanomaterials, combining wide band gap and high carrier density, has become a new integration method for fabricating electronic devices [1]. Among semiconductor materials, zinc oxide has been used in novel transparent electronic devices as forms of epitaxial layer on graphene [2, 3]. Thermodynamically, hexagonal wurtzite ZnO is the common form [2]. The wurtzite structure of ZnO can be transformed to a planar ZnO monolayer in which Zn and O atoms reside in a trigonal planar coordination, instead of the bulk tetrahedral configuration formed when ZnO is thinned down to a few atomic layers [4]. Since ZnO monolayers on graphene can have many applications in electronic devices, growth of thin ZnO layers on graphene has been studied extensively [5]. Here, we provide experimental evidence for the epitaxial growth of a ZnO monolayer on graphene using atomic resolution transmission electron microscopy along with the corresponding image simulations and first principles calculations. Furthermore, we demonstrate through *in situ* observation the atom-by-atom growth of zinc and oxygen at the zigzag edge of the ZnO monolayer on graphene. In addition, we demonstrate the presence of 2–3 nm quantum dots of the epitaxial ZnO monolayer grown by atomic layer deposition (ALD). Unlike conventional bulk ZnO, ZnO quantum dots have potential applications in nanoscale devices, such as photonic and electronic devices, due to the quantum confinement effect [6].

Figure 1 shows a ZnO monolayer grown on pristine graphene and the UV/ozone-treated graphene after 20 ALD cycles. Figure 1a shows the ZnO deposited on the pristine graphene after 20 ALD cycles. The red region indicates the crystallized ZnO monolayer. Figure 1b, however, shows larger size of ZnO crystals epitaxially grown on the UV/ozone-treated hydrophilic graphene after 20 ALD cycles. The ZnO coverage is much larger on the UV/Ozone-treated graphene. The misorientation angle of 0° is the most common.

Figure 2 shows results of band gap measurements with electron energy loss spectroscopy in the scanning transmission electron microscopy for ZnO grown on graphene with different ALD cycles. The results display higher band gap energy for smaller ZnO nanoclusters. For example, a ZnO grown with 10 ALD cycles displays a band gap of 4.0 eV, whereas a ZnO grown with 200 ALD cycles exhibits a band gap of 3.25 eV, which is close to the bulk ZnO value. The observed gradual spectral shift in the band edge with the ALD cycles can be attributed to the expected quantum confinement effect [6].

We demonstrate the formation of ZnO monolayer on graphene, which is the thinnest heteroepitaxial layer of semiconducting oxide on graphene. The optimized UV/ozone treatment enhances the

hydrophilic surface property of the graphene. Moreover, we experimentally determine that the monolayer ZnO on graphene has a wide band gap of up to 4.0 eV, which is different from that of other ZnO nanostructures, due to the quantum confinement effect and the crystallographic structure. The heteroepitaxial stack of the thinnest two-dimensional oxide semiconductors on graphene has potential for future electronic device applications. This study can lead to a new class of two-dimensional heterostructures including semiconducting oxides formed by highly controlled epitaxial growth through a deposition route [7].

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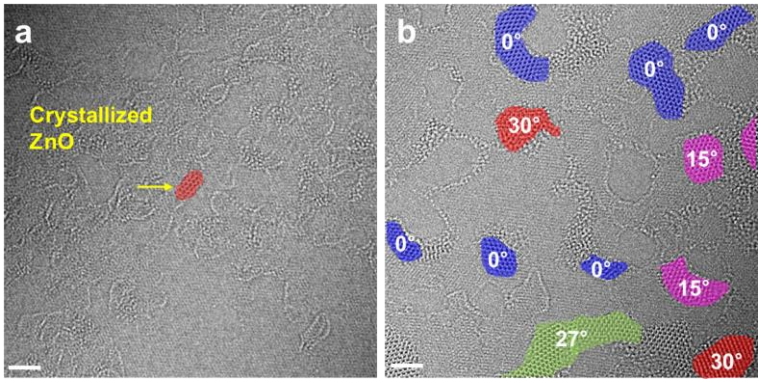

Figure 1. ZnO monolayer on pristine and UV/ozone-treated graphene. (a) Atomic resolution image of ZnO nanocluster on graphene. (b) Atomic resolution image of ZnO nanoclusters on a graphene substrate with 180 s of UV/ozone treatment.

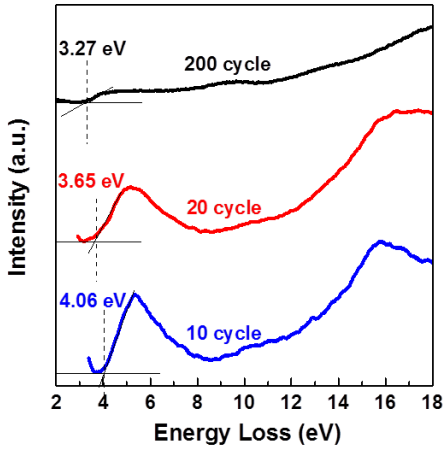

Figure 2. STEM-EELS spectra of ZnO deposited with different ALD cycles on UV/ozone-treated graphene.

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