Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Direct Observation of Quantum Tunneling Charge Transfers between Molecules and Semiconductors for SERS

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Index

1. Preparation of HfO_2/ZnO nanostructures onto graphene films.

First, large-area graphene film-covered SiO_2/Si substrate (300-nm-thick thermal oxide coated silicon wafer) was prepared. Then, 50-nm-thick SiO_2 layer was deposited onto the graphene layer as a growth-controlling mask using commercial system PECVD (STS Co., Ltd.). The mask layer was annealed at 600°C in N_2 to reduce the density of defects in the as-deposited SiO_2 film. Next, hole-patterns to control the position and shape of ZnO nanostructure were defined at the SiO_2 oxide film by an e-beam lithography (EBL) process. After lithography, the mask layer was etched using both dry- and wet-etching processes. Next, ZnO nanostructures were selectively grown on the SiO_2 mask-coated graphene layer using catalyst-free metal-organic vapor phase epitaxy (MOVPE). The detailed process for growing ZnO nanostructure is described in a previous report.[32] After growing ZnO nanostructures, the HfO_2 layer was coated onto the ZnO nanostructures using commercial atomic-layer-deposition system (NCD Co., Ltd.). SEM images of ZnO nanostructures were acquired using Supra 55VP model (Carl Zeiss, Ltd.) at 2 kV acceleration voltage. For GaN substrates, GaN layers were over-grown laterally from pre-fabricated ZnO nanostructures using a similar MOVPE process with tri-methyl gallium and ammonia as sources.

2. SEM images of HfO_2 coated ZnO nanostructures with different coating thicknesses

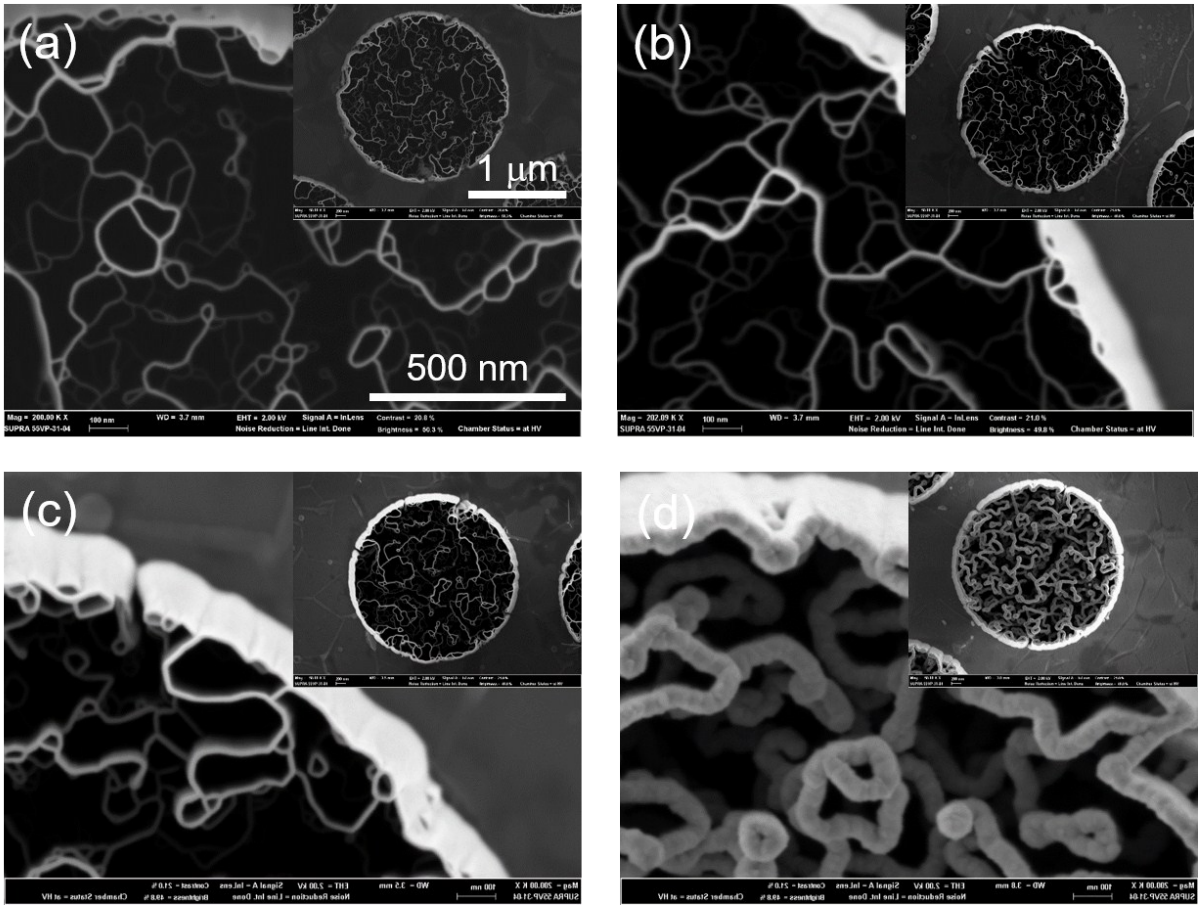

Figure S1. ZnO tubes coated with HfO_2 layers with different cycles of atomic layer deposition; (a) 5, (b) 20, (c) 50, and (d) 200 cycles. Inner nanowall structures are also affected by HfO_2 coating layers. Whole images of the tubes are displayed in the corresponding insets.

The atomically thin and uniform HfO_2 layers were deposited by using a commercial atomic layer deposition (ALD) system (NCD Co., LTD.). Thickness of a single-cycle atomic layer was calibrated to be 0.9 Å/cycle. SEM images of ZnO nanostructures were acquired using Zeiss Supra 55VP model at 2 kV acceleration voltage.

3. Experimental Methods

3.1. Raman data acquisition.

Room-temperature Raman scattering spectra of 4-mercaptopyridine (4-MPY) on ZnO nano-structures were measured by using a McPherson 207 spectrometer equipped with a nitrogen-cooled charge-coupled-device (CCD) array detector. The samples were excited with an Ar+ ion laser (514.5 nm), focused to ~1μm diameter spot using a microscope objective (×50). The excitation power was less than 0.2 mW to avoid laser heating and exposure time was 30 seconds.

3.2. Preparation of 4-MPY molecular samples.

4-MPY molecules were deposited on ZnO nanostructures by drop casting as follows. 10 μls of 10^{-4} M 4-MPY solution was prepared and was divided into 4 equal drops of 2.5 μl each and left to dry naturally. 10^{-3} M and 10^{-2} M 4-MPY solutions were also prepared for ZnO nanostructures coated with HfO_2 layers of different thicknesses and the same deposition procedure was used as for bare ZnO samples.

4. Details of SERS enhancement factor (EF) calculations

The enhancement factor (EF) is defined as $EF = \frac{I_{SERS}}{I_{REF}} \times \frac{N_{REF}}{N_{SERS}}$, where I_{SERS} and I_{REF} are Raman intensities measured from nanostructured samples (SERS samples) and reference samples, respectively, and N_{SERS} and N_{REF} are the number of molecules adsorbed on SERS samples and reference samples, respectively. SERS samples were prepared with 10μl of 10^{-4}M 4-MPY solution, 10^{-3}M 4-MBA, and 4-ATP solution by dropping each molecular solution on each nanostructured micro-rod substrate. Reference samples were prepared on plain Si substrates with 2.5μl of 10^{-1}M 4-MPY solution, 7.5μl 10^{-2}M 4-MBA, and 5μl 10^{-2}M 4-ATP solution, respectively. Schematics of each sample is shown in Fig. S-1. The concentration of each molecular solution was obtained by dropping the molecular solution with the lowest molarity that the molecular peaks were discernable.

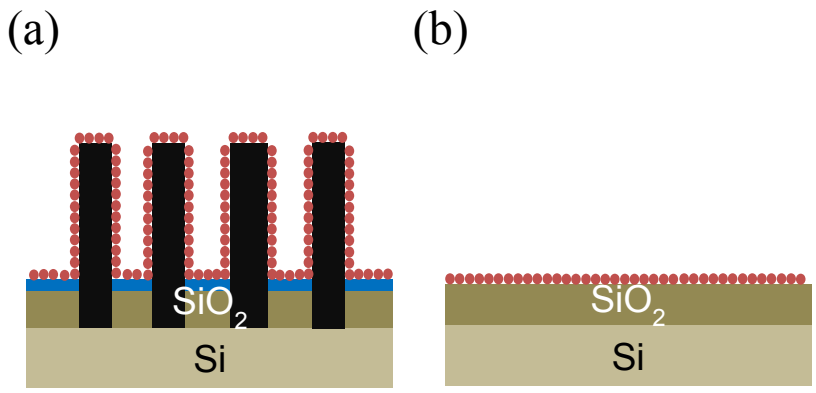

Figure S2. (a) Schematics of a SERS sample. The layer on top of SiO_2 is graphene (see text). (b) Schematics of reference sample. Red dots denote adsorbed molecules in each case.

To calculate the EF of 4-MPY molecules on ZnO nanostructures, we used the peak at 1021 cm^{-1}, which is the C-S stretching mode of 4-MPY. In case of 4-MBA on ZnO and 4-ATP on GaN, we used peaks at 1085 cm^{-1} and 1086 cm^{-1}, respectively. Each peak is indicated by an arrow in Figure S3. The peak intensities of 4-MPY, 4-MBA and 4-ATP on SERS samples are 6631, 208, and 1837, respectively, and those of 4-MPY, 4-MBA, and 4-ATP reference samples are 1481, 128 and 2002, respectively, as shown in Figure S3 (a) and (b).

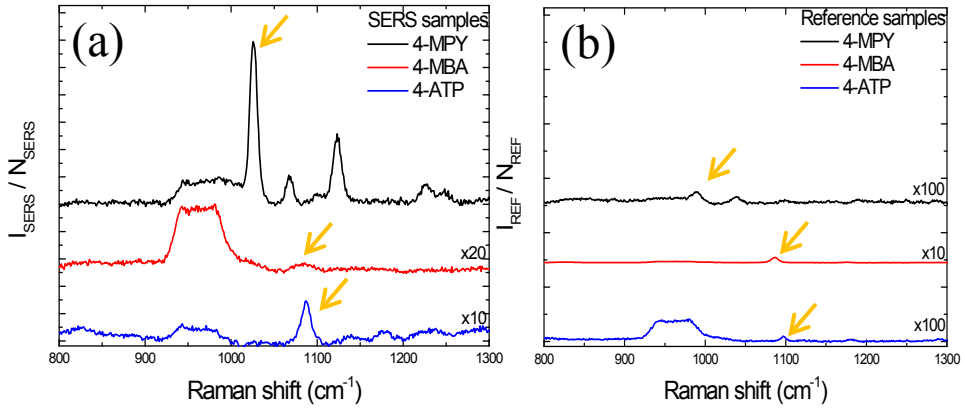

Figure S3. (a) Room temperature Raman spectra measured from molecules adsorbed on SERS samples. Spectra are offset for clarity. (b) Room temperature Raman spectra measured from molecules adsorbed on reference samples. Spectra are offset for clarity.

Since the diameter of the focused laser beam is ~1 μm, we can calculate the illuminated area. By assuming that the molecules were adsorbed on the substrate as a monolayer we can calculate the number of molecules adsorbed on the surface of the reference and SERS samples: N_{REF} of 4-MPY is 3.0×10^{12}, those of 4-MBA and 4-ATP are 1.1×10^{12} and 7.2×10^{11}, respectively. N_{SERS} of 4-MPY is 1.1×10^{-10}, and N_{SERS} of 4-MBA and 4-ATP is 1.1×10^{-11}, respectively. Using these numbers, the EF of 4-MPY, 4-MBA and 4-ATP are calculated to be 1218.7, 6.0, and 16.1, respectively.

5. Schematics of energy diagram

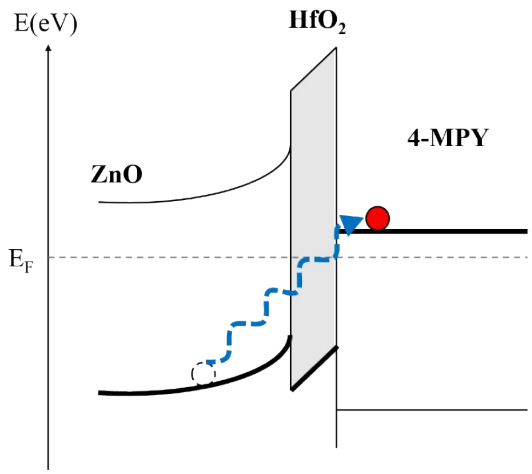

Figure S4. The prebarrier HfO_2 layer may act as a potential well for photo-excited electrons (denoted as a red circle). Drawing is not to scale.