

## Supporting Information

### Semiconductor SERS of Diamond

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#### Experimental Section:

**Synthesis of BDD substrates.** The polycrystalline BDD films were deposited on *p*-type silicon (100) substrates by the microwave plasma chemical vapor deposition (MPCVD) system (at 2.45 GHz). The CH<sub>4</sub> (2.5 sccm) and H<sub>2</sub> (200 sccm) were used as the reaction gases. The flow rate of incorporated boron source was 2 sccm, carried by bubbling H<sub>2</sub> gas with liquid B(OCH<sub>3</sub>)<sub>3</sub>. The microwave power and chamber pressure were 350 W and 8 kPa, respectively. After deposition for hours, the as-grown BDD films were continuously treated in H<sub>2</sub> plasma for an additional 10 min to realize hydrogen-terminated BDD films. The as-grown samples were heated in air at 800 °C for 2 min to produce the oxygen-terminated BDD films.

**BDD film Characterization.** The structure and morphology of the BDD films were characterized by means of X-ray diffraction (XRD, Rigaku D/MAX-RA), scanning electron microscopy (SEM, JSM-6480LV), and Raman spectroscopy (Horiba-Jobin Yvon).

**SERS Measurements.** The Raman spectra were excited using 514 nm line of Ar<sup>+</sup> laser, 633 nm line of a He-Ne laser, and 785 nm line of a semiconductor diode laser. During the measurements, the laser spot on the sample was ~1 μm in diameter, the integration time of the signals was 10 s. The target molecules of MB, 4-MPY, and R6G were dissolved in alcohol, and CV was dissolved in deionized water. To evaluate the enhancement factor, a 10 μL droplet (1×10<sup>-3</sup> M MB in alcohol, 1×10<sup>-4</sup> M 4-MPY in alcohol, 5×10<sup>-5</sup> M R6G in alcohol and 10<sup>-3</sup> M CV in deionized water) was dropped and spread onto the BDD films for the Raman spectroscopy examinations, and the Raman spectra of MB, 4-MPY, and R6G powder on bare glass were examined for comparison.

Figure S1 of 6

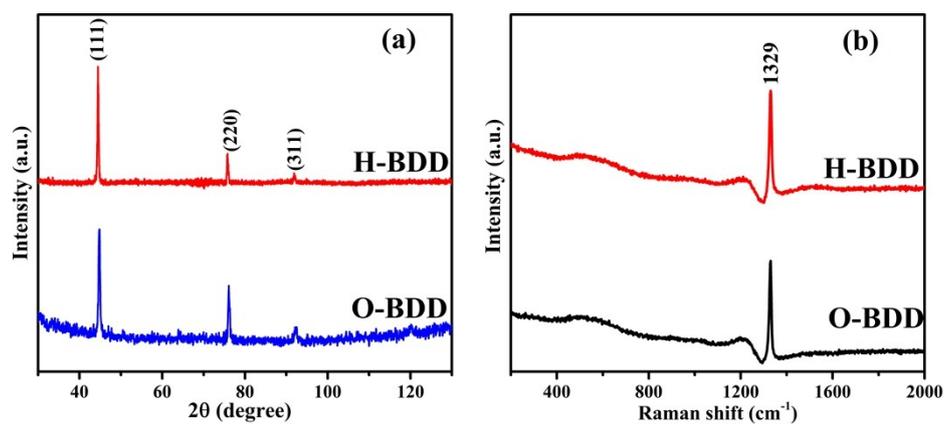
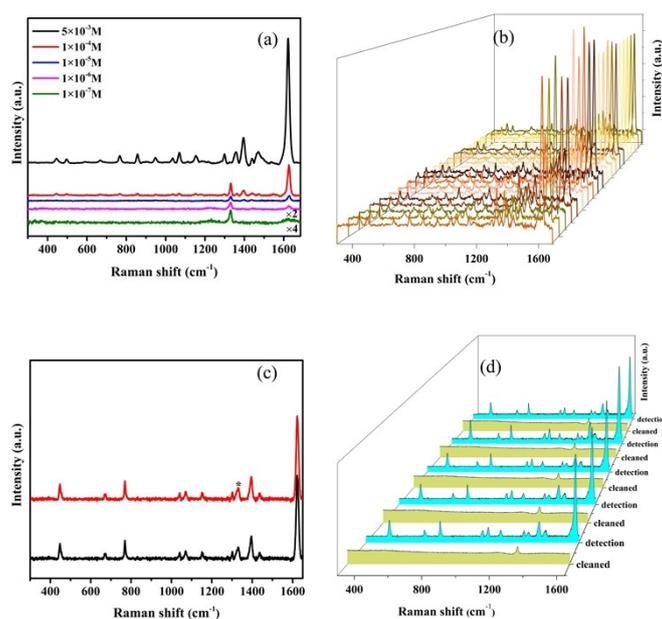


Figure S1 (a) XRD patterns and (b) Raman spectra of H-BDD and O-BDD films.

The diffraction peaks appear at 43.7°, 75.1° and 91.3°, assigning to the characteristic diamond (111), (220), and (311) diffraction patterns, respectively. The asymmetric diamond Raman peak at ~1329 cm<sup>-1</sup> are presented. The features of XRD and Raman spectra of H-BDD and O-BDD are similar, meaning that the diamond phase and boron-doping characteristics are maintained independent on the surface termination.

**Figure S2 of 6**

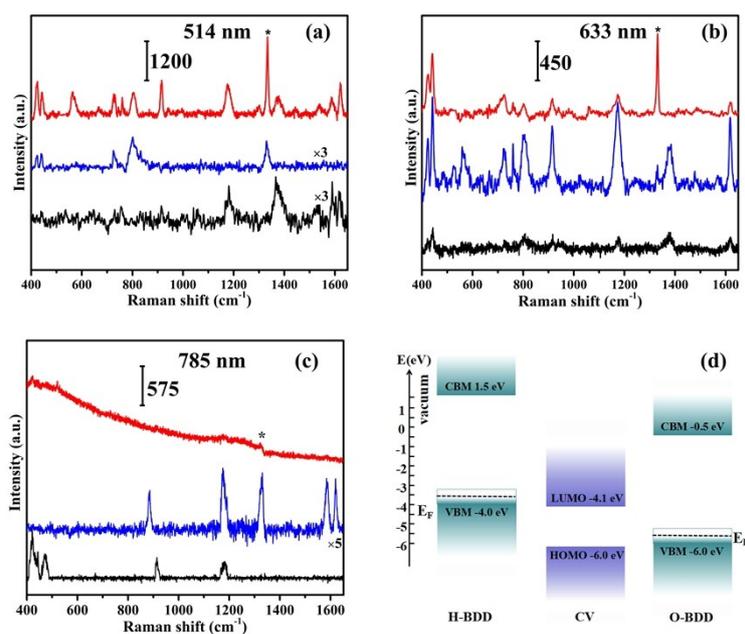


**Figure S2** (a) Raman spectra collected from MB at different concentrations from  $1 \times 10^{-7}$  M to  $5 \times 10^{-3}$  M, (b) SERS reproducibility of MB molecule solution collected from 20 spots on the H-BDD substrate. (c) SERS stability of the target MB molecule obtained from a fresh H-BDD film (red line) and from the film after exposing in atmosphere for 30 days (black line). The diamond Raman peak is labeled by an asterisk (\*). (d) The SERS recyclability examination of the target MB molecule obtained from the H-BDD substrate.

The recyclable experiment is preceded by the following steps: after SERS measurement for MB molecule, the BDD substrate is ultrasonic cleaned for 5 min in ethanol to remove the MB molecules, and then the MB solution with the same concentration is spread on the cleaned BDD surface for the next SERS measurement.

All the measurements indicate that the BDD substrate shows excellent reproducible, stable, and recyclable characteristics.

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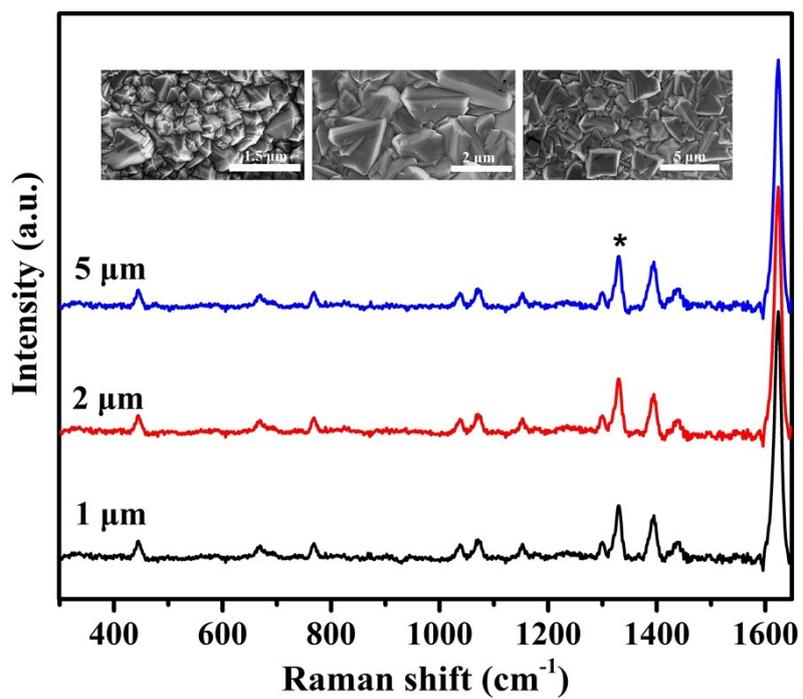


**Figure S3** SERS spectra of target crystal violet (CV) solution ( $1 \times 10^{-3}$  M) spread on the H-BDD (in red) and O-BDD (in blue), and the CV powder on bare glass for comparison (in black), excited at 514 nm (a), 633 nm (b), and 785 nm (c). The diamond Raman peak is labeled by an asterisk (\*). (d) The schematic diagram of the energy levels in the system of semiconductor H-BDD (O-BDD) and CV molecule.<sup>1</sup>

The prominent peaks in the spectra of CV are the bending (C-N-C) at  $\sim 425$  cm<sup>-1</sup>, out-of-plane deformation (C-C-C) at  $\sim 561$  cm<sup>-1</sup>, bending (C-C-C) at  $\sim 803$  cm<sup>-1</sup>, and stretching symmetric (C-C-C) at  $\sim 1170$  cm<sup>-1</sup>. The intensity of 425 cm<sup>-1</sup> band is used to calculate the value of EF excited at 514 nm and 633 nm, and 803 cm<sup>-1</sup> the band is used to calculate the EF excited at 785 nm for O-BDD. The EFs are  $4.7 \times 10^3$  ( $7.1 \times 10^2$ ) excited at 514 nm,  $2.2 \times 10^4$  ( $2.3 \times 10^4$ ) at 633 nm, for H-BDD (O-BDD). The EF is  $1.5 \times 10^2$  when excited at 785 nm for O-BDD.

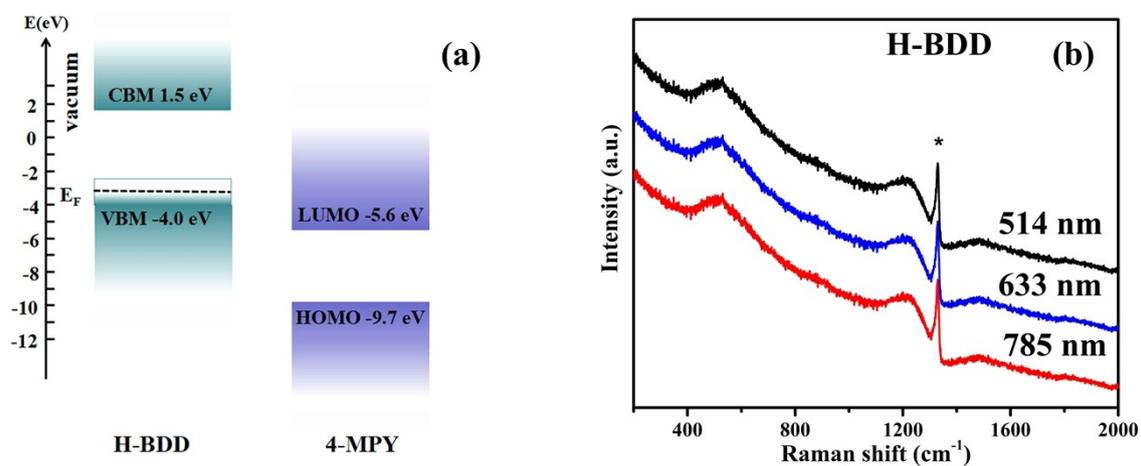
<sup>1</sup> X. Ling, L. M. Xie, Y. Fang, H. Xu, H. L. Zhang, J. Kong, M. S. Dresselhaus, J. Zhang and Z. F. Liu, Nano Lett., 2010, 10, 553.

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**Figure S4** SERS spectra of MB solution ( $1 \times 10^{-3}$  M) spread on the H-BDD films with different grain sizes under identical experimental conditions deposited for 3, 8 and 12 hours. The insets are the SEM images of polycrystalline BDD films with average grain sizes of  $\sim 1 \mu\text{m}$ ,  $\sim 2 \mu\text{m}$ , and  $\sim 5 \mu\text{m}$  from left to right in turn. The diamond peak is labeled by an asterisk (\*).

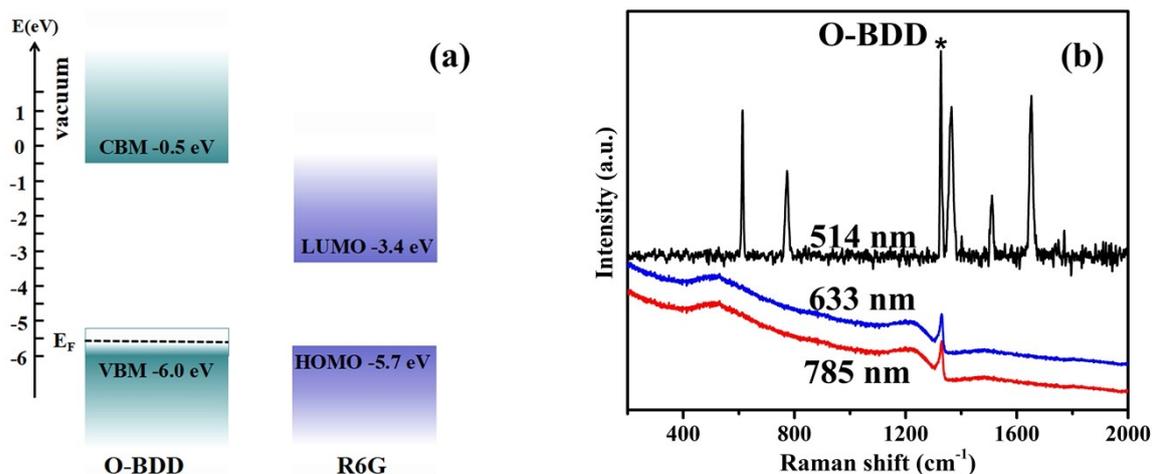
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**Figure S5** (a) The schematic diagram of the non-resonant energy levels in the system of semiconductor H-BDD and 4-mercaptopyridine (4-MPY) molecule.<sup>2</sup> (b) Raman spectra of 4-MPY solution ( $5 \times 10^{-5}$  M) spread on the H-BDD film with the excitation wavelengths at 514 nm, 633 nm, and 785 nm, showing no SERS signals. The diamond peak is labeled by an asterisk (\*).

<sup>2</sup> S. K. Islam, M. Tamargo, R. Moug and J. R. Lombardi, J. Phys. Chem. C, 2013, 117, 23372.

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**Figure S6** (a) The schematic diagram of the energy levels in the system of semiconductor O-BDD and R6G molecule.<sup>3</sup> (b) SERS spectra of R6G solution ( $5 \times 10^{-5}$  M) spread on O-BDD at the excitation wavelengths of 514 nm, 633 nm, and 785 nm. The diamond Raman peak is labeled by an asterisk (\*).

The strong bands at 612, 773, 1360, and 1650  $\text{cm}^{-1}$ , excited by 514 nm laser, are assigned to the in-plane and out-of-plane bending motions of carbon, hydrogen atoms of the xanthen skeleton, and aromatic C–C stretching vibration modes of R6G molecule, respectively.<sup>3</sup>

<sup>3</sup> S. Cong, Y. Yuan, Z. Chen, J. Hou, M. Yang, Y. Su, Y. Zhang, L. Li, Q. Li, F. Geng and Z. Zhao, Nat. Commun., 2015, 6, 7800.