## Binding Energy of Locally Physisorbed Oxygen Molecules in 2D Materials Measured by Laser Terahertz Emission Microscopy



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The properties of 2D materials are highly susceptible to adsorbed gas species. Since surface interaction is very important due to large surface-to-volume ratio, understanding local molecular adsorption/desorption dynamics in these materials is very important. Previously, we have shown that THz emission from InP coated with graphene changes dramatically with  $O_2$  adsorption in the surface of graphene due to modification in the built-in surface field in the semiconductor.<sup>1</sup> Here, we take advantage of this effect to quantify the binding energy of locally adsorbed  $O_2$  molecules in 2D materials like graphene and WS<sub>2</sub> using laser terahertz (THz) emission microscopy.

Graphene and WS<sub>2</sub> prepared by chemical vapor deposition (CVD) and liquid phase exfoliation (LPE) were deposited on InP. Photoexcitation was done using IR pulses ( $\lambda = 800$  nm), and the THz emission was guided using a pair of off-axis parabolic mirrors into a dipole-shaped LT-GaAs photoconductive switch.

By taking the difference in THz emission from unannealed and annealed samples as a function of temperature (Fig. 1a), we were able to quantify the relative decrease in the amount of  $O_2$  adsorbates due to annealing. The data were then analyzed using the Polanyi-Wigner equation for desorption rate, and the binding energy is calculated from the linear fit as shown in Fig. 1b. Calculated binding energies (0.16 eV, 0.15 eV, and 0.25 eV for CVD graphene, LPE graphene, and LPE WS<sub>2</sub>, respectively) agree well with values found in literature for  $O_2$  physisorbed on graphene<sup>2, 3</sup> and WS<sub>2</sub>.<sup>4</sup> Spatial distribution of  $O_2$  molecules during adsorption and desorption in monolayer graphene will also be discussed.



Fig.1 (a) Relative O<sub>2</sub> concentration as a function of temperature and (b) ln(O<sub>2</sub>) vs 1/T plot for calculating binding energy.

This work is partially funded by Grant-in-Aid for Scientific Research (No. 25630149 and No. 26107524), JSPS/MEXT, Air Force Office of Scientific Research (grant number FA9550-14-1-0268 and FA2386-15-1-0004), and Program for Promoting International Joint Research, Osaka University.

## **Reference**:

[1] Y. Sano, et al., Sci. Rep., 4, 6046 (2014).

[2] H. J. Yan, et al., J. Appl. Phys., 112, 104316 (2012).

[3] H. Ulbricht, *et al.*, Phys. Rev. B, *66*, 075404 (2002).
[4] C. Zhou, *et al.*, J. Chem. Phys., *142*, 214704 (2015).