第70回 応用物理学会 春季学術講演会

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First-principles Study on Strain-induced Change of Adsorption Behaviors of NO_2 Molecules on Graphene

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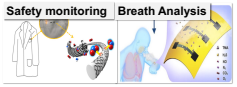
1. Introduction

Background

❑ **Realtime detection of NO_2** is of great importance in health monitoring.

Safety monitoring | **Breath Analysis**



- Long-term exposure above 53 ppm would cause disease even death.
- Exhaled breath → Asthma

A wearable highly sensitive NO_2 gas sensor with selectivity is required.

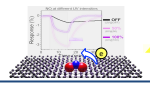
Candidate Material: Graphene

❑ **Graphene:**
- Large sensing area
- High carrier mobility

→ **Sensitive to NO_2 (~ 1ppm)**

Its Sensing Mechanism

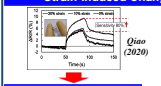
❑ Charge transfer → Change in electrical resistivity



Problem with Improving Sensing Performance

❑ Common approach: Doping/defect
→ unexpected changes (hard to desorb)
→ performance degradation (carrier mobility↓)

Strain-induced Change of Sensitivity



Graphene + H_2O → *strain* → Electrical properties varied drastically

Hint: Strain may improve NO_2 sensing

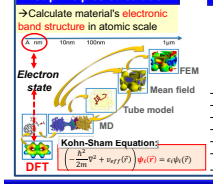
Purpose of This Study

Analysis of the **strain-induced change** of NO_2 adsorption behaviour on graphene and clarification of mechanisms by using first-principles calculation.

2. Methodology and Calculation Details

First-principles calculation

→Calculate material's electronic band structure in atomic scale



Model and Calculation method

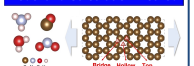
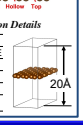


Table 1. Calculation Details

Software	VASP
Potential	GGA-PBE
Cutoff energy	500 eV
EDIFF	10^{-5} eV
EDIFFG	-0.01
K-mesh	12×12×1

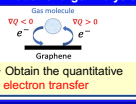


① Adsorption Energy

$E_{ad} = E_{sys} - E_g - E_{gas}$

→ Evaluate the gas adsorption condition

② Bader Charge Analysis



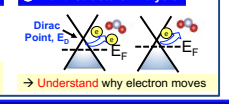
→ Obtain the quantitative electron transfer

③ Projected Density of State

$D_\alpha(E) = \frac{g_s}{N_c}\sum_{\vec{k}}\delta(\varepsilon_{\vec{k}} - E)\left|\langle\chi_\alpha|\psi_{\vec{k}}\rangle\right|^2$

→ Analyze the orbital composition of selected atoms in adsorption systems

④ Band Structure Analysis

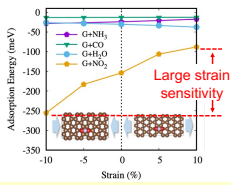


→ Understand why electron moves

3. Calculated Results and Discussions

Strain-induced change of the Adsorption behaviour of NO_2 on graphene

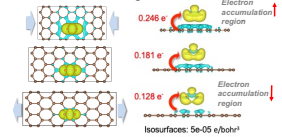
❖ **Strain-effect on adsorption energy**



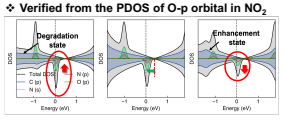
My DFT calculation:
Adsorption energy increased by 70% under 10% compressive strain, while it decreased by 40% under 10% tensile strain.

Our experimental group:
Strain-induced improvement of the NO_2 sensing performance was validated.

❖ **Strain-effect on charge transfer**



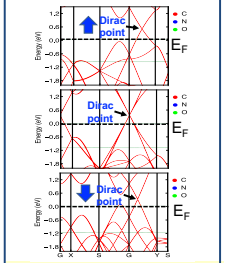
❖ **Verified from the PDOS of O-p orbital in NO_2**



The magnitude of the **charge transfer** between NO_2 and graphene was varied by **orbital interaction**.

Discussions

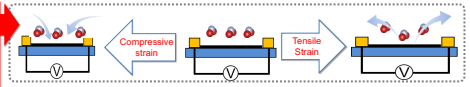
❖ **Strain-effect on the band structure**



Strain causes the **shift of graphene's Dirac point** → larger/smaller doping

4. Conclusions

- ✓ DFT calculation suggests that strain changes the adsorption behavior of gas molecules and improves the sensing performance.
- ✓ The change mechanism was the change in the electronic band structure under strain.



→ **Potential for developing a strain-controlled highly sensitive & selective NO_2 gas sensor**

Acknowledgements

❖ This research activity has been supported partially by Japanese Grants-in-aid for Scientific Research, JSPS KAKENHI Grant Numbers JP20H02022, and Tohoku University.

Improvement of the gas sensitivity of a CNT/graphene hybrid structure sensor by the application of strain

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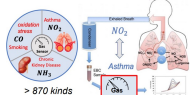
1. Background

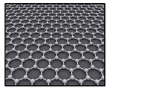
Gas sensor for breath diagnostics



> 870 kinds
1-5000 ppb

Demand for gas sensor
High sensitivity (1 ppb)
Multi objectives
High selectivity
Low cost, etc.

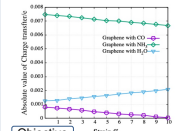
Graphene as a gas sensing material



✓ Large sensing area
✓ High carrier mobility
△ Sensitive to gas adsorption (~1ppm)
× Lack of selectivity

It is necessary to improve the gas sensing performance of graphene

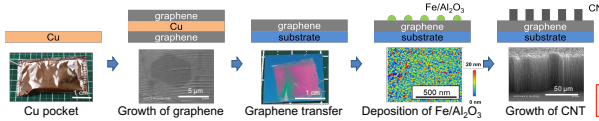
Proposal: mechanical strain & G- CNT hybrid structure



Objective

Experimental validation of the possibility of improvement of the gas sensing performance of graphene by mechanical strain and surface modification by CNT

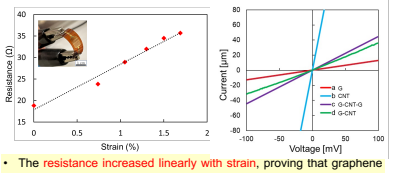
2. Fabrication process of Graphene-CNT hybrid flexible gas sensor



Successfully fabricated graphene-CNT hybrid structure

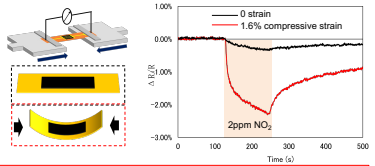
3. Evaluation of the gas sensing performance of the fabricated sensor

3.1 Electrical property of fabricated sensor



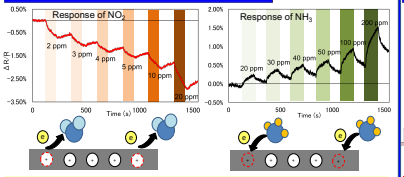
- The resistance increased linearly with strain, proving that graphene was not broken under the bending deformation.
- The linear I-V curve indicated stable ohmic contact between the electrode and graphene, and CNT and graphene.

3.3 Strain-induced change of the sensitivity to NO_2



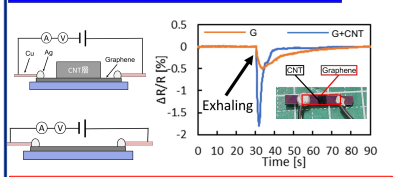
The sensitivity of graphene to 2-ppm NO_2 improved by 6 times under the application of 1.6% compressive strain. This result corresponded to the analytical tesult by DFT calculation.

3.2 Gas sensing test of the fabricated sensor



- The graphene-based flexible gas sensor showed the good sensitivity to NO_2 (accepter) and NH_3 (donor).

3.4 Sensing performance of G-CNT hybrid sensor to H_2O



The sensitivity improved by about 4 times and the recovery time reduced to about 1/5 in the graphene-CNT hybrid structure.

4. Conclusion

1. The fabrication process of CNT- graphene hybrid gas sensor and G-based flexible gas sensor was successfully established.
2. The the sensitivity of the fabricated sensor to NO_2 gas was improved by about 6 times under 1.6% compressive strain. The sensitivity of G-CNT hybrid structure to H_2O was about 4 times larger than that of G-base sensor.
3. It was confirmed that the sensing performance of graphene was improved by mechanical strain & surface modification by CNT.