P_I-28
STEM-EELSによる構造および電子状態の解析

Structures and electron energy states analysis by STEM-EELS

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P_I-29
二段シリンドリカルレンズを使用した新型モノクロメータ

A Novel Monochromater of Double Cylindrical Lenses

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Takashi Ogawa[1], Boklae Cho[1]
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P_I-30
ブラウンミレライト型構造Ca_2FeMnO_5における局所電子構造の研究

Local Electronic Structure Analysis of Ca_2FeMnO_5

治田 充貴[1]，保坂 祥輝[1]，市川 能也[1]，斉藤 貴志[1]，島川 祐一[1]，倉田 博基[1]
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Mitsutaka Haruta[1], Yoshiteru Hosaka[1], Noriya Ichikawa[1], Takashi Saito[1], Yuichi Shimakawa[1], Hiroki Kurata[1]
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P_I-31
EELSによるp（n）-a-Si/i-a-Si/c-Si多層膜におけるSiのディスオーダーの評価

Estimation of Si disorder in p（n）-a-Si/i-a-Si/c-Si heterojunctions by using EELS

東嶺 孝一[1,2]，及川 貴史[1]，小山 晃一[1,2]，大平 圭介[1,2]，松村 英樹[1,2]
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P_I-32
Dual SDDを用いた半導体内ドーパント濃度の検出限界

Detection Limit of Dopant Concentration in Semiconductor using Dual SDD

福永 啓一[1]，遠藤 徳明[1]，鈴木 実[2]，近藤 行人[1]
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P_I-33
孔無し位相板のクライオTEM観察への応用

Cryo TEM application with a hole-free phase plate

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Naoki Hosogi[1], Hirohumi Iijima[1]
([1]JEOL Ltd.)

P_I-34
TEMを用いた高分子材料の液中観察方法の検討

A study of observation method of polymer materials in liquid using TEM

仲野 靖孝[1]，和山 真里奈[1]，渡邉 俊哉[1]，小川 太郎[1]，許斐 麻美[1]，Pin Chang[2]，Lin-Ai Tai[2]，Yu-Ching Chen[2]
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P_I-35
FE-ETEMを用いたガス雰囲気下における電極触媒の*in situ*観察

In situ observation of electrocatalysts in various gasses using FE-ETEM

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Manabu Shirai[1], Hiroaki Matsumoto[1], Isao Nagaoki[1], Toshie Yaguchi[1]
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STEM-EELSによる低次元材料の構造および電子状態の解析

Structures and electron energy states analysis of low dimensional materials by STEM-EELS

越野 雅至[1], Tizei Luiz, H. G[1], Cretu Ovidiu[1], 劉 崢[1], Lin Yung-Chang[1], 飯泉 陽子[1], 岡崎 俊也[1], 末永 和知[1],

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Abstract

We have demonstrated
1. molecule-by-molecule spectroscopy of individual fullerenes [1],
2. atom-by-atom spectroscopy of graphene edges [2],
3. atom-by-atom spectroscopy of N-doped graphene [3],
4. atom-by-atom spectroscopy of tetra-vacancy in h-BN [4],
by means of electron energy-loss spectroscopy (EELS) based on aberration-corrected scanning transmission electron microscopy (STEM).

Methods

Specimen preparations

Fullerene: Encapsulation inside a carbon natnotubes,
Sandwitch between two monolayered h-BN sheets.
Graphene: CVD, PMMA-coat, transfered to SiN TEM grid,
Hexagonal-BN: CVD on Cu, polycarbonate-coat, HCl,

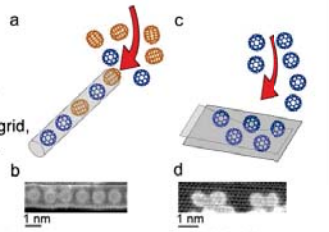
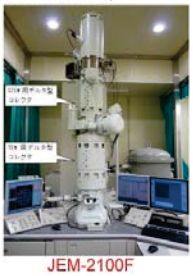


Figure 1-1: Fullerene storages: a-b) Model and ADF (Annular Dark Field) image of C60 (blue) and C70 (orange) molecules stored inside a SWNT. c-d) Model and ADF image of C60 (blue) molecules stored in between two layers of BN. The ADF image was taken at 30 kV for b) and 60 kV for d).

Instruments

S/TEM: JEM-2100F (30 -60 kV)
Electron gun: Cold FEG (W111) , FWHM = 0.35 eV,
Probe size =0.1 nm,
Current 6-20 pA,
Delta-type aberration corrector (JEOL)
EELS: Gatan Quantum 965 for low voltage,
65 counts / electron,
50μ-1 sec for EELS,
Holder: A single tilt JEOL (Heating) holder
Data Processing:
Gatan Digital Micrograph 2,
HREM plugin (MSA, DeconvEELS),
ImageJ, Cornell Spectrum Imager (CSI) plugin,

Gatan Quantum 965



JEM-2100F

Results & Discussion

1. Molecule-by-molecule spectroscopy of individual fullerenes [1].

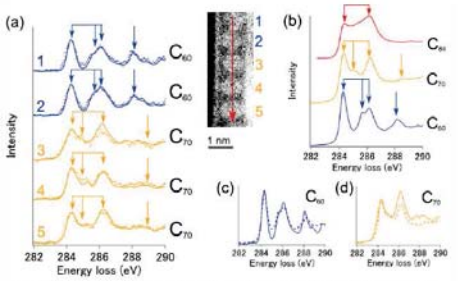


Figure 1-2: Core-level spectroscopy of individual fullerene molecules. a) ELNES carbon K edge spectra extracted from aligned five molecules shown in the inset on the right. Note that the contribution of carbon nanotube to the carbon K edge spectra has been extracted by recording separately the carbon K edge of an empty nanotube. The solid lines are spectra after Richardson-Lucy deconvolution and the dots are the raw data after background subtraction. Blue and orange arrows point to common features of C60 and C70, respectively (see text). From these spectra peak configurations, the discrimination of C60 and C70 molecules is indeed possible. c) The same common features can be seen in b) where reference spectra from crystalline C60, C70 and C84 are shown The C84 spectra was extracted from Kuzuo et al[5] and obtained at 60 kV, while the others were obtained at 30 kV, as in the other experiments described here. Reference spectra for C60 and C70 crystals have been deconvoluted using the maximum entropy method. c-d) Comparisons of the bulk crystalline spectrum (dashed-lines) with a single molecule spectrum (solid-lines) for C60 (blue) and C70 (orange), respectively.
[5] R. Kuzuo, M. Terauchi, M. Tanaka, Y. Saito, & H. Shinohara, Phys. Rev. B 49, 5054 (1994).

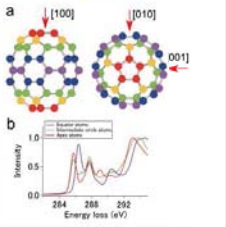


Figure 1-3. EELS simulation of C70 molecules: a) Depiction of a C70 molecule in two different orientations. Five non-identical carbon atoms are painted in different colors b) Simulation of ELNES for different carbon atoms. Between the 285.7 eV and 287.7 eV peaks, the additional peak shifts for different atoms. This could explain the shifting peaks for the experimentally measured molecules. Note that C60 has 60 identical carbon atoms and will show no spectral variation due to the atoms involved in a spectrum.

3. Atom-by-atom spectroscopy of N-doped graphene [3],

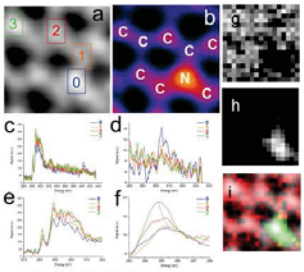


Figure 3-1. (a) ADF-STEM image taken simultaneous as the EELS map. (b) ADF-STEM image with high signal to noise of the same N dopant in graphene. (c-f) EELS corresponding to the boxed regions indicated in (a). (d - f) Magnified N K-edge, C K-edge, and π* region of the C k-edge EELS corresponding to the boxed regions in (a). (g) 2D spectroscopic map based on the carbon k-edge EELS. (i) Overlap of carbon EELS map (red) and N EELS map (green) with ADF-STEM image.

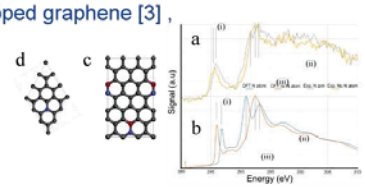


Figure 3-2. Density functional theory simulations of the EELS. Comparison of the experimental (a) and EELS of the C K-edge for nearest neighbour C atoms bonded to the N atom and C located several atoms away from the N atom and not bonded to it. (b) Comparison of the DFT EELS of the C K-edge for nearest neighbour C atom bonded to the N atom in N-doped graphene (blue line and modeled in c) and that in graphene (red line and modelled in d). Dashed vertical lines with labels (i)-(iii) indicate peaks for (i) π*, (ii) σ*, and (iii) peak for N bonded C atoms. (c) The N-doped graphene model has Amm2 symmetry with nitrogen atoms colored in red and carbon atoms with a core-hole colored in blue. *(d) The graphene model has P-9m symmetry* with carbon atom with a core-hole colored in blue.

Results & Discussion

2. Atom-by-atom spectroscopy of graphene edges [2],

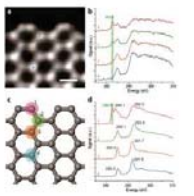


Figure 2-1. STEM:EELS mapping of an armchair graphene edge. (a) ADF-STEM image of armchair edge. Scale bar: 2Å. (b) EELS from the numbered regions in (a). (c) Density functional theory atomic model of armchair edge. (d) Simulated EELS from the numbered regions in (c).

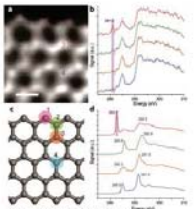


Figure 2-2. STEM:EELS mapping of a zig-zag graphene edge. (a) ADF-STEM image of zig-zag edge. Scale bar: 2Å. (b) EELS from the numbered regions in (a). (c) Density functional theory atomic model of zig-zag edge. (d) Simulated EELS from the numbered

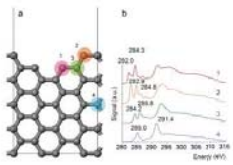


Figure 2-3. Model of stair edge (combination of armchair and zigzag edge) and ELNES simulation. Carbon K-edges of individual atoms numbered from 1 to 4 and marked by red, orange, green and blue colours in (a) are simulated in (b). The ELNES shape of stair edge is different from zigzag edge or armchair edge.

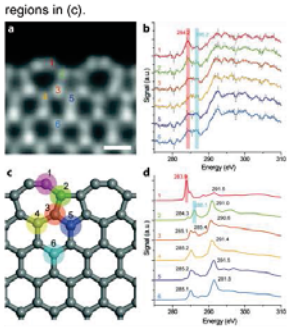


Figure 2-4. STEM:EELS mapping of reconstructed 5-7 graphene edge. (a) ADF-STEM image of rec 5-7 edge. Scale bar: 2Å. (b) EELS from the numbered regions in (a). (c) Density functional theory atomic model of rec5-7 edge. (d) Simulated EELS from the numbered regions in (c).

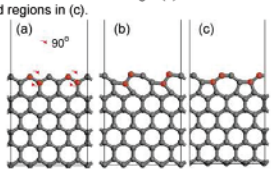


Figure 2-5. Modeling of 57 edge structure. A pair of carbon atoms at zigzag edge (a) was rotated by 90 degrees (b). (c) The structure was then geometry optimized by CASTEP using GGA-PBE functionals. The unitcell in the figure corresponds to the calculation of ELNES but the unit cell with a half distance of a-axis is used for geometry optimization.

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Table 1. Summary of EELS Peak Positions for Different Graphene Edges

peak (eV)	zig-zag (P_z)	Klein (P_k)	armchair (P_a)	heptagon (P_h)	bulk (P_b)	pentagon (P_p)
experiment	281.0	282.8	282.8	284.2	285.0	286.2
DFT	282.7	283.5	282.6	283.9	285.0	286.1
shift (exp.)	−4.0	−2.2	−2.2	−0.8	0	+1.2
shift (DFT)	−2.3	−1.5	−2.4	−1.1	0	+1.1

4. Atom-by-atom spectroscopy of B-terminated tetra-vacancy in h-BN [4],

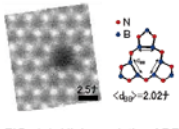

FIG. 4-1. High resolution ADF image of a VB_1N_3 tetravacancy in h-BN (left) and corresponding atomic model of the defect (right). Data acquired using 60 kV electrons @ 500 °C.

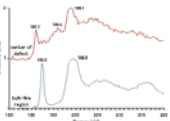

FIG. 4-2. The B K-edge EELS signature of a tetravacancy. The two spectra are acquired from the center of the defect and near the defect, respectively. The spectra have been PCA-filtered. The data was extracted from a 16x14 pixel map acquired using 60 kV electrons @ 600 °C, with an exposure time of 0.5 s/pix and an energy dispersion of 0.1 eV/ch.

TABLE I. h-BN defect types as a function of imaging conditions. The data in the shaded cells is taken from the literature.

	Voltage	80 kV		60 kV
	Temperature	20 °C	500 °C	500 °C
Mode	TEM	V_{B3N1} [6] [8]		V_{B3N3} V_{B1N3}
	STEM	V_{B3N3}	V_{B3N3}	V_{B1N3}

[6] C. Jin, et al., Phys. Rev. Lett. 102, 195505 (2009).
[7] N. Alem, et al., Phys. Rev. B 80, 155425 (2009)
[8] J. C. Meyer, et al., Nano Lett. 9, 2683 (2009)

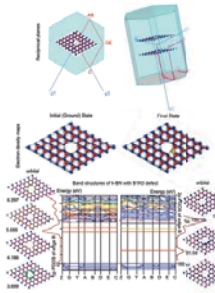

FIG. 4-3. Electron density maps, band structures for the ground and excited states electron configurations and partial density of states (PDOS) of 2p of the B atoms at the edge of the VB_1N_3 defect. The spatial distributions for bands (orbitals) corresponding to representative peaks in the PDOS are plotted for each case. See main text for details.

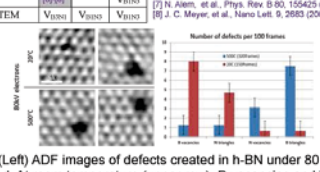

FIG. 4-4. (Left) ADF images of defects created in h-BN under 80 kV electron irradiation. The images have been FFT-filtered. At room temperature (upper row), B vacancies and VB_3N_1 defects dominate, while at high temperatures (lower low), N vacancies and VB_1N_3 defects are predominant. (Right) Distribution of the various types of defects created at 80 kV as a function of temperature. The error bars have been introduced in order to account for inaccuracies in structure assignment.

Summary

We have demonstrated the feasibility of low voltage STEM-EELS analysis for low dimensional materials by interpreting our experimental data with theoretical calculations, which provides deeper insights of the molecular and atomic science.

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[1] Luiz. H. G. Tizei, Zheng Liu, Masanori Koshino, Yoko Iizumi, Toshiya Okazaki, and Kazu Suenaga. Single Molecular Spectroscopy: Identification of Individual Fullerene Molecules. Phys. Rev. Lett. 113, 185502-185502, Oct. 2014.
[2] Warner, J. H.; Lin, Y.-C.; He, K.; Koshino, M.; Suenaga, K. Nano Lett., 14, 6155, Oct. 2014.
[3] J. H. Warner, Y.-C. Lin, K. He, M. Koshino, K. Suenaga, Stability and Spectroscopy of Single Nitrogen Dopants in Graphene at Elevated Temperatures. ACS Nano, 8, 11806-11815, Dec. 2014.
[4] O. Cretu, Y.-C. Lin, M. Koshino, L. H. G. Tizei, Z. Liu, K. Suenaga. Structure and Local Chemical Properties of Boron-Terminated Tetravacancies in Hexagonal Boron Nitride. Physical Review Letters, 114(7), 075502-075502, Feb 2015.

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STEM-EELSによる構造および電子状態の解析

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