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Article / Book Information

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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	Organic and Polymeric Materials 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 (Engineering) Doctor of
学生氏名： Student's Name	Maxim Ziatdinov	指導教員（主）： Academic Advisor(main)	Takehiko Mori
		指導教員（副）： Academic Advisor(sub)	Manabu Kiguchi

要旨（和文 2000 字程度）
Thesis Summary（approx.2000 Japanese Characters ）

In my thesis, I was working on the creation and characterization of the defects in graphene and graphite. I was particularly interested in the connection between the exact chemical composition of the defects and their electronic and magnetic properties. I started with studying single atomic vacancies in the topmost graphene layer of graphite. Such monovacancy defects are considered to be an attractive tool for tailoring the electronic, magnetic, and mechanical properties of the graphene layers. First, I created the single vacancies by sputtering the graphite topmost layer with low-energy Ar^+ ions. The as-prepared monoatomic vacancy possesses two types of localized electronic states located close to the Fermi energy: a zero-mode π state originating from a local sublattice imbalance in graphene bipartite lattice and a dangling bond σ state due to the broken C–C sp^2 chemical bond. The presence of the dangling bonds at the Fermi level implies the enormous chemical reactivity of the monovacancy defects and therefore understanding how foreign chemical species bond to these defects can advance our ability to tailor the electronic and magnetic properties of defective graphenic materials. Among various ways to functionalize graphenic single atomic vacancies, I chose a passivation with hydrogen because it is likely to be employed in a future graphene industry. Using the ultra-high vacuum scanning tunneling microscopy (UHV-STM) with a sub-nanometer resolution, I found a dramatic difference in the topographic images of the vacancies before and after the H passivation. The central question was, What exact arrangement of hydrogen atoms in the graphenic vacancy gives rise to the observed novel patterns? To answer this question, I utilized a density functional theory (DFT) to determine the thermodynamic stability of a various vacancy-hydrogen complexes under the employed preparation conditions, and compared the DFT-simulated STM images of the most stable structures with the experimental data. The monoatomic vacancies passivated with three (V_{111} complex) and four (V_{211} complex) hydrogen atoms were found to be the most stable in our experiments, and their simulated STM images showed a remarkable agreement with the experimental ones. Here, the V_{111} complex, where each σ dangling bond is passivated with one hydrogen atom, exhibits a

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a well-defined signal from the zero-mode π state, which penetrates into the bulk with a $\sqrt{3}a$ periodicity (*a*: graphene lattice constant). However, in the V_{211} complex adsorption of an additional hydrogen atom at one of the vacancy's monohydrogenated carbon sites leads to the complete quenching of the low-energy localized states.

Next, I studied the electronic states at the H-passivated edges of the 2D graphenic nanopores (structures with 10^2-10^3 missing carbon atoms). There are two main types of edges in a graphene lattice: zigzag and armchair. The pseudospin (sublattice) symmetry of Dirac fermions in graphene is broken at the zigzag edge leading to the emergence of the new branch of π electronic states with nearly zero energy localized along the edge boundary (edge state), while no such states are expected at the armchair edges, where the pseudospin symmetry is preserved. I used the monoatomic vacancies as nucleation centers to create the nanopores with predominantly zigzag hydrogenated edges. In analogy with the study on the monoatomic vacancies, I showed, by means of STM and DFT, that key low-energy electronic properties of the graphene zigzag edge (presence/absence of the edge localized state, details of its spatial localization, and character of electron scattering at the edge) in fact depends on the number and bonding arrangement of hydrogen atoms attached to the edge. This leads to the existence of at least two distinct types of the linear zigzag edge, namely monohydrogenated edge, and edge with periodic repetition of two mono and one dihydrogenated sites. The monohydrogenated edge constitutes about 70-80% of all observed zigzag edges in nanoholes, and supports the edge localized state at its outermost carbon atoms. STM spectroscopy measurements at this edge reveal a presence of two peaks in the positive and negative bias regions, with the interpeak separation of about 0.16 V. Using ab-initio calculations, I was able to explain the observed features by the Stoner-type spin splitting of the edge electronic state and found that the best quantitative agreement with the experimental spectrum is achieved by assuming a local bending of the monohydrogenated edge towards an underlying graphite substrate.

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Finally, I showed that one can also induce the edge state at the armchair edge of graphene by breaking the sublattice symmetry at the edge through the appropriate chemical functionalization. The electronic structure of the H-passivated armchair edge in graphene step edges was visualized using the low-temperature UHV-STM. Two types of the armchair edge were revealed: i) perfectly monohydogenated armchair edge without the edge state and characterized by profound standing wave pattern, and ii) armchair edge where every second C atom at each "armrest" is dihydrogenated, with the well defined edge-localized state. I further studied theoretically spin correlations at the edges of the narrow armchair ribbon and showed that it can be switched between the antiferromagnetic (AFM) and ferromagnetic (FM) ground states by simply changing the sequence of mono- and dihydrogenated sites at the opposite edges. I also studied, both experimentally and theoretically, an effect of structural reconstructions in the carbon backbone at the armchair graphene edge (e.g. formation of the pentagon-heptagon (5-7) pairs) on the edge's electronic properties.

I believe that my findings mark an important step towards bringing together chemical and physical aspects of graphene defects and may have strong implications for the research field of graphene-based nanoscale systems. I was able to provide first experimental evidence that key electronic properties of graphene edges and atomic vacancies can be controlled through their functionalization with foreign chemical species (e.g., hydrogen). This may open a way for tuning electronic and magnetic properties of graphene structures not only by changing the geometrical shape of graphene defects as was assumed earlier (e.g. zigzag edge vs. armchair edge, or monovacancy vs. divacancy) but also by controlling how specific chemical species are attached to the defect of a given geometry/shape.

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