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博士学位論文
論文内容の要旨および審査結果の要旨

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１．論文内容の要旨

Two-dimensional (2D) materials or monolayer materials refer to solids that consist of only one layer of atoms and have a 2D sheet structure in which atoms are arranged on a plane, such as graphene and transition metal dichalcogenides, which received lots of attention in recent years. It has been expected to be applied as a new material that takes advantage of the unique properties derived from its two-dimensional structure. 2D materials such as MoS_2 or graphene are the most promising for applying electronic devices due to their strong hardness, excellent heat conduction, charge transfer, and impressive electronic properties. In 2D materials, atoms inside each layer are bonded by covalent bonds, and the layers are combined by van der Waals-like force, which makes it easy to exfoliate from bulk crystals. However, there are challenges in applying 2D materials, such as the existence of lattice vacancy, which is easy to introduce during the fabrication, and difficulty in introducing of impurities for chemical modification.

In this study, the monolayer sample of graphene (zero-gap semiconductor), MoS_2 (direct-gap semiconductor), and TaS_2 (metallic) were fabricated by mechanical exfoliation method and examined from the viewpoint of modifying and verifying the properties of 2D materials. Irradiation of the Ar / Au / I / Fe ions beam, including Noble gas / nonmetallic / metallic / magnetic elements, was used to modify the 2D materials to introduce defects or impurities under a well-controlled condition. The properties of 2D materials on the structure were evaluated by Raman spectroscopy, and the electronic properties were evaluated by photoluminescence and conductivity measurements using the FET (Field Effect Transistor) device structure. This thesis consists of 6 chapters.

Chapter 1 is a general introduction of 2D materials and the objective of this thesis.

In Chapter 2, we propose a low-energy Ar^+ ion beam irradiation method to introduce vacancies into monolayer MoS_2 in a controlled manner. Since the presence of vacancies in 2D materials, such as monolayer MoS_2, significantly affects their structural and electronic properties, a complementary study that combines multiple evaluations was performed to verify the role of vacancies in the structural and electronic properties of MoS_2. Raman spectroscopy and conductivity measurements reveal that the S vacancies, introduced into the MoS_2 lattice prior to Mo vacancies at the lower ion-beam dose region, cause electron doping. The E' lattice vibration mode was more sensitive to vacancies than the A'_1 mode in a Raman spectrum of MoS_2. According to photoluminescence studies, irradiating Ar^+ at a lower dose of less than 3.8×10^{13} cm^{-2} does not change the band gap. It only introduces mid-gap states, consistent with the smaller and larger influences of vacancies in carrier scattering and doping, respectively, in the electrical conductivity. This study compares several measurement methods to confirm the mechanism of vacancy formation in MoS_2, providing a reference for future research and applications of 2D materials.

In Chapter 3, we discussed tuning the carrier transport properties of graphene as the fundamental structure of carbon materials to meet various requirements for the application to next-generation electronic devices related to carrier density, electric mobility, spin-orbit coupling, etc. We attempted to modify graphene by irradiating Au / I ion beam at 200 keV with dosages of 10^{13} - 10^{14} cm^{-2} using a NaCl sacrificial layer to introduce ions as guest chemical species into a two-dimensional graphene sheet as a quantitative chemical modification method. After removing the sacrificial layer, the ion-irradiated graphene was evaluated by Raman spectroscopy, electrical conductivity measurement, and Rutherford backscattering spectrometry. By irradiating the ion beam at the dosage of 10^{14} cm^2, both vacancies of carbon atoms, and Au atoms of 2.1×10^{13} cm^{-2} / I atoms of 1.2×10^{13} cm^{-2} are introduced into graphene, the latter of which act as charged impurities, resulting in the Raman D' band and the downshift of the Fermi energy through hole carrier doping. Using the sacrificial layer method, the modification of 2D materials by high-energy ion beam irradiation becomes available, which could be expected in future applications.

In Chapter 4, we focus on the spin-orbit interaction of MoS_2, which can be expected to be applied to spin-valley electronics. By utilizing this valley-spin polarized state as an information carrier, a next generation communication could be developed, which is different from conventional electronics that only utilize the charge degree of freedom of electrons. Since the selective valley polarization in monolayer MoS_2 is affected by internal magnetic fields inside a material, the Fe atom, a magnetic atom, can be used to improve the valley polarization properties of MoS_2. We attempted to irradiate the Fe ion beam at 200 keV with dosages of 10^{12} - 10^{15} cm^{-2} using a NaCl sacrificial layer to introduce the Fe ion into monolayer MoS_2 sheet as a modification method. After irradiation, circularly polarized photoluminescence measurements were used to measure the change in selective valley polarization property in room and low-temperature conditions.

In Chapter 5, we evaluated the layer number dependence of Raman spectroscopy on TaS_2, a type of metallic 2D material exhibiting a charge density wave (CDW) transition around room temperature and the Ar^+ irradiation effects. The temperature hysteresis of the Raman peak height related to the CDW transition decreases as the number of 1T-TaS_2 layers decreases. The difference in the dimensionality of the CDW superstructures and the competition between the pinning potential of defects and thermal energy explains this. The defect introduction by Ar^+ irradiation significantly broadened and decreased peaks related to the CDW superstructure.

Chapter 6 is the conclusion of this thesis. In this study, the monolayer sample of graphene (zero-gap semiconductor), MoS_2 (direct-gap semiconductor), and thin-layer TaS_2 (metallic) were fabricated by mechanical exfoliation method and examined from the viewpoint of modifying and verifying the properties of 2D materials. From this comprehensive study, the mechanism of ion beam irradiation on 2D materials has been clarified, and it will be a useful tool for defect engineering in the fabrication process of devices based on 2D materials.

２．審査結果の要旨

2D materials have attracted much attention due to the significant advantage of the unique properties derived from their two-dimensional structure. However, there are challenges in applying 2D materials, such as the existence of lattice vacancy, which is easy to be introduced during the fabrication, and difficulty in introducing impurities for chemical modification. The dissertation gives clarified knowledge about the influences on the structure and electronic properties of irradiating 2D materials with Ar / Au / I / Fe ion species, which will help lead to a new class of material development for electronics and spintronics. The novelty and effectiveness of this dissertation were confirmed in the following points.

1) Although there have been attempts to modulate the properties of 2D materials by ion beam irradiation, they all involve direct irradiation of high-energy ion beams, which only introduce vacancies and large-scale structural breakdown. Applying the sacrificial layer method developed in this dissertation enables the intrinsic introduction of irradiated ions as chemical species achieved in a two-dimensional material, leading to the modulation of the degrees of freedom of charge and spin based on the irradiated ion species.

2) The ions beam irradiation in the wide dose range of 10^{12} – 10^{16} cm^{-2} modified 2D materials by introducing defects or impurities under well-controlled conditions, where the influences in the electronic properties, such as carrier transport and optical phenomena, become significant with much lower ion beam doses than that in the lattice dynamics.

3) By clarifying the effects of ion-beam irradiation for 2D materials with various electronic ground states, such as zero-gap semiconductors, semiconductors, and metallic metals, this dissertation provided broadly applicable material design guidelines for their application to electronic devices, environmentally friendly materials, and so on.

The oral examination results on this thesis and other related scholarly fields indicated that the applicant has sufficient academic knowledge.

Based on all of these, this examination committee is unanimous that the submitted doctoral thesis is fully qualified as a Doctor of Philosophy (Science).