論文の内容の要旨

Carrier dynamics at surfaces of WSe_2 studied by time-resolved photoemission spectroscopy

（時間分解光電子分光による WSe_2 表面のキャリアダイナミクス研究）

氏　名　　劉 若亞

Two-dimensional transition metal dichalcogenides (TMDC) have nowadays attractedattention in research on valley-, spin-, and opto-electronics. Performance of these novel technologies depends on carrier dynamics in the materials, however, understanding of the non-equilibrium electronic structure has remained uncertain. Photoemission spectroscopy has been the most powerful experimental technique to probe electronic states in materials directly and recently developed time-resolved measurements allow us to trace them in real time.

In the present work, ultrafast carrier dynamics at surfaces of WSe_2 crystals, and monolayer WSe_2 crystals are investigated by time-resolved photoemission spectroscopy. Using two types of light sources, high-harmonic generation laser and highly-brilliant synchrotron radiation, the time-evolution was chronologically traced from femotosecond to nanosecond after the pumping optical trigger. Dynamical data are systematically discussed in terms of the electronic structure.

In the femtosecond-time scale, various types of non-equilibrium states were observed in the semiconducting WSe_2 crystals, depending on the photon energy of the pumping optical pulse. The light-induced electronic state is generated as Floquet replica bands when pumping photon energy is lower than the bulk direct band gap. When the pumping photon energy is larger than the bulk band gap, photo-excitation to the bulk conduction band is valley-dependent, showing the polarization dependence. Occupations of the conduction band at the K point of the hexagonal Brillouin zone become maximum or minimum by the right-handed or left-handed circular polarized light, respectively, and the optical response reverses at the K’ point. At the monolayer WSe_2 surface, a significant band shift is observed in the fs range after intense excitation by above-band-gap pump pulses. This band shift can be attributed to the band gap renormalization due to the population inversion and strong electronic interaction. The band shift decay within a ps due to the carrier recombination.

In the following picosecond-time scale, photoemission intensity of the bulk valence band shows an oscillation that is found to have a frequency of 6.7 THz by the Fourier-transformation analysis and to be related to a coherent phonon. Since it corresponds to twice the frequency of 3.2 THz of the

maximum single acoustic phonon density in WSe_2, the observation indicates formation of the two-phonon squeezed state.

In the nanosecond-time scale, relaxation of the surface photovoltage (SPV) effect, induced simultaneously by the photo-excitation, is apparently observed. The dynamical phenomena are associated with carrier transfer between the surface and the bulk region. By formation of the heterojunction on a WSe_2 surface with the donor (K) - or acceptor (C_{60})-adlayer, the generation and the relaxation of SPV are modified, showing possible opto-electronic regulation.

The present work has revealed temporal variations of the non-equilibrium electronic structure of WSe_2 after the optical pulse by time-resolved photoemission spectroscopy. The various dynamical phenomena happen on different time scales, which are consistently described by the light-matter interaction and carrier dynamics in the material. The concepts, developed in this work, are expected to be a landmark in developing photo-science and opto-electronic devices.