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変革を駆動する先端物理・数学プログラム（FoPM）

国外連携機関長期研修　報告書

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From February 21st until March 30th, 2024, I visited the Fritz-Haber Institute (FHI) in Berlin, Germany, for joint research with the Shiotari group. FHI is a research institute that mainly specializes in surface science, and the Physical Chemistry Department of FHI is pushing forward with cutting-edge research using light sources of various wavelengths, pulse widths, and powers to study surfaces, solid materials, and molecular dynamics. In the department, some groups investigate atomic-resolution scanning probe microscopy (SPM), including scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning near-field optical microscopy (SNOM) combined with optical systems. I joined the Shiotari Group with advanced SPM techniques integrated with several laser excitations. STM measures the tunneling current between a tip and a sample surface while applying the bias between the tip and surface, allowing us to get an image of individual molecules on the surface. So far, STM imaging has provided less chemical and physical information about the molecules. The dynamics of molecules can be investigated by vibrational spectroscopy, such as infrared (IR) absorption spectroscopy and Raman scattering spectroscopy. The SPM machines in the Shiotari Group take advantage of the atomic resolution STM/AFM imaging in low temperature (LT) and ultra-high vacuum (UHV) conditions together with laser excitation, which allows tip-enhanced Raman spectroscopy (TERS) measurements.

On the other hand, at The Institute for Solid-State Physics (ISSP), Japan, I study molecular dynamics at surfaces by sum-frequency generation (SFG) spectroscopy, one of the vibrational spectroscopic methods. Although SFG spectroscopy probes molecules at surfaces with high sensitivity, the phenomenon observed by SFG spectroscopy is spatially averaged across a hundred μm regions. Because of the recent advances in catalysts designed at the nanoscale, I would like to observe molecular dynamics on surfaces at the nanoscale. Therefore, I decided to visit the Shiotari Group in FHI to learn TERS and its related techniques in the LT-UHV environment.

Firstly, I learned how to perform STM and AFM measurements in LT and UHV conditions using an Ag(111) surface model system. Then, I constructed the optical setup (Fig. 1) to introduce the laser beam to the SPM junction; the bright field image of the junction illuminated by a laser and the scattered light from the junction could be observed simultaneously. Finally, the laser illumination at the SPM junction was adjusted based on field emission resonance (FER) and SNOM signals.

FER is a Stark effect affected by laser illumination; in principle, the bias required to overcome the energy barrier for electron tunneling between the tip and sample shifted to the lower energy region. Comparing the bias spectrum with/without laser illumination after adjusting the laser optical path, a decline of the bias peak was observed, but peak shift was not. As high-power laser illumination for this detection destabilized the SPM junction, we decided to change the alignment method to SNOM-based signal detection. The SNOM signal was measured by lock-in detection at the resonance frequency of the tapping Ag tip to separate the scattering light from the tip and background. We found a weak but specific signal localized in the junction in optical alignment. Further improvement is required for this equipment to increase the signal intensity and detect higher-harmonics signals.

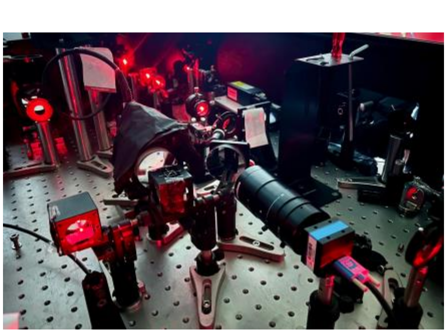

Fig. 1. My arrangement of the optical setup for an LT-UHV SPM apparatus in FHI

Secondly, I reformed an optical system to introduce many laser sources (at 355, 532, and 633 nm) to another

STM-TERS equipment to increase the number of possible molecular targets for dynamics measurements. With this new installation, the optical paths for different lasers became switchable. Also, I designed an optical system to realize TERS measurement down to the Tera-Hertz (THz) region (10-30 cm^{-1}) by using specially designed optical filters. Until now, I have assembled optical systems that introduce multiple beams of light to a sample placed in the UHV chamber, and this experiment has given me a new perspective on designing optical systems in which various laser sources can be switched depending on the application. Adjusting the laser beam to focus tightly at the LT SPM junction in the UHV chamber is challenging because of equipment constraints. I also felt it necessary to assemble a system to reproduce the optical alignment. Because I am planning SFG spectroscopy experiments using a vacuum chamber in the future in the Yoshinobu Lab, ISSP, this experience in the Shiotari Group will be useful.

In addition to my experimental study, I attended a joint workshop between ISSP and FHI: "THz and SFG spectroscopy and related phenomena in Solid-State Physics and Surface Science**" (March 11-12th, 2024),** where I gave a presentation on my recent study in the Yoshinobu Lab (Fig. 2). It was an exciting workshop where we could exchange ideas on each other's perspectives on surface science and photophysical research. During the workshop event, I visited several laboratories, for example, using THz spectroscopy, THz STM, and free electron laser facility. Although ISSP has similar THz pulse sources, I was inspired by possible directions for utilizing such advanced optical equipment. I also participated in the German Physical Society (DPG) Spring Meeting of the Condensed Matter Section and the European Physical Society (EPS) Forum in Berlin. I primarily listened to oral presentations on plasmonic catalysis and the THz STM technique, which recently attracted much attention. It was the first time I had attended a conference overseas in person. Initially, I felt nervous and upset because there were not many Asian participants, and I could not catch up with "European English". However, I was impressed by young presenters in an area of interest. Learning about exciting research and the abilities and presence required to research abroad actively benefited me.

Fig. 2. My presentation in the joint workshop between ISSP and FHI

Throughout this stay, the research environment in FHI seemed better to me than in Japan because German thinks that it is vital to balance work and life; they usually work hard in set working hours and enjoy their private life on their days off doing some activities such as hiking (Fig. 3). Also, there is a high understanding of "researchers' childcare," which is still under discussion in Japan. FHI established a culture of mutual respect regardless of position, gender, age, or race. It is not because they are business associates but because Germany has an immigrant population. Although I was initially intimidated by the small number of Asians in the institute, the people there were kind and helpful, and I completed my month-long stay with peace of mind. I thank the members of the Shiotari Group and the people in FHI. I want to thank Prof. Martin Wolf, the director of the Physical Chemistry Department, for allowing me to stay in his department for this valuable time.

Fig. 3. Krumme Lanke, a lake near FHI.

To summarize my visit to FHI, despite the short period of one month, it was significant for me to apply my background in optics for the present research in FHI that I was interested in. Also, I learned a lot about the research and living environment in Germany. The FoPM program supported this stay. I appreciate this valuable opportunity.