Photo-Induced Dynamics and Reactions at Solid Surfaces

Solid surfaces provide an interesting environment where two completely different electronic systems meet to each other: Localized electronic system, i.e., atoms and molecules and delocalized one, i.e., solid bulk surfaces. Charge transfer at surfaces is fundamental to adsorbate-metal interactions and reactions. Moreover, dynamic processes including chemical reactions on surfaces, particularly metal surfaces, are associated with continuous nonadiabatic transitions. This research program aims for understanding electron and nuclear dynamics at surfaces. Photo-induced processes including photochemistry at surfaces are the major focus in this program. Photons are used for not only exciting electronic states of adsorbate and substrate, but also for probing those states with various types of nonlinear optical spectroscopy.

1. Ultrafast Dynamics at Well-Defined Surfaces

To understand the mechanism of surface photochemistry, it is vital to know how photoinduced electronic excitation induces adsorbate nuclear motions that ultimately lead to chemical reactions. We have demonstrated the real-time observations of surface phonons and adsorbate-substrate vibrational modes by fs time-resolved second harmonics generation (TRSHG). If an excitation light pulse has a duration sufficiently shorter than a period of a vibrational mode or a phonon mode, it can excite the mode with a high degree of temporal and spatial coherence. This coherent nuclear motion modulates the second-order susceptibility $\chi^{(2)}$. Thus, by monitoring the intensity modulation of the second harmonics (SH) generation of a probe pulse, we can observe the evolution of the coherent nuclear motion subsequent to the electronic excitation at the surfaces. We have focused on the excitation mechanism of coherent surface phonons at Na-covered Cu(111) surfaces.

Changing the photon energy of the pump pulse (25 fs) from 2.0 to 2.5 eV, the oscillation amplitude derived from the Na–Cu stretching motion is enhanced. As shown in Figure 1, the careful measurements of photon-energy dependence indicates that the excitation efficiency mimics the absorbance of bulk Cu. Holes created in the d-bands by the optical transitions could be filled by electrons in the adsorbate-induced occupied state of the metallic quantum well by an Auger-type transition. Hence, holes can be created in the adsorbate-induced occupied state. Moreover, since this Auger decay can occur significantly faster than the oscillation period of the Na–Cu stretching mode, the substrate excitation may be a possible excitation mechanism for the coherent oscillation.

Figure 1. Action spectrum for the initial amplitude of the oscillating component in TRSHG traces due to the coherent Na–Cu stretching mode.
2. Spectroscopy of Molecules at Interfaces in Organic Field Effect Transistors by a Sum Frequency Generation Microscope

Organic field effect transistors have gained substantial attentions recently. In order to understand the efficiency of the device and the mechanism of charge transport, it is important to know carriers at the interface between a gate electrode and an organic semiconductor thin film. Since the interface is buried in the device, there are a few methods to investigate what is really happening at the interface. Sum frequency generation (SFG) is one of promising methods to realize it, since this is sensitive to the molecules at interfaces. SFG is a nonlinear optical process and, in particular, when visible and infrared beams are used, SFG is a powerful means for vibrational spectroscopy. We have developed a SFG microscope and applied it to the interface between pentacene and silicon oxide at the gate electrode. SFG signals generated at the interface are spatially resolved by the SFG microscope. We found that SFG signals are largely enhanced when carriers are injected at the interface.

3. Chemistry of One-Dimensional Nano-Surface Compounds

The fluctuating configurations of low-dimensional structures can be thermodynamically favorable at finite temperatures, because the energy gain overcomes the energy cost that accompanies local structural fluctuation. In particular, one-dimensional (1D) systems have a propensity to be sensitive to these fluctuations as described by one of the maxims of condensed matter physics, i.e., one chain does not make a crystal. Thus, the dynamical formation of active species and sites by these fluctuations is a key factor in establishing a microscopic model for chemical reactions at surfaces and nano-structured compounds. It is well known that the adsorption of O on Ag(110) results in the formation of quasi-1D structures, AgO chains, accompanied by the mass transfer of substrate atoms.

We have studied the structures of continuous and truncated AgO chains on Ag(110) surfaces by using density functional theory (DFT) calculations. In addition, the thermal fluctuations of truncated chains are simulated by using the Monte Carlo method. Although it is known that oxygen elimination by CO from one dimensional AgO chains takes place exclusively at chain ends when the chains keep a linear structure at low temperatures, the structure of chain ends has been unexplored. The DFT calculations reveal that oxygen-terminated chains are more stable than silver-terminated ones and have an enhanced density of states near the Fermi level at the terminal oxygen, which is consistent with scanning-tunneling microscope (STM) observations. The Monte Carlo simulations with pairwise interactions between AgO units reproduce characteristic features observed in STM studies, including the existence of an onset temperature for the chain fluctuations and the oxygen-coverage dependence of average chain length. The onset temperature, on the one hand, is largely controlled by attractive interactions in the direction parallel to chain growth. On the other hand, the spatial distribution of fragmented AgO chains depends strongly on repulsive interactions in the direction perpendicular to chains. In particular, the repulsive interactions ranging ten units of the lattice constant in the direction perpendicular to the AgO chains are essential to mimic STM observations, where fragmented chains almost keep the mutual distance inherent to the (n×1)-O phase even under thermal fluctuations.

Reference