

## VIII-L Photochemistry on Well-Defined Surfaces

Upon the irradiation of light in the wavelength range from visible to ultraviolet, a number of adsorbed molecules on metal surfaces reveal variety of photochemical processes, including photo-stimulated desorption, rearrangement of adsorbed states, photodissociation, and photo-initiated reactions with coadsorbates. A central and fundamental question in the surface photochemistry is to clarify how adsorbate-substrate systems are excited by photon irradiation. In addition, since photo-initiated reactions can be induced without any thermal activation of reactants, they may provide good opportunities for studying a new class of surface reactions that may not be induced thermally. We have studied photochemistry of various adsorption systems on well-defined metal and semiconductor surfaces mainly by temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), work function measurements, near edge x-ray absorption fine structure (NEXAFS) and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation.

### VIII-L-1 Photo-Induced Oxygen Elimination on Silver Surfaces

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We have investigated the structural changes in the added-rows of Ag–O chains at a Ag(110)(2×1)-O surface due to photo- and CO-induced elimination of O by using scanning tunneling microscopy. The photo-induced elimination occurs only on the surface contain-

ing carbidic carbon, resulting in the structural change of the added-rows from (2×1) to (4×1) according to the reduction of O coverage ( $\theta_{\text{O}}$ ). The structural change due to the CO-induced elimination depends on the carbon coverage: the (2×1) structure is retained in spite of the decrease of  $\theta_{\text{O}}$  for the C-contained surface, while the structure changes sequentially from (2×1) to (4×1) and (6×1) for the carbon-free surface. Furthermore, the CO-induced elimination rate in the low  $\theta_{\text{O}}$  on the carbon-free surface is much faster than that on the C-contained surface. These results indicate that the small amount of C atoms play an important role not only in the structural changes associated with the oxygen elimination reactions but also in the kinetics of the oxidation reaction of CO.

## VIII-M 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 demonstrate the real-time observations of substrate 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.

### VIII-M-1 Coherent Surface Phonon at a GaAs(100)-c(8×2) Surface

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Coherent surface phonon at a GaAs(100)-c(8×2)-Ga reconstructed surface has been investigated by time resolved TRSHG. The phonon mode is impulsively excited by an ultrashort laser pulse and subsequent coherent nuclear motion is monitored through the intensity modulation of the second harmonics of a probe pulse. Oscillatory traces are clearly observed in TRSHG signals and their Fourier transformation show two peaks

at 8.2–8.6 THz and 8.9 THz. Fitting these traces with two oscillatory components shows that the oscillatory signals are contributed by the bulk LO-phonon at 8.8 THz and the surface phonon at 6.0–8.6 THz. The relative amplitude of the surface phonon modes is sensitive to sputtering and annealing of the surface. Clear dips appear at 8.7 THz in the Fourier spectra, which is caused by the initial phase difference between the surface phonon and the bulk phonon modes. The frequency of the surface component shows red shifts as the pumping power increases. The shifts are indicative of a marked electron phonon interaction or anharmonicity of the surface phonon modes.

### VIII-M-2 Impulsive Excitation of a Vibrational Mode of Cs on Pt(111)

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We have performed TRSHG measurements regarding a Cs–Pt stretching mode on a Cs-covered Pt(111) surface under an ultrahigh vacuum condition. The TRSHG trace obtained from the clean surface shows an instantaneous sharp rise right after the excitation. This is followed by a fast decaying component ( $t < 1$  ps) and a slowly decaying one persistent to the longest delay ( $t = 6$  ps) of the measurements. When the surface is covered

with Cs, SH signals are enhanced by about 70 times and strongly modulated waveforms are superimposed on the TRSHG traces. The power spectrum obtained from the Cs-covered Pt(111) surface shows a strong peak at 2.3 THz; this is assigned to the Cs–Pt stretching mode. The dephasing time of the coherent vibration was estimated to be 1.4 ps. The strong modulation is observed only the Cs-coverages larger than 0.24 ML. At these coverages alkali metal adsorbates are known to make metallic quantum wells. Thus, the resonant impulsive Raman process between quantum well states is responsible for the creation of the vibrating nuclear wavepacket motion in phase along the Cs–Pt stretching coordinate.

## VIII-N Multiphoton Photoelectron Spectroscopy of Electronic States of Nano-Structured Materials on Surfaces

Electronic structure and excited state dynamics of nano-structured materials on surfaces are very important for exploring their properties, thermal reactivity and nonthermal processes including photochemistry and photo-induced charge transfer. For this purpose, we performed multiphoton photoelectron spectroscopy with fs lasers. This year we applied this method to a single-layered nano-graphite crystalline grown on a metal surface.

### VIII-N-1 Anomalous Quenching of Electronic States of Nanographene on Pt(111) by Deuterium Edge Termination

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The electronically excited state and its decay dynamics of graphite nano-crystals on metal surfaces have been investigated by fs time-resolved multi-photon photoelectron spectroscopy. Single-layer graphite nano-

crystals are formed on a Pt(111) surface. The 3-photon photoelectron spectra taken from this surface reveal two peaks whose intensities are strongly correlated with the graphite coverage. By combining with the measurements of photoemission of adsorbed xenon used as another probe for local work functions, we can clearly identify for the first time that one of the peak is due to the electronically excited  $\sigma^*$  state of the graphite nano-crystal. Moreover, this state is extremely sensitive to hydrogen termination of the edge of the nano-crystal in contrast to the occupied  $\pi$  state. These findings clarify the properties of the electronic states of graphene and finally settle the controversy on the location of the interlayer band and its split-off state of bulk graphite.

## VIII-O Chemistry of One-Dimensional Nano-Surface Compounds Studied by Scanning Tunneling Microscopy

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.

### VIII-O-1 Role of Structural Fluctuation in a Surface Reaction Studied by Scanning Tunneling Microscopy: The $\text{CO} + \text{O} \rightarrow \text{CO}_2$ Clean-Off Reaction on $\text{Ag}(110)(2 \times 1)\text{-O}$

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It is well known that the adsorption of O on  $\text{Ag}(110)$  results in the formation of quasi-1D structures, AgO chains, accompanied by the mass transfer of substrate atoms.

AgO chains arrange periodically to form  $(n \times 1)$  ( $n = 2 \sim 7$ ) depending on the fractional O coverage due to repulsive inter-chain interactions. While the chains appear as rigid straight lines in the  $(2 \times 1)$  structure at room temperature, the structures fluctuate to appear as

segmented and sometimes “fizzy” chains in the  $(n \times 1)$  ( $n \geq 4$ ) structures. Energetically-equivalent structures of different configurations of segments exist, reflecting the 1D nature of the chains. Thus, chains fluctuate between configurations rather than freezing into a single configuration, and consequently segmented or fizzy chains are observed. Therefore, AgO chains on  $\text{Ag}(110)$  is a good system for investigating the effects of structural fluctuation on reactivity.

The kinetics of the clean-off reaction of O adatoms by CO on  $\text{Ag}(110)(2 \times 1)\text{-O}$  is investigated by scanning tunneling microscopy. The reaction is accelerated in the lower O coverage range where AgO chains with  $(n \times 1)$  ( $n \geq 4$ ) configurations show significant structural fluctuation. Simulations based on the Ising model are used to provide a quantitative understanding of the acceleration, which originates from the dynamical formation of active O adatoms by fluctuation of AgO chains.

## VIII-P Adsorbate Structure and Surface Chemistry on Well-Defined Surfaces

Surface reactions have been playing an important role in production of many useful compounds and also fabrication of electronic devices. In particular, investigations on the structures of adsorbates and their reactivity are the first step for understanding more complicated catalytic reactions. We investigate surface reactions and kinetics by means of various techniques including temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), work function measurements, Auger electron spectroscopy (AES), infrared reflection absorption spectroscopy (IRAS) and scanning tunneling microscopy (STM).

### VIII-P-1 Thermal Decomposition of Acetylene on $\text{Pt}(111)$ Studied by Scanning Tunneling Microscopy

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The adsorption and the thermal decomposition processes of  $\text{C}_2\text{H}_2$  on  $\text{Pt}(111)$  have been investigated by the use of STM. For a high  $\text{C}_2\text{H}_2$  coverage, a  $(2 \times 2)$  structure is observed locally after the  $\text{C}_2\text{H}_2$ -covered  $\text{Pt}(111)$  surface is heated to 120 K. By heating to 220 K, the sample surface is covered with the  $(2 \times 2)$  structure separated with brighter lines. After heating up to 370 K,  $(2 \times 2)$  domains related to ethynylidyne species appear with larger and brighter protrusions. For a low  $\text{C}_2\text{H}_2$  coverage, adsorbates are located randomly and no ordered islands are observed after heating to 120 K. In contrast, heating to 220 K leads to the formation of  $(2 \times 2)$  islands. This indicates that the adsorbate-adsorbate interaction in the  $(2 \times 2)$  structure observed by 120 K heating is different from that in the  $(2 \times 2)$  structure observed by 220 K heating; the former is repulsive, but the latter attractive. Therefore, it is suggested that different sur-

face species are formed by the decomposition of  $\text{C}_2\text{H}_2$  at 220 K. The detail of the decomposition processes of  $\text{C}_2\text{H}_2$  and the relation between the adsorbate-adsorbate interaction and the surface species are discussed. The results are also reported measured by heating up to higher temperatures above 400 K.

### VIII-P-2 Reaction Intermediates in the Oxidation of Methanol on a $\text{Pt}(111)\text{-}(2 \times 2)\text{O}$ Surface

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The oxidation of methanol on a  $\text{Pt}(111)\text{-}(2 \times 2)\text{O}$  surface has been investigated by infrared reflection absorption spectroscopy and temperature-programmed desorption. Methanol is dehydrogenated to produce methoxy species in the annealing temperature range from 130 to 170 K. At above 170 K, the reaction proceeds differently, depending on methanol coverage. At the saturation coverage, methanol adsorbates partly desorb molecularly and partly react with precovered

oxygen atoms to produce CO, H<sub>2</sub> and H<sub>2</sub>O. No detectable formaldehyde or formate is formed. In contrast, at submonolayer coverages, methoxy species is dehydrogenated to yield formaldehyde at ~ 180 K and further oxidized to formate at ~ 200 K. Formate is decomposed by 300 K. Defect sites such as steps are not relevant to the formation of the intermediates. When CO is coadsorbed on the surface, it destabilizes the reaction intermediates. The destabilization by coadsorbed CO makes the reaction intermediates short lived as not to be detectable at high initial coverages of methanol.