

論文の内容の要旨

論文題目

Electronic Structure and Dynamics of Molecules on Oxide Surfaces

(酸化物表面における分子の電子構造とダイナミクス)

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The interaction between molecule and solid consists of the exchange of matter, energy, and angular momentum. Compared to molecules as isolated systems and solid as condensed matter, the interacting system breaks symmetry and lowers dimensionality. Furthermore, sometimes the system is in non-equilibrium. These make the understanding difficult and, as a result, most all of the system remains to be elucidated. General purpose of this study is to elucidate the mechanism of the interaction. The understanding of the interaction enables us to elucidate and design catalysis, fuel cell reaction, process in semiconductor-device fabrication, and generation of stars in the future.

In this dissertation, we firstly focus on the interaction of molecules with $\text{SrTiO}_3(001)$ surfaces. The surface of SrTiO_3 has received greater attention in recent years due to the photocatalytic activity under visible light and the generation of a two-dimensional electron gas, as well as because of the use as a substrate in oxide-based devices.

For this oxide, in common with others, oxygen vacancies on the surface have an influence on the electronic properties of the surface and promote the interaction with gas molecules. Controlling the oxygen vacancy density is thus of particular importance

for understanding the dynamics on oxide surfaces. It has been shown and well-established that electron irradiation induces desorption of oxygen on an oxide surface following the Knotek-Feibelman mechanism. This electron stimulated desorption (ESD) is of particular interest because O vacancies are expected to be formed only at the topmost layer in a controlled manner. We have studied the effects of electron irradiation and subsequent oxygen adsorption on the electronic and atomic structure of the SrTiO₃(001) surface with ultraviolet photoemission spectroscopy (UPS) and low energy electron diffraction (LEED). While electron irradiation induces an in-gap state due to oxygen ESD on the topmost surface, the vacancy-free surface is restored by molecular oxygen dosage. The ESD cross section with irradiated electron energy of 1500 eV was estimated to be $1.8 \times 10^{-18} \text{ cm}^2$. The cross section increases as irradiated electron energy rises. There have been several discussions on how the doped electrons are localized in the band gap forming the in-gap states, such as the polaronic effect and Ti 3d-O 2p hybridization effect. Electron irradiation also induces downward band bending, which seems to result in the formation of a conductive layer in the surface. This allows us to control the area density of the oxygen vacancies at the surface, thereby enabling us to switch the surface between semiconducting and metallic regimes.

The behavior of hydrogen on the SrTiO₃ surface is of particular interest, because molecular hydrogen is formed as a result of photolysis of water and the surface is metalized by adsorption of hydrogen. In order to elucidate hydrogen behavior on the surface, we have studied the interaction of hydrogen with the electron-density-controlled SrTiO₃ surfaces. On a nearly-vacancy-free (NVF) SrTiO₃(001) surface, atomic-hydrogen exposure induced in-gap states at 1.3 eV below the Fermi level, which is observed by ultraviolet photoemission spectroscopy (UPS). The hydrogen coverage was quantitatively evaluated to be $3.1 \pm 0.8 \times 10^{14} \text{ cm}^{-2}$ with H-specific ¹H(¹⁵N, α γ)¹²C nuclear reaction analysis (NRA). Upon molecular hydrogen exposure to an oxygen-deficient (OD) SrTiO₃(001) having in-gap states due to oxygen vacancies, on the other hand, the in-gap state intensity was reduced with a hydrogen coverage of $0.9 \pm 0.7 \times 10^{14} \text{ cm}^{-2}$. We argue that H is positively charged on the NVF surface by being coordinated to the O atom, whereas H is negatively charged on the OD surface by occupying the oxygen vacancy site.

In addition, we have studied the rotational-state transition in the scattering of molecular hydrogen on electron-density-controlled SrTiO₃(001) surfaces. Molecular hydrogen exists in two nuclear-spin isomers, ortho-H₂ ($I=1$) and para-H₂ ($I=0$). The transition between the ortho and para state is slow in the gas phase with a conversion

time of the order of 10^{20} s. On the other hand, transition between ortho- H_2 and para- H_2 is promoted in physisorption through interaction with solid surfaces. Rotational and spin-state transition in dynamic processes remain to be elucidated. The surface electron density was controlled by electron-stimulated desorption of oxygen. For the scattering experiments, we have constructed a molecular-hydrogen beam with a flux of $\sim 10^{15}$ $cm^{-2} s^{-1}$. The H_2 beam was incident to metallic and non-metallic phases SrTiO₃(001), and scattered H_2 was state-selectively detected by (2+1) REMPI via E,F $^1\Sigma_g^+$. Possible rotational and spin-state transition is discussed.

Next, we have studied the behavior of molecules on stainless steel surface covered with complex of oxides.

Pressure decay during an evacuation process of a vacuum chamber often shows a power-law dependence on time, which is considered to reflect the distribution of the adsorption energy of particles on the surface of the chamber. We derive an analytical formula that directly transforms the pressure change into the adsorption density of states. This method shows that the power-law behavior is equivalent to the situation in which the chamber surface has a constant-or exponential-type adsorption density of states for particles under a quasi-static condition

On the basis of this formula, we analyzed the pumping-down curves reported in literatures to obtain ADOS of water molecules. The ADOS was dependent on the initial exposure pressure of water. The origin of the pressure dependence is discussed.

In order to discuss the ADOS from the other points, temperature dependence of hydrogen depth distribution in a stainless steel surface was investigated by NRA. Activation energy of desorption of hydrogen was analyzed from the temperature dependence of NRA profiles. The activation energy distribute from 0.8 eV to 2.4 eV, which is consistent with the form of ADOS analyzed from pressure decay curves.