

III-I In-Situ Observation of Surface Reactions by Variable Temperature Scanning Tunneling Microscopy

Chemical reactions at a well-defined single crystal surface has been intensively investigated as a prototype for heterogeneous catalytic reaction, electrochemical reaction and corrosion. The surface chemical reactions are heterogeneous in nature reflecting the structural and electronic imperfections relevant to steps, vacancies and impurities. In addition, the surface reactions are significantly influenced by the presence of reactants and products which often form ordered arrays. Therefore, in order to get better understanding of the surface reactions, it is vital to unravel the nature of these local properties which are closely linked to catalytic activity. The advent of scanning tunneling microscopy (STM) has enabled us to tackle the challenge with the ability to image the surface reactions in both real-time and real-space with atomic resolution. We investigate the reactivity of novel one-dimensional (1D) -Ag-O-Ag-O- compounds formed upon the dissociative adsorption of oxygen molecule on Ag(110) using variable temperature STM (VT-STM). The 1D compounds are arranged periodically to form $(n \times 1)$ ($n = 2-7$) reconstructed structures. In addition, the 1D compounds show structural fluctuation in low O coverage regime reflecting the low dimensionality. These characteristics make them promising as a model system to explore physical and chemical properties of nano-structured materials.

III-I-1 Spontaneous Formation of Stripe Phase under the Dynamic Equilibrium between Adsorption and Desorption of H_2O on O-Covered Ag(110) Surfaces

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The surface structure variation under the equilibrium condition achieved by the adsorption-desorption of H_2O ($\text{H}_2\text{O} + \text{O}_{(\text{ad})} \leftrightarrow 2\text{OH}_{(\text{ad})}$) on the Ag(110)(2×1)-O surface at room temperature was investigated using VT-STM. We found that the (2×1)-O and OH phase alternately arrange to form periodic stripes. The STM observations were made by initially preparing the (2×1)-O surface and then exposing the surface to H_2O of $P_{\text{H}_2\text{O}} = 1 \times 10^{-8}$ mbar. The initial surface is the (2×1)-O structure with small bare patches that are not covered with the AgO chains. These patches are randomly distributed and appear as darker lines. When the surface was exposed to H_2O , the darker lines wander and become frizzy because the deconstruction of AgO chains upon the reaction occurs at the boundary. In addition, the lines coalesce to extend from step to step, become bright and finally arrange periodically to form a stripe pattern. The average interval between the stripes was estimated to be 6–7 nm. When H_2O was fully evacuated, the stripe pattern became disordered and finally the structure similar to the initial structure was restored. This indicates that the spontaneous formation of the stripe pattern occurs only under the equilibrium.

The formation of phase boundary is generally unfavorable because energy cost related to the phase boundary increases the surface energy. Thus, the formation of the stripe pattern needs the energy gain which overcomes the energy cost accompanied by the interface formation. According to Vanderbildt,¹⁾ the interactions characterized by $1/r^3$ scaling are responsible for the stabilizing the stripe pattern formation. The elastic and electrostatic interactions between the (2×1)-O and the OH phases are dominant candidates. Simple estimation based on the theory suggests that the energy gain originating from the electrostatic interaction is not sufficient

and thus the elastic relaxation is responsible for the formation of the stripe pattern.

Reference

1) D. Vanderbilt, *Surf. Sci.* **268**, L300 (1992).

III-I-2 Direct Observation of a Propagating Chemical Wave in Disproportionation Reactions of Water on Oxidized Ag(110) Surface by Scanning Tunneling Microscopy

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Scanning tunneling microscopy was used for studying spatiotemporal evolution of the disproportionation reaction of H_2O with O adatoms on oxidized Ag(110) surfaces where quasi-one dimensional AgO chains form ordered structures. Initially the reaction takes place slowly on Ag(110)-(5×1)O at the end of AgO chain, whereas the reaction accelerates explosively upon the appearance of a chemical wave that propagates along the direction perpendicular to the chain. The surface morphology of the region swept over by the chemical wave completely changes from (5×1)-O to that with many rectangular islands, indicating the formation of H_2O (OH)₂. The induction time and explosive acceleration with the propagating chemical wave imply that the reaction is autocatalytic. Water clusters hydrating OH produced likely play a central role in serving as a reservoir of H_2O to feed to the reaction and enhancing the reactivity of H_2O with O adatoms in AgO chains.