主　論　文　の　要　約

論文題目　Thickness dependence of growth and structure of ultrathin cerium oxide films on Rh(111) (薄膜層依存性を有する Rh(111)上の酸化セリウム超薄膜のエピタキシャル成長と構造)

氏　　名　陳　立航

論　文　内　容　の　要　約

Ultrathin films of metal oxides, such as Ti, Ce, V or Fe oxides, are important materials for a wide range of catalytic processes. In the field of catalysis, an important example is the so-called oxide "monolayer" catalyst, which consists of an ultrathin metal oxide film on other metal substrate. On the other hand, the controlled growth of arrayed metal nanostructure on solid surface by self-organized method is of great interest both from the fundamental and technological points of view. So far, a monolayer vanadium (V)-oxide film on Pd(111) is known to form a (4×4) nanomesh structure. Group 14 elements, Si, Ge, Sn, and Pb, were chosen because they exhibit a variety of physical and chemical properties depending on mass number and environmental factors and show catalytic properties on a transition metal surface. In the present study, I study the crystalline structure of monolayer and submonolayer cerium (Ce)-oxide films on Rh(111) and examine the adsorption site of group 14 elements on monolayer Ce-oxide films and (4×4) V-oxide nanomesh. The geometric structure of ultrathin Ce-oxide films on Rh(111) was investigated using scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and density functional theory (DFT) calculations. I prepared ultra-thin Ce-oxide films on Rh(111) with layer thickness dependence by postoxidizing the metallic Ce films in an oxygen atmosphere. For quantitative analysis of Ce-oxide films, I used the combined techniques of X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS) to determine the concentration of Ce and O atoms. The number of Ce and O atoms in the unit cell was successfully estimated. The phase diagram of the surface structure of Ce-oxide films on Rh(111), as a function of Ce coverage and annealing temperature under an oxygen atmosphere, was obtained from LEED patterns and STM images. The first-oxide-monolayer Ce-oxide film on Rh(111) with (4×4) structure was formed at Ce coverage lower than 0.5 ML. The structure of monolayer Ce-oxide film with the (4×4) phase was determined using the missing Ce atoms model with a nanomesh-like structure. The adsorption site of group 14 elements on the monolayer (4×4) Ce-oxide film was investigated using DFT calculations. On the (4×4) V-oxide nanomesh, the adsorption site of group 14 elements in the nanohole or on the nanomesh has been investigated.

(1) Growth and structure of Ce-oxide films on Rh(111) (Chapter 3)

The Ce-oxide films were obtained by annealing the metallic Ce films at the Ce coverage less than 2 ML at various temperatures in an oxygen atmosphere. The atomic-scale surface structures of Ce-oxide films with layer thickness dependence were observed by STM. The surface phase of the Ce-oxide films on Rh(111) was investigated using the LEED patterns and displayed an overview of surface phase structures as a function of Ce coverage and annealing temperature. The concentration of the Ce^{4+}/Ce^{3+} and O ion in the Ce-oxide films at various thicknesses was measured by XPS and was estimated by fitting the Ce 3*d* and O 1*s* spectra.

(2) Quantitative analysis of Ce-oxide films on Rh(111) (Chapter 4)

For quantitative analysis of Ce-oxide films, I used the combined techniques of XPS and RBS. The Ce or O concentration was quantitatively analyzed using calibration curves with reference data points, which are measured by Ce-oxide films on graphite substrates and standard samples. Calibration curves were obtained as a function of the XPS Ce 3*d* or O 1*s* intensity and the Ce or O coverage was determined by RBS measurement. Structural models of Ce-oxide film were discussed based on a cross comparison with alternative techniques. The number of Ce and O atoms in the unit cell was successfully estimated.

(3) Computational study of geometrical structure of monolayer Ce-oxide film and adsorption sites of group 14 elements (Chapter 5)

I determined the structural models of Ce-oxide films on Rh(111) with layer dependence from total energy using first principle calculations based on DFT analysis. The simulated STM image of structural model is in good agreement with the experimental STM image. The adsorption behavior of group 14 elements in monolayer Ce-oxide film on Rh(111) has been systematically investigated by DFT calculations.

(4) Growth and structure of group 14 elements in (4×4) V-oxide nanomesh on Pd(111) (Chapter 6)

I prepared the (4×4) V-oxide nanomesh on Pd(111) by postoxidizing the metallic V film at coverage of 0.3 ML in an oxygen pressure of 3.0×10^{-7} mbar at annealing temperature of 550 K. I deposited the group 14 elements on the (4×4) V-oxide nanomesh films at coverage of 0.001 ML at room temperature. The adsorption behavior of group 14 elements in the (4×4) V-oxide on Pd(111) has been systematically investigated by STM and DFT calculations.

(5) Conclusions (Chapter 7)

Quantitative analysis of the Ce-oxide films using XPS in combination with RBS led to the successful estimation of the number of Ce and O atoms in the unit cell. A monolayer Ce-oxide film with a nanomesh-like structure was obtained. The adsorption site of group 14 elements on V or Ce-oxide films on metal surface has been successfully determined.