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STM and XPS study of $CeO_2(111)$ reduction by atomic hydrogen

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ABSTRACT

Reduction of $CeO_2(111)/Ru(0001)$ surface by atomic hydrogen was investigated using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). We observed the formation of oxygen vacancy trimers and hydroxyl trimers on the stoichiometric $CeO_2(111)$ surface when it was exposed to atomic hydrogen at room temperature. The reaction of an impinging hydrogen atom with a surface oxygen atom yields a hydroxyl species, which diffuse on the surface until stabilized by the formation of OH trimers. The hydrogen atoms were located at atop sites of the oxygen atoms in the topmost surface layer. A reaction between the hopping hydrogen atom and the hydroxyl species yields a water molecule, which is desorbed from the surface leaving an oxygen defect. The oxygen vacancies were also observed as a trimer of vacancies. XPS measurements showed an increase of a reduced Ce and hydroxyl species with an amount of exposed hydrogen atoms. The former was estimated by measuring the ratio of Ce^{3+}/Ce^{4+} in the Ce 3d components. Our study shows the formation of hydroxyl trimer species in atomic scale upon atomic hydrogen exposure to $CeO_2(111)$ surface which could offer new catalytic activity.

1. Introduction

Rare earth metal oxide, cerium dioxide (CeO_2, ceria), has attracted a large attention due to its applications in automotive technology and various industrial processes [1–4], which is due to the fact that cerium ions can change the oxidation states from Ce^{4+} to Ce^{3+} in a reversible way [5,6]. Since in many catalytic processes ceria may come in contact with hydrogen, the reduction study of a ceria surface mediated by hydrogen is of great technological importance.

Several experimental studies on ceria powders reported the formation of hydroxyl species and oxygen vacancies when exposed to molecular hydrogen [7–10]. Chen et al. reported the interaction of atomic hydrogen with stoichiometric and reduced ceria surfaces by means of XPS and TDS measurements. Surface hydroxyls on $CeO_2(111)$ surface can undergo two reaction paths depending on the concentration of the oxygen vacancies, which are the formations of water and molecular hydrogen [11]. Hydroxyl species were reported to recombine and desorb as water or molecular hydrogen depending on the substrate temperature during hydrogen dosing. The interaction of hydrogen with the ceria surface was calculated to be a strongly exothermic process [12–16]. Alam et al. reported that consecutive attacks of two different hydrogen atoms on the same surface oxygen atom results in the abstraction of oxygen atom preceded by Ce – O bond breaking [12]. Chen et al. showed that the hydrogen reduction of Ce^{4+} to Ce^{3+} is accompanied by water desorption [14]. These theoretical studies have predicted the formation of hydroxyl species when hydrogen atoms are chemisorbed on the ceria surface. Since surface hydroxyls play a key role as Lewis acid or base sites on metal oxides in many catalytic processes [17], hydroxyls on oxide surfaces have attracted attention of intensive experimental and theoretical research [14,18–34]. However, none of them provided an atomic scale characterization of the defects and hydroxyl species on a ceria surface.

In this study, we examined the reduction of $CeO_2(111)$ surface by exposing the clean $CeO_2(111)$ surface to hydrogen atoms. The surface characterizations were executed by using scanning tunneling microscope (STM) and X-ray photoelectron spectroscopy (XPS). An epitaxial film of $CeO_2(111)$ was formed on Ru(0001) surface with atomically flatness and small defect density [35]. The $CeO_2(111)$ surface after being exposed to H atoms at room temperature showed characteristic protrusions and depletions in STM images, which were attributed to hydroxyl species and oxygen defects, respectively. These interpretations were further supported by XPS spectra, which clearly indicated the change of oxidation states in the Ce 3d and O 1s components. Interestingly both the protrusions and depletions always appeared as trimers, indicating the bonding nature of the interactions between hydroxyls.

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2. Experimental

All experiments were carried out in the ultra-high vacuum (UHV) condition (base pressure below 1×10^{-8} Pa) equipped with variable temperature STM (Omicron LT-STM), low-energy electron diffraction (LEED) optics, a hemispherical analyzer (Omicron EA125HR), a Mg/Al twin anode X-ray source (Omicron DAR400) and standard surface cleaning system [36]. The Ru(0001) single crystal (8 mm diameter and 2 mm thick, Mateck), used as substrate for $CeO_2(111)$ thin film, was cleaned by repetitive cycles of Ar^+ sputtering (1 keV) followed by annealing at 1073 K in an O_2 ambient of 5×10^{-5} Pa to remove hydrocarbons. The surface was finally annealed at 1423 K for 60 s to remove the oxides. Clean Ru(0001) was confirmed by LEED, XPS and STM. Epitaxial $CeO_2(111)$ thin film was prepared on the clean Ru(0001) substrate by evaporating Ce atoms in oxygen ambient [37–39]. We used a deposition rate of 0.22–0.35 Å/min and a partial pressure of O_2 of 5.5×10^{-5} Pa. A formation of an atomically flat and stoichiometric $CeO_2(111)$ surface was confirmed by using LEED, XPS and STM. It was confirmed that enlarged islands of $CeO_2(111)$ surface can be formed when the substrate temperature during the evaporation is kept slightly lower than the temperature at which surface reduction occurs (~1096 K). Non-contact atomic force microscopy (NC-AFM) measurement was performed in air with using a commercial available instrument (XE-100, Park Systems, Inc.).

Hydrogen molecules were cracked to hydrogen atoms using a hot tungsten filament of 1500 K which was placed in the vicinity of the $CeO_2(111)$ surface. The amount of dosing was calibrated using Langmuir ($1\ L = 10^{-6}$ Torr-s) estimation from the pressure of the chamber. All of the STM measurements were carried out at 150 K, while atomic hydrogen dosing and XPS measurements were conducted at room temperature. Mg Kα ($E = 1253.43$ eV) X-ray source was used and binding energy scale was calibrated using Au4f feature at 84.0 ± 0.05 eV for known standards. To calculate Ce^{3+}/Ce^{4+} ratio Shirley background was subtracted from all spectra and the peaks were deconvoluted using the Gaussian–Lorentzian peak fitting.

3. Results and discussion

We formed an epitaxial $CeO_2(111)$ film on the Ru(0001) surface. Since a high temperature annealing (~1000 K) is required to obtain well-ordered $CeO_2(111)$ films, it is preferable to use a metal substrate with a high melting temperature [37–41]. The Ru metal satisfies this condition and there are no reports of a formation of Ru–Ce alloy at ~1000 K [40].

Fig. 1 shows STM images observed on the $CeO_2(111)$/Ru(0001) film. We prepared the ceria film on the Ru(0001) substrate considering full coverage, large islands, and minimum reduction. NC-AFM observation in micron scale (image is not shown here) confirmed the compact ceria islands on the Ru(0001) islands. The maximum height of the islands was more than ~10 ML. However, the actual island height remained unknown in our measurement technique because the Ru(0001) was not exposed. Bare Ru(0001) substrate was not observed so far in both AFM and STM observations. Moreover, no substrate spots were revealed in LEED pattern also. The fully covered ceria film on Ru(0001) facilitated the hydrogen reduction study on oxide surface avoiding the substrate effect. The substrate temperature was kept at ~1070 K during the deposition. We found that enlarged islands could be obtained by using this substrate temperature, which was slightly lower than the temperature where the reduction of the surface started (see Fig. 1a). On the terrace of the film of second layer, we found a moiré pattern in the atomic lattice, which is shown in Fig. 1b. The observation of the moiré pattern indicates a good commensurate film growth on the Ru(0001) surface [41]. Each bright spot corresponds to a surface oxygen atom [42–44]. The lattice shows the three-fold symmetry and the nearest neighbor distance was 0.38 nm, which agrees well with lattice parameter of the $CeO_2(111)$ surface. We note that there are circular protrusions in the terrace part. Similar circular protrusions were observed on the Ru(0001) surface after the cleaning. Jakob et al. reported a similar protrusion for Ru(0001) surface after the cleaning process of Ar sputtering and annealing, which was explained by the subsurface gas bubbles induced by Ar ion-bombardment/implantation [35,45].

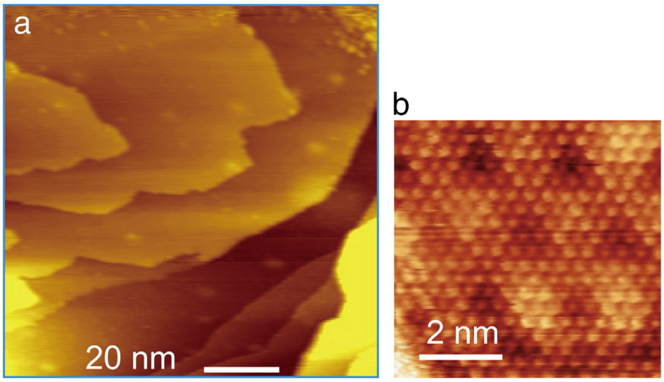

Fig. 1. (a) $CeO_2(111)$ epitaxial film on Ru(0001) grown at the temperature of 1060 K. STM image is $100 \times 100\ nm^2$ in size and obtained with tunneling conditions of $Vs = -2.0$ V, $I = 0.1$ nA. (b) A magnified image of the terrace part of (a). Oxygen atoms are images with a three-fold symmetry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We show the variation of the STM images before and after the dosing of hydrogen atoms in Fig. 2a and c, respectively. These two STM images were visualized by showing an error signal of the tunneling current from the set-point value. The image of this mode is equivalent to a differentiated topographic image, which is sensitive to small changes in height even if different height structures coexist in a wide scanning area.

In Fig. 2a, we see the straight step edges which appeared as white/black lines. In the terrace part, there were no noticeable structures except circular structures that correspond to the Ar-gas bubble related structure mentioned above. A topographic STM image of the terrace part shown in Fig. 1b reveals a defect free stoichiometric surface of $CeO_2(111)$. Note that the moiré pattern is less obvious than that shown in Fig. 1b, due to the higher film thickness at the terrace where the STM image was obtained.

The prepared defect-free $CeO_2(111)$ surface was exposed to hydrogen atoms of 0.53 L at RT. In Fig. 2c, we see newly appeared dots in the terrace parts which cannot be seen in Fig. 2a. In the topographic image shown in Fig. 2d, two types of new features can be clearly identified, which were observed as protrusions and depressions in the STM image and are marked with a circle and a triangle, respectively.

A magnified topographic image of the bright protrusion is shown in Fig. 2e. It is found that each protrusion consists of three equivalent protrusions which are separated by ~0.38 nm arranged in an orthogonal triangle shape. The center of the bright spot was located at the atop site of the oxygen atoms of $CeO_2(111)$. The height of the protrusion was estimated ~50 pm from the oxygen layer. We like to stress that they always appear as trimers, and we could observe neither monomer nor dimer of protrusions.

A similar trimer feature was observed in previous reports by using NC-AFM [46] and STM [47] when the $CeO_2(111)$ surface was exposed to water. It is most likely that the protrusions observed in this experiment were a trimer of hydroxyls, in which an atomic H atom is attached to an oxygen atom in the top-most surface, which is consistent with previous reports [7–9]. In addition a hydroxyl on other metal oxide surfaces also appears as a protrusion in STM image [26,48].

Another interesting feature is the depleted area, which appeared after the H exposure, is composed of a trimer of defects. Fig. 2f shows a magnified image of a depleted area. Most plausible origin of the depleted area is an oxygen defect. We analyze the depleted area by superimposing the lattice of oxygen sites (see Fig. 2f). The lattice points