The growth of CeO\textsubscript{x}(111) thin films on Ru(0001)

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Abstract. Ceria has attracted great attention in recent years in the catalysis community. Metal catalysts supported on ceria exhibit a promising catalytic activity due to the ceria’s unique redox properties and oxygen storage capacity. The purpose of this paper is to look at the fundamental aspect of CeO\textsubscript{x}(111) thin films on Ru(0001). The investigation presented in this paper utilizes the surface science method to understand the properties of CeO\textsubscript{x}(111). In one component, through a series of XPS studies, it is shown that the deposition of Ce in the presence of oxygen on Ru(0001) can produce ceria thin films. Fully oxidized CeO\textsubscript{2} can be obtained with an oxygen pressure of 2 \times 10^{-7} \text{Torr}. With the decrease in the oxygen pressure, partially reduced CeO\textsubscript{x} films can be prepared. Moreover, STM images are collected from the CeO\textsubscript{2} growth in the presence of 2\times10^{-7} Torr of oxygen and partially reduced ceria with oxygen pressures of 8\times10^{-8} Torr. These films can completely cover the Ru(0001) substrate. The measured step height is about 0.3 nm, which is consistent with the 0.313 nm spacing of O-Ce-O tri-layers in the CeO\textsubscript{2}(111) fluorite bulk structure.

1. Introduction
Cerium oxide or ceria is a rare-earth metal oxide. Among several relevant applications of ceria are catalytic support for three-way catalyst [1], solid-oxide fuel cells [2-4], and solar cells [5]. Ceria possesses some distinctive properties, such as its flexible convertibility between Ce\textsuperscript{4+} and Ce\textsuperscript{3+} and its ability to store oxygen. These unique properties are the following requirement for ‘well-defined oxides’, according to Barteau.[6] Figure 1 is a depiction of cubic fluorite of ceria. In the ceria crystal structure, there are four oxygens and eight ceria. The structure is a tetrahedron with ceria as the center, and each

![Figure 1: The Fluorite structure of CeO\textsubscript{2}](image)
of the corners is inhabited by oxygen atoms. Ce\textsuperscript{4+} cations are positioned at the corner and face center of the cube. Oxygen anions are located at the tetrahedral sites. Every Ce\textsuperscript{4+} cation is coordinated by eight O\textsuperscript{2-} anions whereas O\textsuperscript{2-} is coordinated with four Ce\textsuperscript{4+} cations. The lattice constant of ceria is 5.41 Å. There are three most known low-index crystallographic planes of ceria. They are (111), (110), and (100). The (111) surface is oxygen-terminated consisting of neutral repeatable (O-Ce-O) sandwiches with zero perpendicular dipole moment. It has an outmost layer of oxygen anions and an exposed subsurface layer of cerium cations, which are surrounded by seven oxygen anions and have one coordination vacancy relative to those in the bulk. There are two folds of factors to explore ceria with a specific plane. Firstly, the surface structures of the catalytic supports can influence the structural and electronic properties of the metal catalyst, which can influence its catalytic reactivity. Secondly, it has been proposed in the literature that oxygen vacancies and lattices can greatly influence the reactivity of the metal particle [7, 8]. The different surface structures of the ceria can provide different oxygen surfaces, which may affect the reactivity of the metal differently.

To gain a fundamental understanding of ceria, the surface chemistry method is utilized. This means ceria is studied on a well-defined surface and inside a clean environment (pressure in the ultra-high vacuum region). To mimic the bulk material, ceria is made into a thin film form. Moreover, the epitaxial method is employed for growing ceria thin film. Furthermore, the implementation of the metal substrate is of importance. In this paper, the synthesis of the (111) ceria surface is performed. The choice of (111) surface is made because it is the most stable among all ceria surfaces. There are many metals that can be used as a substrate for growing ceria(111). Several low index metals have been utilized such as Pt(111) [9], Cu(111) [10], Ni(111) [11], and Ru(0001) [11]. This paper focuses on ceria thin film growth on Ru(0001).

The paper aims at achieving two objectives. The first objective is to determine the effect of different oxygen pressure on the stoichiometric value of ceria. The second objective is to reveal whether well-ordered ceria can be grown on top of Ru(0001). Studies [11-13] suggested that there is no alloy formation between Ru(0001) and ceria thin film, and ceria thin film can be easily removed from Ru(0001) by using Ar sputtering method. The aforementioned items are the advantage of using Ru(0001) as a metal substrate. Moreover, based on the properties of ceria, it can be observed that the reducibility of ceria can be controlled by using different oxygen pressure.

2. Method
The experiments were conducted in an ultra-high vacuum (UHV) chamber manufactured by Omicron Technology. The base pressure of the chamber is below 5 × 10\textsuperscript{-11} Torr. Briefly, the chamber is equipped with a variable-temperature scanning tunneling microscope (VT STM XA 650), an EA 125 U1 hemispherical electron spectrometer, a DAR 400 twin-anode X-ray source, and 4-grid SPECTALEED optics. Additionally, it contains an ISE 5 cold cathode sputtering ion source for sample cleaning, homemade water-cooling metal evaporation sources for Ce deposition. The Ru crystal (Princeton Scientific Corp., diameter 10 mm, one side polishing, roughness < 0.03 μm, orientation accuracy < 0.1 degrees) was mounted to a solid tantalum plate by spot-welded Ta straps. The Ru surface was cleaned by repeated cycles of Ar ion sputtering (1 KeV, ~3 μA sample current) followed by annealing to 1300 K for 45 s. The surface cleanliness of Ru single crystal can be confirmed by scanning tunneling microscope (STM), X-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED).

3. Results and Discussions

3.1. Scanning Tunnelling Microscopy (STM) of Ru(0001) and CeO\textsubscript{2}(111)
STM analysis of clean Ru(0001) was performed immediately after the cleaning process. Before ceria's growth, it is crucial to clean Ru(0001). Figure 2 implies that there is no contaminant present in the Ru(0001). The Ru(0001) surface was scanned in at least 5 different regions, but only STM images around the center of the crystal are shown. Figure 2(a) is a measurement of bright spots on the Ru(0001).
Measurement of each of the bright spots yields a height of less than 0.2 nm. This is an indication of Ar bubbles. Ru(0001) is cleaned using Ar sputtering methods, which, due to its repetition, occasionally causes an embedding of Ar on Ru(0001). Fortunately, these Ar bubbles do not disturb the growth of ceria. The measurement indicates that the height of Ar bubbles is only at a level of atomic height. The bright circle in Figure 2 is a result of Argon bombardments. The measurement of the bright feature gives a number of around 0.2 nm and can be seen in Figure 2(b). Once ceria is grown on top of Ru(0001), Ar bubbles disappear. The terrace of Ru(0001) is wide, and it has an atomic step. From line profile 2(a), the Ru(0001) terraces have around 40-50 nm width and 0.2 nm height in between terraces.

![Figure 2](image)

**Figure 2** Scanning tunneling microscopy of Ru(0001) (a) is the size Ru(0001) terraces and (b) is the Ar bubbles.

The deposition flux of ceria is determined by using STM. For this purpose, sub-monolayer ceria was prepared as an example (Figure 3). Ceria grows in triangular and hexagonal islands with the Ru substrate partially exposed. Using the STM data analysis software WSXM [14], the ratio between the area of ceria and area of Ru is found to be 0.5. The CeO$_2$(111) fluorite bulk structure consists of atomically flat terraces consisting of O-Ce-O tri-layers with a spacing of 0.313 nm. The measured height of the ceria islands is about 0.5 nm.

![Figure 3](image)

**Figure 3** (a) Scanning tunneling microscopy of sub-monolayer of CeO$_2$(111) (b) Line profile analysis of sub-monolayer CeO$_2$(111).
These islands are two-layer high. Considering the area ratio between ceria and Ru, the layer thickness, and a deposition time of 10 minutes, the flux for the ceria is determined to be 0.01 ML/min. Figure 2(a) is the XPS spectra of clean Ru(0001), which is obtained after the cleaning process (data not shown). There is no impurity present on the surface. All peaks are corresponding to Ru(0001).

After growing sub-monolayer ceria, the next step is growing ceria thin film in two different oxygen pressure. The first oxygen pressure is $8 \times 10^{-8}$ Torr and the second oxygen pressure is $2 \times 10^{-7}$ Torr. The first oxygen pressure will give the STM images of Figure 4(a). STM images indicate that there are many surface defects and oxygen vacancies that are present in the CeO$_x$.

![Image](a)

**Figure 4** The height and width analysis of sub-monolayer CeO$_x$(111).

Ceria thin films are prepared by deposition of Ce onto a Ru (0001) single crystal while keeping the Ru(0001) temperature at 700 K from a homemade water-cooling e-beam evaporator in the presence of oxygen and subsequently by annealing the surface to 1150 K for 2 min by electron bombardment. Ce flux of 0.07 ML/min was used. Figure 2 exhibits several STM images that indicate the growth process of ceria. At 10 min, CeO$_x$(111) on Ru(0001) display triangle and hexagonal island. Since the method that we are using is epitaxial growth, the ceria surface is tailored into the Ru(0001) surface. When a shorter time is used, CeO$_x$(111) prefers to land on Ru(0001). There is no ceria on top of ceria at the initial growth (see Figure 3). The line profile of CeO$_x$(111) at 10 min growth (see Figure 3(a)) shows a triangle and hexagonal islands at the surface, which indicates the presence of (111) plane. The height of the ceria island is around 0.6 nm. By further increasing the growth time to 25 min (see Figure 4 (a)), ceria is started to land on top of other ceria surfaces. The height from bright contrast in the surface to the dark pit is around 1 nm. The dark protrusion in the STM image is an indication of the uncovered part of Ru(0001). Figure 4(c) is the STM image of ceria with 40 min time growth. The terraces in Figure 4(d) is not as wide as in Figure 4. The STM images indicate that time of growth influences the morphology of ceria on Ru(0001). The dark pit in Figure 4(c) is lesser compared to the one in Figure 4(a). Ceria has a thickness of 0.07 nm for 10 minutes of growth. By increasing the growth time to 20 minutes, the thickness of the ceria is increased to 0.52 nm.
3.2. X-Ray Photoelectron Spectroscopy (XPS) of Ru(0001) and CeO$_x$(111)

XPS survey scan is used to examine the elemental composition of the Ru(0001) surface. A survey scan with binding energy ranging between 0 – 1100 eV from Ru is shown in Figure 5. In the spectrum, we identify the XPS peaks of photoelectrons that originated from different core levels of Ru. We conclude that no other peaks not associated with Ru are visible. Main contaminations for Ru include oxygen and carbon. We did not observe O 1s peak in the range between 522 and 542 eV. It is difficult to identify C from Ru based on XPS studies since C 1s XPS peak overlaps with the Ru 3d region. Our STM data indicate that the surface is free of C as discussed later. Ru 3d XPS region (290 eV – 275 eV) was also collected (data not shown). One of the purposes of acquiring Ru 3d region is to use it as an XPS instrument calibration by comparing Ru 3d peak positions and intensities at various experimental dates.

Upon the growth of ceria thin films, XPS survey scan spectrum is first collected. Shown in Figure 5(b) is a survey scan from a partially reduced CeO$_x$ film grown with an oxygen pressure of 8 x 10$^{-8}$ Torr. We conclude that all peaks are correlated to cerium, oxygen, and ruthenium. No contaminants are found in the grown film. Ce 3p, 3d, and 4p XPS peaks, as well as x-ray induced Ce MNN Auger peak, were observed. The most intense peak for Ce is the Ce 3d with the binding energy range between 870 – 925 eV. By monitoring Ce 3d XPS region at different locations on the Ru crystal and comparing their intensities, it is established that the grown ceria film is uniform across the Ru surface.

By monitoring the Ce 3d XPS region using XPS, we can also determine the oxidation state of Ce in ceria thin films. The Ce 3d XPS region consists of a collection of 10 peaks originated from different Ce oxidation states (Ce$^{3+}$ and Ce$^{4+}$) and their 4f configurations. For example, the initial state for Ce$^{3+}$ is 3d$^{10}$ 4f$^1$. Its final state can have two forms (3d$^9$ 4f$^2$ V$_{n-1}$ and 3d$^9$ 4f$^1$ V$_n$). Here, V denotes the valence band. Therefore, there are four peaks in the Ce 3d XPS region corresponding to two pairs of spin-orbit doublets characteristic of Ce$^{3+}$. These peaks are labeled u, u', v, and v; u and v refer to the 3d$_{3/2}$ and 3d$_{5/2}$, respectively. For Ce$^{4+}$, the initial state is 3d$^{10}$ 4f$^0$. The final state can have three forms including 3d$^9$ 4f$^1$ V$_{n-2}$, 3d$^9$ 4f$^1$ V$_{n-1}$, and 3d$^9$ 4f$^0$ V$_n$. Thus, there are six peaks in the Ce 3d XPS region associated with Ce$^{4+}$ (u, u', u'', v, v', and v''). Partially reduced ceria thin film grown in the study consists of cerium with oxidation states of both +4 and +3. Peak fitting of Ce 3d XPS spectrum is used to determine the percentage of Ce$^{4+}$ and Ce$^{3+}$ ions in the ceria film and the stoichiometric value x in CeO$_x$. Peak fitting of Ce 3d from partially reduced ceria is shown in Figure 6. From this figure, it can be clearly seen that all the corresponding peaks have a specific location. The stoichiometric value of ceria can be determined based on the area percentage of each peak. Hence, different oxygen pressure during ceria growth gives us different stoichiometric value.
Figure 6 XPS spectra of Ce 3d from CeO$_x$(111)

Figure 6 compared the different sets of Ce 3d spectra. Ce 3d from CeO$_2$ and Ce$_2$O$_3$ is used as an indicator for Ce 3d analysis from CeO$_x$(111). XPS analysis of CeO$_x$ also includes the analysis of O 1s region (535 – 524 eV). The O 1s region (see Figure 7) has a single peak at the binding energy of ~529.2 eV. Literature studies (see, for example, [15]) establish the fact that the oxygen peak 529.2 eV indicates the presence of lattice oxygen in ceria. The shoulder peak at 531.9 eV is a new feature and can be ascribed to defective oxides or surface oxygen ions with low coordination in the literature [11, 15, 16]. XPS studies have shown that the deposition of Ce in the presence of oxygen on Ru(0001) can produce ceria thin films. Fully oxidized CeO$_2$ can be obtained with an oxygen pressure of 2 x 10$^{-7}$ Torr. With the decrease in the oxygen pressure, partially reduced CeO$_x$ films can be prepared.

Figure 7 XPS spectra of Ce 3d from CeO$_x$(111).
The black dash line indicated the shoulder peak area.

3.3. Low Energy Electron Diffraction (LEED) of Ru(0001) and CeO$_x$(111)

LEED can also be used to determine whether Ru crystal is contaminated with oxygen. It is known that oxygen can form (2x2) and (2x1) adsorption on Ru (0001), which can contribute additional spots in the LEED pattern of Ru.131. From Figure 8(a), we did not observe additional LEED spots from oxygen. This also suggests that the Ru crystal is free of oxygen. Figure 8(a) is a LEED image of clean Ru(0001). The six spots in the LEED images represented the (0001) plane of Ru(0001). The epitaxial growth of
ceria on Ru(0001) can be checked by investigating the LEED image of ceria on Ru(0001) (Figure 8(b)). The ability to take LEED images for ceria on Ru(0001) means that the epitaxial growth is possible for ceria on Ru(0001). The spots of ceria on Ru(0001) is indicated as p(1.4×1.4). As alluded to earlier, Ru(0001) is probably the most suitable substrate for ceria. This is true because no alloying between ceria and Ru(0001) can occur. The LEED pattern for grown CeOx(111) thin films are collected to examine the long-range order. Shown in Figure 8(b) as an example from CeO1.86, the LEED pattern of ceria shows six spots forming a hexagonal structure, confirming the formation of the ceria film with the (111) orientation. This comparison also indicates that the crystallographic direction of the ceria thin film is an alignment with the principle azimuth direction of the Ru(0001). No LEED pattern from the Ru substrate was visible that suggests that the film fully covers the Ru surface. The LEED pattern collected from CeO2 is comparable to that from reduced CeO1.86 crystal and is covering the Ru(0001) surface (data is not shown).

![Figure 8 LEED images of (a) Ru(0001) and (b) CeOx(111)](image)

4. Conclusions
Ceria, successfully used as additives in three-way automobile emission-control catalysis, has attracted great attention in recent years in the catalysis community. Metal catalysts supported on ceria exhibit promising catalytic activity due to the unique redox properties and oxygen storage capacity of ceria. In these studies, XPS studies have shown that the deposition of Ce in the presence of oxygen on Ru(0001) can produce ceria thin films. Fully oxidized CeO2 can be obtained with an oxygen pressure of 2 x 10⁻⁷ Torr. With the decrease in the oxygen pressure, partially reduced CeOx films can be prepared. Furthermore, STM images were collected from the CeO2 growth in the presence of 2×10⁻⁷ Torr of oxygen and partially reduce ceria with oxygen pressures of 8×10⁻⁸ Torr. These films can completely cover the Ru(0001) substrate. The measured step height is about 0.3 nm, consistent with the 0.313 nm spacing of O-Ce-O tri-layers in the CeO2(111) fluorite bulk structure. In summary, the overall data clearly demonstrate that the oxide thin film approach provides a novel easy method to prepare well-ordered CeOx(111) thin films with controlled degrees of Ce reduction.

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