

Oxidation kinetics for Ni(111) and the structure of the oxide layers

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The oxidation kinetics for Ni(111) surface and the structure of the oxide layers grown at room temperature were analyzed by high-resolution medium energy ion scattering using isotopically labeled $^{18}\text{O}_2$. Initially, the surface showed a reflection high energy electron diffraction (RHEED) pattern of the Ni(111)-(2×2)-O chemisorption structure at an oxygen exposure of a few langmuir (1 L: 10^{-6} Torr s) and started to form NiO(111) layers above 10 L. The oxide thickness was saturated with six atomic layers at oxygen exposure of 160 L. The saturated NiO(111) surface shows a (1×1) RHEED pattern not $p(2\times 2)$ and consists of two domains: NiO(111)-[112̄]/Ni(111)-[112̄] (primary) and NiO(111)-[110̄]/Ni(111)-[112̄] (a small fraction). The elemental depth profile corresponds to the octopolar reconstruction terminated with Ni (0.25 ML) [1 ML = 1.33×10^{15} atoms/cm²: areal density of NiO(111)]. The oxide surface grown epitaxially probably takes a precursor state of the octopolar structure with significant distortion because of a large lattice mismatch of 19% between NiO(111) and Ni(111). Two step oxidation using $^{18}\text{O}_2$ and $^{16}\text{O}_2$ clearly indicates that oxidation takes place at the top surface obeying the Cabrera-Mott mechanism. The potential barrier for the jump from Ni into the NiO layer is derived to be 2.36 eV.

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Polar rocksalt surfaces were long believed to be unstable because of a nominally infinite surface energy. In fact, it was experimentally evidenced that the clean surfaces faceted into neutral {100} type planes.¹ However, Wolf² predicted that the (111) surfaces of rocksalt crystals were stabilized by taking a $p(2\times 2)$ -octopolar structure. Indeed, the $p(2\times 2)$ structure was observed for the NiO(111) surfaces grown epitaxially on Au(111) (Refs. 3 and 4) and on single crystal NiO(111).⁴ Rohr *et al.*⁵ oxidized Ni(111) to form the NiO(111) surface and observed a diffused $p(2\times 2)$ pattern for the surface after annealing that covered with hydroxyl groups. According to the report of Barbier *et al.*,⁴ the octopolar reconstruction formed on the single crystal NiO(111) takes a single Ni termination and that on NiO(111) thin films grown on Au(111) has both Ni and O terminations.

In this work, we oxidize the single crystal Ni(111) to grow epitaxially NiO(111) layers at room temperature (RT) and clarify the surface structure of the NiO(111) by means of high-resolution medium energy ion scattering (MEIS). In addition, analysis using isotopically labeled $^{18}\text{O}_2$ reveals the oxidation kinetics. The present MEIS analysis using a toroidal electrostatic analyzer (ESA) allows a layer-by-layer analysis.⁷ The NiO(111) surface exhibits a (1×1) RHEED (reflection high energy electron diffraction) pattern not the $p(2\times 2)$ but takes a layered structure of Ni(0.25 ML)/O(0.75 ML)/NiO(111) suggesting a octopolarlike structure terminated with Ni. Here, 1ML (monolayer) is defined as the areal density of the NiO(111) plane (1.33×10^{15} atoms/cm²). The oxidation kinetics of Ni has been studied for a long time in terms of the Cabrera-Mott oxidation mechanism.⁶ In this study, we clearly evidence that Ni ions are transported to the surface and oxidation takes place at the top surface.

We prepared the clean surface of a single crystal Ni(111) by repetition of sputtering with 0.75 keV Ar⁺ and annealing

at 650 °C under an ultrahigh vacuum condition. The RHEED observation showed a clear (1×1) pattern [see Fig. 1(a)] and no surface contaminations were confirmed by MEIS using 120 keV He⁺ ions under a double alignment condition ([011] incidence and [211̄] emergence). The clean surface was then exposed to O₂ at a pressure ranging from 1×10^{-8} to 1×10^{-6} Torr at RT. At an initial stage of oxidation with O₂ exposure from 1 to 3 L the surface showed a (2×2)-RHEED pattern [see Fig. 1(b)] indicating oxygen chemisorption.⁸⁻¹⁰ The NiO(111) phase starts to grow for O₂ exposure above 10 L [see Fig. 1(c)] and oxidation was saturated at O₂ exposure of 160 L. As seen from the RHEED pattern [Fig. 1(d)], the NiO(111) layer grows epitaxially and has two types of domains: NiO(111)-[110̄]/Ni(111)-[110̄] (primary) and NiO(111)-[112̄]/Ni(111)-[110̄] (a small fraction).

Figure 2(a) shows the MEIS spectra observed for the

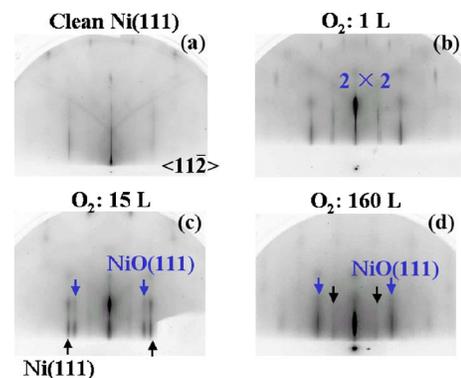
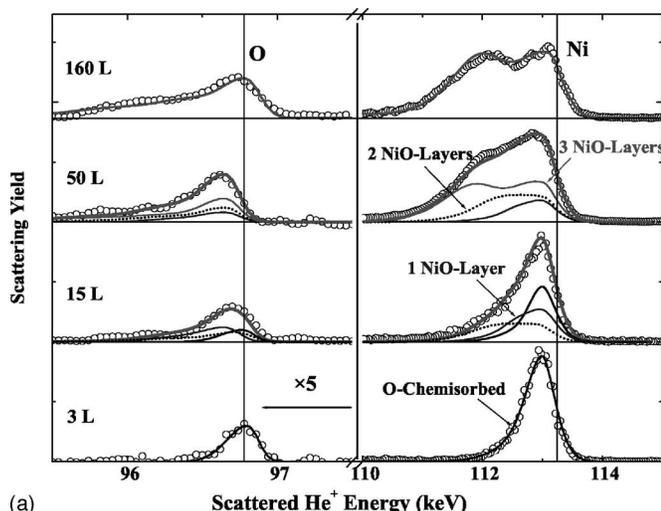
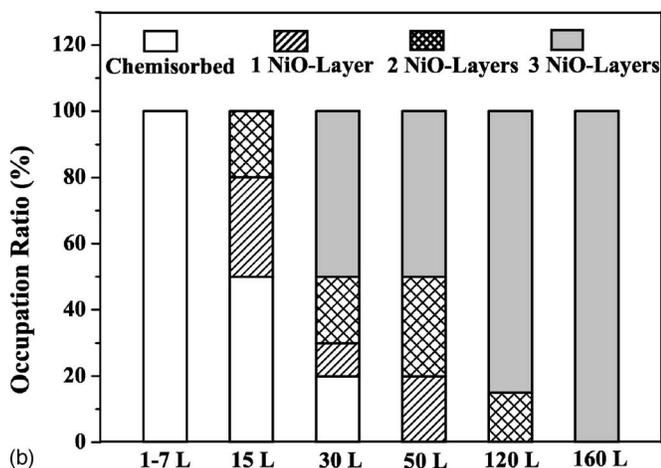


FIG. 1. (Color online) (a) RHEED patterns observed for clean Ni(111) surface, oxidized with O₂ exposure of (b) 1 L, (c) 15 L, and (d) 160 L. Here, 30 keV electron beams were incident along the [112̄] axis of Ni(111).



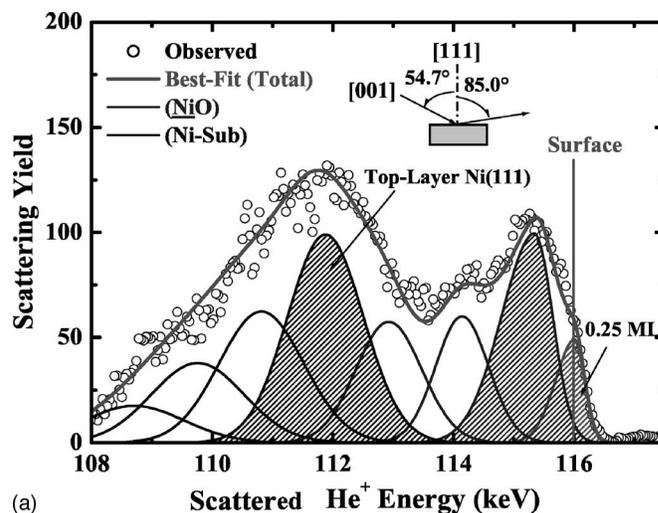
(a)



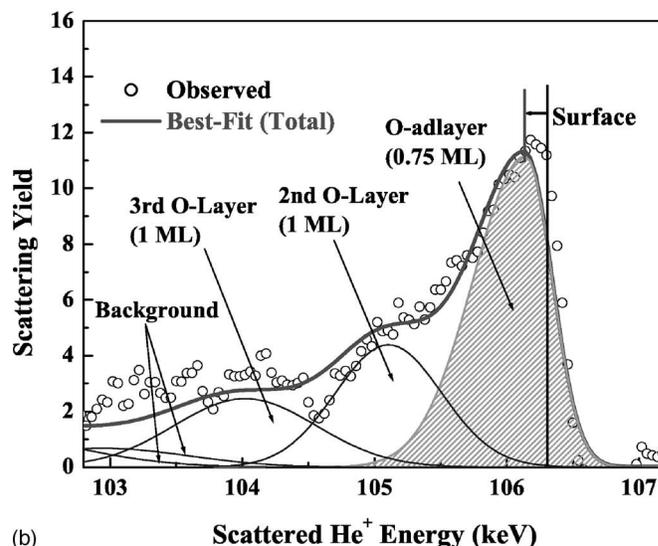
(b)

FIG. 2. (a) MEIS spectra observed for the Ni(111) surfaces oxidized at RT for O₂ exposure of 3, 15, 50, and 160 L. 120 keV He⁺ ions were incident along the [001] axis and backscattered to 70.0° with respect to the surface normal. The vertical lines indicate the energy positions for He⁺ ions backscattered from O and Ni atoms on the top surface. The solid curves are the simulated MEIS spectra best-fitted to the observed ones assuming the elemental depth profiles, which are indicated in Fig. 2(b).

Ni(111) surfaces oxidized at RT for O₂ exposure of 3, 15, 50, and 160 L. The solid curves are the simulated spectra best-fitted to the observed ones assuming the depth profiles indicated in Fig. 2(b). The growth mode is not in a layer-by-layer fashion. With increasing oxygen exposure, the oxidation rate drastically drops. The saturated oxygen and nickel coverage was estimated to be $3.9 \pm 0.05 \times 10^{15}$ and $4.1 \pm 0.04 \times 10^{15}$ atoms/cm², respectively, corresponding to about three NiO(111)-double layers, O(1 ML)/Ni(1 ML)/O(1 ML)/Ni(1 ML)/O(1 ML)/Ni(1 ML) on Ni(111). In order to estimate precisely the absolute amounts of O and Ni, it is essential to determine the He⁺ fractions dependent on an atomic species of scatterer and the emerging velocity and angle.¹¹ Here, it must be noted that the toroidal ESA detected He⁺ ions only. The He⁺ fractions were determined in advance using polycrystals of SiO₂ and Ni films



(a)



(b)

FIG. 3. MEIS spectra observed for the Ni(111) surface oxidized with O₂ exposure of 160 L. Scattering components from (a) Ni and from (b) O. Scattering geometry was set to [001] incidence and backscattering to 85.0° with respect to the surface normal. The solid curves denote the simulated MEIS spectra giving the best fit to the observed ones assuming the elemental depth profile of Ni(0.25 ML)/O(0.75 ML)/Ni(1 ML)/O(1 ML)/Ni(1 ML)/O(1 ML)/Ni(1 ML)/Ni(111).

and a NiO(001) single crystal. Another important factor to determine absolute amounts of composite elements is the scattering cross sections, which were calculated from the ZBL potentials.¹²

In order to analyze the fine structure of the top surface, we performed the MEIS analysis taking a glancing emergence geometry, where 120 keV He⁺ ions were incident along the [001] axis and backscattered to 85.0° with respect to the surface normal. Figure 3 shows the MEIS spectra, in which the scattering component from each atomic layer is clearly resolved. As a result, it is seen that the topmost layer consists of 0.25 ± 0.03 ML Ni sitting on the O plane (0.75 ± 0.04 ML). The underlying Ni/O/Ni/O/Ni layers were significantly shadowed, because the domain of

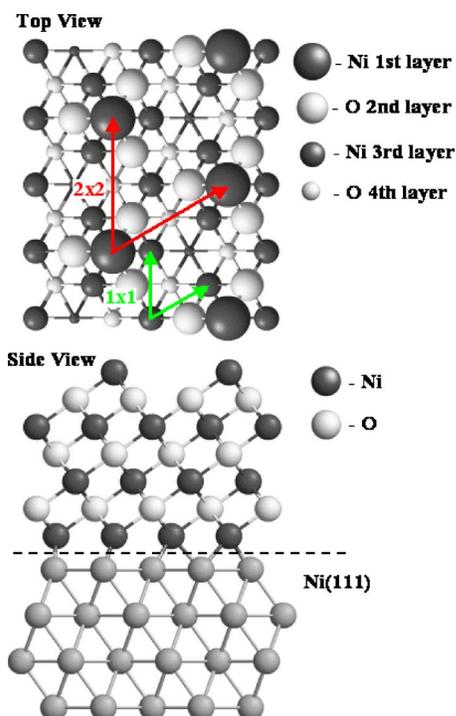


FIG. 4. (Color online) Top and side views of octopolar reconstruction terminated with Ni.

NiO(111)- $[1\bar{1}0]$ //Ni(111)- $[1\bar{1}0]$ is dominant. It must be noted that top layer Ni(111) is visible for the He⁺ ions incident along the [001] axis but the underlying Ni(111) layers are shadowed. The adatoms [Ni(1/4 ML)] and adlayer [O(3/4 ML)] are located on the bulk-truncated NiO(111) with thickness of five atomic layers on the Ni(111) substrate. Such a surface structure coincides with the octopolar reconstruction terminated with Ni (see Fig. 4). However, the present NiO(111) surface grown on Ni(111) showed the (1×1) RHEED pattern not the $p(2 \times 2)$ image. This is probably due to some stress imposed by the underlying thin NiO(111) layer, which may be caused by a large lattice mismatch of 19% between NiO(111) and Ni(111). This adatoms-adlayer structure may correspond to a precursor state of the $p(2 \times 2)$ -octopolar reconstruction. Here, it must be noted that the clear $p(2 \times 2)$ pattern was observed for an NiO(111) single crystal⁴ and NiO(111) films grown epitaxially on Au(111) (Refs. 3 and 4) [the lattice mismatch between NiO(111) and Au(111) is 2%].

Next, we analyzed the oxidation kinetics using isotopically labeled ¹⁸O₂ (purity: 95%) and ¹⁶O₂. The clean Ni(111) surface was first oxidized in ¹⁸O₂ at RT with an exposure of 20 L. The average thickness of the Ni¹⁸O(111) is estimated to be about 2.9 atomic layers derived from MEIS analysis [see Fig. 5(b)]. Then the surface was reoxidized in ¹⁶O₂ at RT with an exposure of 140 L. Figure 5(a) shows the MEIS spectra observed for the NiO(111)/Ni(111) oxidized in ¹⁸O₂ (top) and that reoxidized in ¹⁶O₂ (bottom). The simulated MEIS spectra best-fitted to the observed ones give the elemental depth profiles, as indicated in Fig. 5(b). Apparently, Ni atoms(ions) diffuse to the surface and the oxidation takes

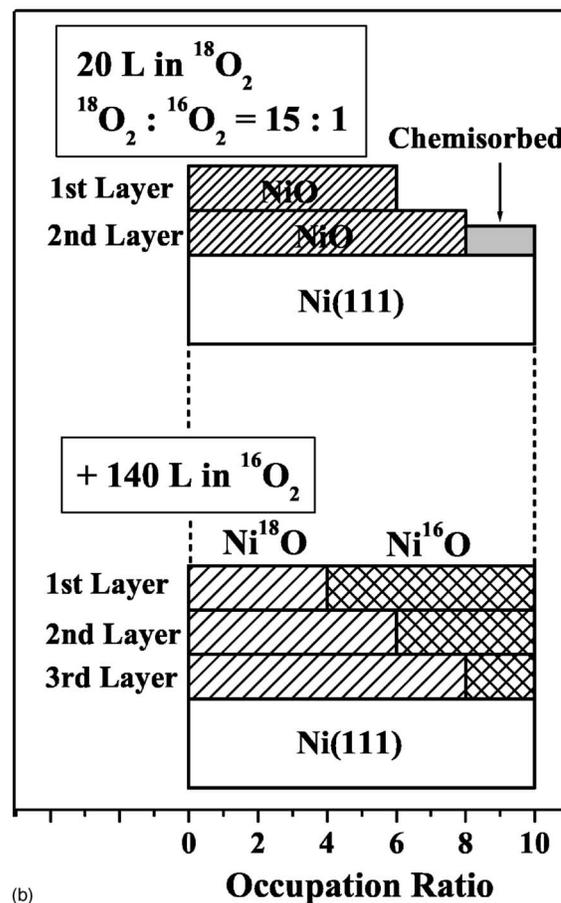
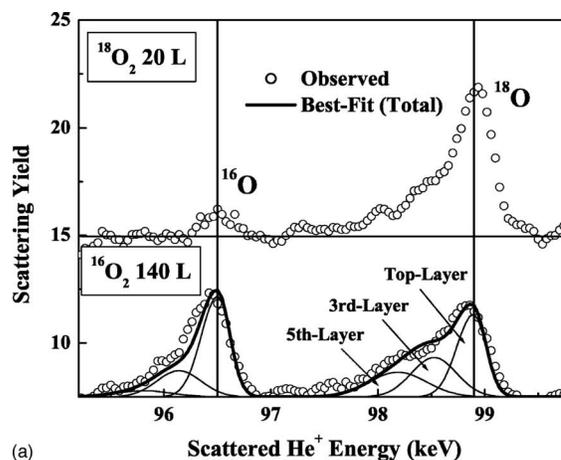


FIG. 5. MEIS spectra observed for the NiO(111)/Ni(111) oxidized in ¹⁸O₂ with an exposure of 20 L (upper) and that reoxidized in ¹⁶O₂ with an exposure of 140 L (bottom). The scattering geometry takes the [100] incidence and backscattering to 70.0° with respect to the surface normal. Best fit was obtained assuming the elemental depth profiles, indicated schematically in Fig. 5(b). For exposure to ¹⁸O₂ (20 L), the surface was covered with three kinds of domains with different thicknesses, four atomic layers of NiO(60%), two atomic layers of NiO(20%), and O chemisorbed (20%). For exposure to ¹⁶O₂ (140 L), oxidation is saturated with the depth profile of Ni(0.25 ML)/O(0.75 ML)/Ni(1 ML)/O(1 ML)/Ni(1 ML)/O(1 ML)/Ni(1 ML)/Ni(111).

place on the top surface. The average thickness of the reoxidized NiO(111) layer is estimated to be 3.1 atomic layers. According to the Cabrera-Mott model,¹³ for a thin oxide film (less than 3 nm), electrons tunnel from a metal to an adsorbed oxygen atom through a dielectric film (oxide film) in order to equalize the electrochemical potential. This creates an electric field across the oxide film, which in turn allows metal ion transport to the top surface. A dissolved Ni⁺ ion jumps to the oxide layer against a potential barrier (W) and then drifts to the top surface. The drift velocity u is limited by the barrier height and thus expressed by

$$u = N\Omega\nu \exp[-W/k_B T], \quad (1)$$

where N , Ω , ν , k_B , and T are the areal density of the dissolved Ni⁺, the volume per one Ni⁺, frequency of thermal lattice vibration, Boltzmann constant, and temperature, respectively. The growing oxide thickness X on time t is expressed by

$$\frac{X_L}{X^2} ut = \exp\left[-\frac{X_L}{X}\right], \quad (2)$$

where X_L is a constant [2 nm for oxidation of Ni (Ref. 6)]. If the Cabrera-Mott model is applied to the above reoxidation in ¹⁶O₂ after oxidation in ¹⁸O₂, one obtains the potential barrier W of 2.36 eV. Here, we used the average thickness of the reoxidized NiO(111) $X=3.73 \times 10^{-8}$ cm, $\nu=\nu_D$ ($=9 \times 10^{12}$ s⁻¹: Debye cutoff frequency), $N\Omega=2.035 \times 10^{-8}$ cm, $k_B T=0.03$ eV, and $t=1400$ s. This is consistent with the pre-

vious prediction (2.56 eV) based on the Cabrera-Mott model.⁶

In summary, the oxidation kinetics for Ni(111) surface and the structure of the oxide layers grown epitaxially at RT were analyzed by high-resolution MEIS using isotopically labeled ¹⁸O₂. Initially, the surface showed a RHEED pattern of the Ni(111)-(2×2)-O chemisorption structure at an oxygen exposure of a few L and started to form NiO(111) layers above 10 L. The growth mode is not in a layer-by-layer fashion. The oxide thickness was saturated with six atomic layers at oxygen exposure of 160 L. The saturated NiO(111) surface showed a (1×1) RHEED pattern not $p(2 \times 2)$ and consists of two domains: NiO(111)-[11 $\bar{2}$]/Ni(111)-[11 $\bar{2}$] (primary) and NiO(111)-[1 $\bar{1}0$]/Ni(111)-[11 $\bar{2}$] (a small fraction). The elemental depth profile corresponds to the octopolar reconstruction terminated with Ni(0.25 ML). The oxide surface grown epitaxially probably takes a precursor state of the octopolar structure with significant distortion because of a large lattice mismatch of 19% between NiO(111) and Ni(111). Two step oxidation using ¹⁸O₂ and ¹⁶O₂ clearly indicates that oxidation takes place at the top surface obeying the Cabrera-Mott mechanism. The potential barrier for the jump from Ni into the NiO layer is derived to be 2.36 eV, which is compatible with the previously predicted value of 2.56 eV for migration of Ni ions through the NiO lattice.

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