Surface Science 606 (2012) 378–382

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Surface electronic structure of polar NiO(111) films

Shuai Wang, Shuming Liu, Jiandong Guo, Kehui Wu, Qinlin Guo *

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100190, China

ARTICLE INFO

Article history:
Received 5 July 2011
Accepted 25 October 2011
Available online 31 October 2011

Keywords:
Polar surface
NiO films
Surface state
Surface defects
Photoelectron spectroscopy
Electron energy loss spectroscopy

ABSTRACT

The surface and electronic structure of polar NiO(111) films with or without facets, prepared on a Mo(110) substrate, were in situ studied using various surface analytical techniques. A new surface state located at 0.8–1.8 eV measured by electron energy loss spectroscopy was observed on faceted NiO(111) films, which is originated from surface Ni vacancies. This surface state is decreased by annealing or deposition of Ni atoms. The experimental results indicate that the charge transfer occurs between surface and bulk of the faceted NiO(111) films. Present work provides a model surface with polarity and facets, which can be used for further investigation on chemical adsorption of atoms or molecules as well as selective reaction.

1. Introduction

Metal oxide and oxide supported metal system are important aspect of material and catalytic sciences. Various surface defects including surface vacancies [1–7] in metal oxides play an important role in the chemical reactivity, e.g. FeO with coordinatively unsaturated ferrous sites used for the preferential oxidation of CO [6], and CeO_2 with oxygen vacancies for water–gas shift [7]. However, their electronic structures of surface/interface with defects related to catalytic properties remain poorly understood.

Recently, polar surfaces of metal oxides have attracted much attention in fundamental research and technological applications [8] due to their rich stabilization mechanisms and unusual adsorption and catalytic properties [9–17]. The polar surface of metal oxides consisting of alternate stacking of cation layers and oxygen layers brings a net dipole moment normal to the surface, which leads to a surface instability. To get the surfaces stabilized, the polar surfaces undergo several possible processes, i.e. adsorption of contaminations [11], hydroxylation [5,18,19], modification of surface electronic structure [20], reconstruction [5,10,18,19], faceting [5,10,21–23] and charged surface nano-defects [24]. For example, Ni vacancies are formed on NiO(111) films due to stabilization of $p(2\times2)$ reconstruction [25], and a large-scale facet was observed on NiO(111) [10]. Those facets consist of a series of trigonal pyramids containing (100), (010), and (001) faces, and each face is inclined by 54.7° to the original surface normal [21]. The formation of {100} pyramid facets on NiO(111) surface may result in a different surface electronic structure compared to that of non-polar NiO(100) films. These processes to stabilize the polar surface may provide peculiar surface defects and new surface states. Since the defect states are generally located in the gap, the surface oxygen and cations may become more basic or acid, which provide important implication on catalysis [26].

In this work, we have prepared NiO(111) thin films with or without facets in ultra-high vacuum (UHV) systems at room temperature (RT), and in situ studied their surface structure and electronic structure by using various surface analytical techniques including low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES) and high resolution electron energy loss spectroscopy (HREELS). The NiO films are thick enough to have properties of bulk NiO yet are thin enough to circumvent the surface charging problem in order to use electron probe techniques. Based on the photoelectron spectroscopies and electron energy loss measurements, a new surface state caused by Ni vacancies located on boundaries around facets is assumed. The surface electronic structure and thermal stability are discussed.

2. Experiments

The experiments were conducted in two UHV systems: ELS-22 (LEYBOLD-HERAUS GMBH) and ESCA LAB-5 (VG SCIENTIFIC) with base pressure of 2×10^{-10} and 2×10^{-9} mbar, respectively. The former machine is equipped with LEED, UPS, AES and HREELS, and the latter one with LEED, UPS and XPS.

Single crystals of Mo(110) and Mo(100) were used as substrates to grow NiO(111) and NiO(100) films, respectively. A C-type thermocouple was spot welded to the substrates for temperature measurements. The clean and well ordered Mo substrates were obtained by

---

* Corresponding author. Tel.: +86 10 8264 9435.
E-mail address: qlguo@iphy.ac.cn (Q. Guo).

0039-6028/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2011.10.026

annealing at ~1100 K in ~10^{-7} mbar O_2 to remove the surface contamination (mainly carbon), followed by a subsequent flash to 1700 K without O_2. No impurities were detected on the substrates by XPS or AES except a small residual oxygen signal, which was proved to have no influence on growth of the Ni oxide films.

The source of nickel was made of high purity Ni (99.994%) wire wrapped tightly around tungsten wire, which can be resistively heated for deposition. The thickness of the NiO films was calculated based on the deposition rate of Ni (about 0.7 ML (monolayer) /min) monitored either by a quartz crystal oscillator in ELS-22 chamber or by the XPS in ESCA LAB-5 chamber. The faceted NiO(111) films and NiO(100) films were prepared by evaporating Ni in ~10^{-7} mbar O_2 at RT on Mo(110) and Mo(100), respectively. However, by using the same preparation procedure, facet free NiO(111) films were obtained in an incompletely baked UHV system. The thicknesses of films are around 4–6 nm. Deposition of Ni with 0.2–1.0 monolayer equivalent (MLE) on the NiO(111) films at RT were conducted in order to investigate the interfacial interaction. The Fe_3O_4 films [27] were prepared by deposition of Fe in 4×10^{-7} mbar O_2 at 600 K and subsequently annealing at 850 K as a buffer layer between Mo(110) and NiO(111).

In the XPS measurements, Mg K_α X-ray source ($h\nu = 1253.6$ eV) and the pass energy of 50 eV were used. The analyzer takeoff angle is about 15° with respect to the surface normal. The binding energy (BE) in XPS was calibrated using Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.7 eV) lines. The He I ($h\nu = 21.2$ eV) source was used for UPS. In HREELS and EELS measurements, electron primary energies of 4.7 and 20 eV were used for investigations of surface vibrational and electronic structures, respectively. All data were collected at RT.

3. Results and discussion

Fig. 1 shows the XPS spectrum of Ni 2p core level for as grown nickel oxide films on Mo(110) substrate. The shape of Ni 2p peaks and BE position of Ni $2p_{3/2}$ at 854.6 eV are consistent with that of NiO reported elsewhere [28,29]. The AES spectrum (not shown) of these films is also virtually identical to the NiO. The HREELS spectrum of the films is shown as inset in Fig. 1. The Fuchs-Kliewer phonon loss at 66.4 meV as well as its overtone loss at 132.9 meV is typical character of NiO. The results agree well with that previously reported [17,29,30]. The loss peak at 452 meV is assigned to surface hydroxyl groups adsorbed from residual OH or H in vacuum during the preparation of the NiO(111) films, which can stabilize the polar surface of NiO(111) films [5].

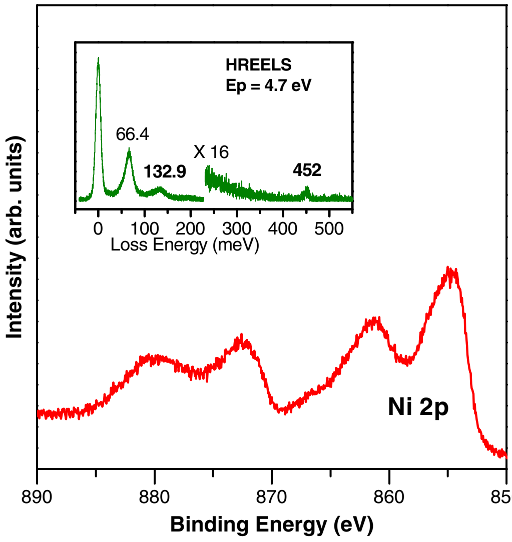

Fig. 1. XPS spectrum of Ni 2p core levels for faceted NiO(111) films. Inset shows the HREELS spectrum of the films.

The LEED patterns of the films are shown in Fig. 2a and b with primary energies of 60 and 88 eV, and the schematic drawings of the patterns are given in Fig. 2c and d, respectively. Two sets of LEED spots are observed, one is from (1 × 1) hexagonal symmetry (solid circles in Fig. 2c) of (111) face and the other is extra spots as indicated by the open circles in Fig. 2c. These extra spots moved in non-radial directions with a slight change of primary energy, as seen in Fig. 2b and d. This is a typical character of facets structure. A similar structure was also found on MgO(111) surface [21]. For facet free NiO(111) films, the peaks shape of Ni 2p lines is the same as that of faceted films as seen in Fig. 1. However, on this surface, only (1 × 1) LEED pattern from (111) face is observed (Fig. 2e and f).

The EELS spectrum of faceted surfaces is shown in Fig. 3a. A broad peak at 0.8–1.8 eV and a peak at 0.6 eV are detected. Interestingly, the broad peak is not consistent with the EELS spectra of NiO(100) or NiO (111) reported else [17,31,32], from which the loss peaks at 0.6, 1.1, 1.6 and 2.9 eV are observed and assigned to d–d transitions of the surface and bulk states. Apparently, this loss is indicative of a new surface state (NSS). Contrastively, for facet free NiO(111) films prepared in our experiments, the NSS is not observed (Fig. 3b), and this spectrum is in good agreement with that of NiO. The NSS is also absent for the NiO(100) films, a non-polar surface, grown on Mo(100) at RT (Fig. 3c). However, after annealing the faceted NiO(111) films at 500–650 K in UHV, the NSS is disappeared (Fig. 3d), and the loss at 0.6 eV remains basically unchanged. Also, the peaks at 1.1 and 1.6 can be resolved.

The UPS spectra of faceted NiO(111), facet free NiO(111) and NiO (100) films are shown in Fig. 4a, b and c, respectively. The valence band of faceted films is different from others and shows a shift of 0.5 eV towards to E_F. The peaks at about 1.6 and 3.3 eV represent the screened Ni 3d emissions, while the peak at about 4.7 eV is assigned to O 2p emission [33]. After annealing at 500 K, the valence band of faceted films in Fig. 3d shows a rigid band shift of 0.5 eV to

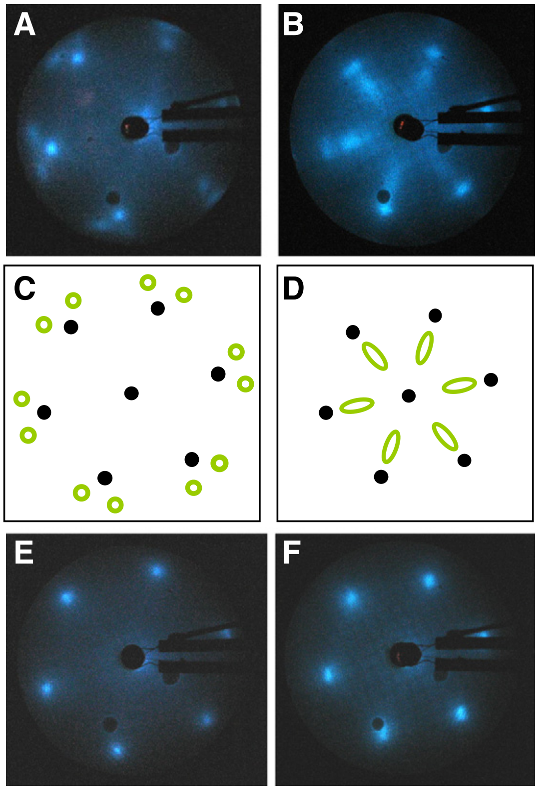

Fig. 2. LEED patterns of faceted NiO(111) films with $E_P = 60$ eV (a) and 88 eV (b). (c) and (d) schematic drawings of (a) and (b), respectively. LEED patterns of facet free NiO(111) films with $E_P = 60$ eV (e) and 88 eV (f).