Epitaxial growth of ZnO films on thin FeO(111) layers

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Abstract

Thin FeO(111) buffer layers prepared on Mo(110) substrate were used to grow ordered ZnO films under ultrahigh vacuum condition, and were in situ characterized by various surface analytical techniques. A chemical interaction between Zn (or ZnO) and FeO(111) can effectively lower the interfacial energy, which is in favor of an epitaxial growth of ZnO on FeO layers. Compared with the MgO(111) buffer layer used for the growth of ZnO(0 0 0 1) on sapphire (0 0 0 1) surface, the FeO(111) thin films might be a better one because it is more thermally stable. Our experimental results provide constructive information on the growth mechanism of ZnO-based materials, which is helpful for further understanding the growth mechanism of related oxide materials.

1. Introduction

Metal oxides including metal oxide films have absorbed considerable attention due to their importance in technological applications, such as catalysis, electrochemistry, electronics and magnetic recording [2–4]. For a better understanding of their properties, it is of significance and necessity to obtain a high-quality single crystal or well-ordered film. In practice, for some hard-preparing metal oxides (such as ZnO), to optimize the growth techniques is very beneficial to improve their crystallographic quality [2–4].

Among metal oxides, ZnO as well as ZnO-based materials have received great interest owing to their unique semiconducting properties in short-wavelength optoelectronic devices, transparent electrodes and solar cells [3–5]. To prepare high-quality ZnO on different substrates, e.g., on Al₂O₃, Si, GaN and SiO₂, various growth methods including molecular beam epitaxy, pulse laser deposition, metal organic chemical vapor deposition and magnetron sputtering, have been employed [5]. However, in many cases, the quality of ZnO films was not obviously enhanced due to lattice mismatch, the existence of oxygen vacancies as well as the difficulty in creating effective nucleation centers [3,6]. To grow high-quality ZnO films on sapphire, a buffer layer of MgO(111) thin film has been used [3]. In this case, the buffer layer can lower the surface energy and provide nucleation centers. However, MgO(111) surface is a typical polar surface with thermodynamic instability and is easily diverged into MgO{10 0} facets [7,8], which is unfavorable for the initial growth of ZnO films. In a previous study [9], we reported that an ultra-thin layer of Fe₂O₃(111) can be a better buffer layer used to grow ZnO(0 0 0 1) films on sapphire (0 0 0 1) surface, and predicated that Fe₂O₃(0 0 0 1) and FeO(111) layers are also good candidates as buffer layers to grow ZnO.

In this paper, we present ZnO(0 0 0 1) film grown on a thin FeO(111) buffer layer, prepared on Mo(110) substrate, under ultrahigh vacuum (UHV) condition. Here the choice of metal Mo(110) substrate, instead of insulated sapphire, can effectively avoid surface charging during the measurements of surface electronic and geometric structures while using an electron incidence beam with lower energies. The as-prepared films were in situ characterized by various surface analytical techniques. The experimental results suggest that a thin FeO(111) layer can be used as an effective buffer layer for epitaxial growth of ZnO(0001) films on sapphire (0 0 0 1) substrate.

2. Experimental details

The experiments were performed in two UHV systems. One is ESCALAB-5 (VG UK) chamber with a base pressure of $8 \times 10^{-10}$ Pa.
mbar equipping with optical facilities for low-energy electron diffraction (LEED), dual-anode X-ray sources (Mg and Al) and a He I (hv = 212.2 eV) source for X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), respectively. The other is ELS-22 (Leybold-Heraeus GmbH, Germany) chamber with a base pressure of 1 x 10^-10 mbar for Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS) and LEED studies. In both chambers various metal and gas sources were installed.

The Mo(1 1 0) single crystal (10 mm diameter disk, 1-mm-thick) was used as a substrate to grow FeO(1 1 1) films, which could be either resistively heated to 1300 K or annealed to temperature > 2000 K with an electron beam heating assembly at the backside of the sample. A C-type thermocouple (5%Re–W/26%Re–W) was spot welded to the edge of the Mo(1 1 0) substrate for temperature measurements. The substrate surface was treated at ~1200 K in ~10^-7 mbar oxygen to remove the surface contamination (mainly carbon), followed by a subsequent flash to 1800 K without oxygen until obtaining a clean surface monitored by XPS/AES and LEED.

The iron and zinc sources were made of a pure iron wire (purity > 99.95%) and a zinc wire (purity > 99.995%) wrapped tightly around a tungsten wire, respectively. Before growth, the two sources were thoroughly degassed by thermal treatment. The deposition rates of Fe and Zn were about 0.15 and 0.05 monolayer (ML)/min, respectively, calibrated via the intensity ratios of Fe 2p_3/2 to Mo 3d_5/2 and Zn 2p_3/2 to Mo 3d_5/2 lines as a function of deposition time by XPS in ESCALAB-5 chamber, and measured by a quartz crystal oscillator in HREELS chamber. The ordered iron oxide thin films with 3–5-nm-thickness were prepared by evaporating Fe in ~10^-7 mbar O_2 ambience at a substrate temperature of 600 K, and then annealed at 850 K without O_2 for 20 min. Then, the iron oxide films were used as a template to prepare ZnO films by depositing Zn in ~10^-6 mbar O_2 at a substrate temperature of 300–450 K.

In XPS measurements, the Mg Kα X-ray source (hv = 1253.6 eV) with a pass energy of 50 eV was used. The binding energy (BE) was calibrated with respect to the pure bulk Au 4f_7/2 (BE = 84.0 eV) and Ag 3d_5/2 (BE = 368.3 eV) lines, and the accuracy of measured BE is better than 0.15 eV. In AES, the primary electron beam energy of 3 keV was used. In the HREELS measurements, a 5.0 eV primary electron beam energy was used with a typical resolution of 10–12 meV obtained by the full width at the half maximum height of the elastic peak from the substrate. The HREELS data were recorded at the specular direction (60° with respect to the surface normal). All data were recorded at room temperature (RT).

3. Results

3.1. Preparation of FeO(111) thin films

Fig. 1(a) shows the AE spectrum of as-grown iron oxide film. There are only the Auger peaks from Fe MNN, Fe LMM and O KLL lines, being indicative of a clean iron oxide surface. By combining the signal intensities and the relative elemental sensitivity factors of Fe and O, the estimated atomic ratio of Fe to O is 0.94:1, being close to 1:1. The inset in Fig. 1(a) shows the corresponding LEED pattern with a hexagonal symmetry. Since the surfaces of three iron oxides (FeO(1 1 1), Fe_3O_4(1 1 1) and Fe_2O_3(0 0 0 1)) are of the same symmetry with a hexagonal structure [10], the LEED pattern as shown in Fig. 1(a) may come from any of them. Therefore, more information regarding the chemical states and composition of as-prepared iron oxide film is needed.

XPS was used to identify the chemical state of the films. For Fe, the most intense Fe 2p core level is split into 2p_3/2 and 2p_1/2 due to the spin-orbit coupling. It is known that the BEs of Fe 2p_3/2 core levels in Fe, FeO, Fe_3O_4 and Fe_2O_3 are 707.0, 710.0, 710.6 and 711.0 eV, respectively [11–14]. In addition, for Fe^{2+} or Fe^{3+} 2p core level, observable satellite peaks with different BE position originating from shake-up processes can also be used to characterize their chemical states [10,13]. Fig. 1(b) gives the XPS result of Fe 2p core level of the iron oxide film. This spectrum with BE values of 710.1 and 723.6 eV for Fe 2p_3/2 and 2p_1/2 lines as well as their shake-up satellite lines at about 716.0 and 730.2 eV levels in Fe, FeO, Fe_2O_4 and Fe_3O_4 are 707.0, 710.0, 710.6 and 711.0 eV, respectively [11–14]. In addition, for Fe^{2+} or Fe^{3+} 2p core level, observable satellite peaks with different BE position originating from shake-up processes can also be used to characterize their chemical states [10,13]. Fig. 1(b) gives the XPS result of Fe 2p core level of the iron oxide film. This spectrum with BE values of 710.1 and 723.6 eV for Fe 2p_3/2 and 2p_1/2 lines as well as their shake-up satellite lines at about 716.0 and 730.2 eV
implies Fe$^{2+}$ state, being in well agreement with reported data \cite{12,13}. All these results from XPS, AES and LEED strongly suggest that ordered FeO(111) thin films have been formed on Mo(110) substrate.

The lattice constant of rock-salt FeO is 4.28 Å with O–O distance of 3.04 Å on (111) surface, while the lattice constants of oblique Mo (110) surface are $a_0 = 2.74$ Å and $b_0 = 3.17$ Å. The angle between $a_0$ and $b_0$ is 125.3° in Mo(110) face, which is larger than 120° from hexagonal structure of FeO(111). The lattice mismatch between FeO(111) and Mo(110) faces is 10.9% and −4.3% along $a_0$ and $b_0$ directions, corresponding to tensile and compressive stress, respectively. Interestingly, however, even though both lattice mismatch and angle mismatch can cause FeO(111) lattice parameter strained at the interface as well as a mismatch/change in crystallographic direction, the FeO(111) is formed on the substrate. The possible reason is that the tensile strain along $a_0$ direction fitly reduces the compressive strain along $b_0$ direction to release strain energy, inducing a structural transformation from an oblique surface symmetry of Mo(110) face to a hexagonal symmetry of FeO(111) face. A similar result was also found in a previous study of MgO(111)/Mo(110) system \cite{15}. However, the detailed strain process at the interface is unclear, and the further study on its growth mechanism is needed.

### 3.2. Growth of ZnO thin films

Zinc oxide films were prepared on as-prepared FeO(111) thin films by evaporating Zn in $\sim 10^{-6}$ mbar oxygen at substrate temperature of 300–450 K. Fig. 2(a) shows the XPS results of Zn 2p core levels and Zn LMM Auger lines. The value of BE is 1021.5 eV for Zn 2p$_{3/2}$ core level, corresponding to either ZnO or metallic Zn \cite{16}. In XPS measurements, it is difficult to distinguish various chemical states of Zn-based materials by measuring 2p$_{3/2}$ line alone due to close BE values between Zn$^{2+}$ and Zn$^{0}$ states \cite{14}. However, the corresponding Auger parameter ($z = BE (Zn 2p_{3/2}) + KE (Zn LMM)$, KE = kinetic energy) value is 2010.6 eV, which strongly suggests the existence of Zn$^{2+}$, i.e. the formation of ZnO for as-prepared thin films \cite{16–18}. In addition, from AE spectra, the ratio of Zn to O being 0.95:1 supports the formation of ZnO film.

Fig. 2(b) is the UP spectra of corresponding ZnO films. In the valence region, the large peak at about 4.0 eV is from the non-bonding O 2p orbital, while the shoulder peak at around 6 eV is thought to relate with a mixed bulk state of O 2p and Zn 4s
orbitals [4,19]. The main peak at about 10.4 eV resulting from the filled Zn 3d band is obviously different from that of unfilled Zn 3d band (9.7 eV) for metallic Zn [20]. This peak (10.4 eV) is very close to the BE value (10.5 eV) of Zn 3d in bulk ZnO as reported previously [4,21]. Therefore, the UPS result also indicates the formation of ZnO film.

It is known that HREELS can be used to measure surface optical phonons (as known as Fuchs–Kliewer model) from a single-crystal surface. The electron energy losses in many solids are dominated by long-range electric fields associated with dipole-active excitations [22,23]. Fig. 3 presents the HREELS result for as-prepared ZnO film. That the main loss peak at 67 meV as well as the multiple loss peaks observed at 134, 200 and 268 meV characters the lattice vibration of Zn–O, which is in well agreement with that from single crystals of ZnO [24]. These features of the surface phonons from long-range ordered ZnO surface are different from polycrystalline ZnO films reported previously [25]. The inset in Fig. 3 demonstrates the LEED pattern with the hexagonal spots, indicating the epitaxial growth of ZnO on FeO(111) films. All data from XPS, AES, HREELS and LEED confirm the formation of long-range ordered ZnO film on FeO(111) thin film.

4. Discussion

Structurally, ZnO and FeO are of wurtzite and NaCl-type structures, respectively. In 2D cells, both ZnO(0 0 0 1) (O–O distance: 3.25 Å) surface and FeO(111) surface are characteristic of hexagonal symmetry, and their mismatch in oxygen sublattice is smaller (6.9%), providing a possibility for the epitaxial growth of ordered ZnO films on FeO(111) thin films. Moreover, the FeO(111) surface is of a polarity resulting from alternative stacking of Fe and O layers along [1 1 1] direction. As the FeO(111) is prepared at high temperature (850 K), it can keep stability below 850 K. The topmost surface of as-grown FeO(111) films is most likely O-terminated in our experiments because of the preparation process with O2 ambience as described in previous section. The O-terminated layer formed by a close-packed oxygen matrix is of advantage to attract cationic species onto the surface. Thereby, Zn or Zn–O species can site on the oxygen layer to form a wetting layer of ZnO, following to construct Fe–O–Zn–O–Zn layers along the surface normal. Subsequently, this interfacial layer is vital for further growth of ordered ZnO films. Once there is the chemical interaction taken place between O-terminated layer and Zn [2,19], it will help ZnO to spread onto FeO(111) surface.

To prove the chemical interaction between Zn and O-terminated FeO(111) at the interface, Zn was deposited step-by-step on FeO(111) surface without O2. Fig. 4(a) gives the Zn LMM Auger lines as a function of Zn coverage. For initial deposited Zn, the main peak is at about 988.9 eV in KE. With increasing Zn coverages, the peak gradually becomes strong, and another peak at 992.7 eV starts to appear at 0.4 ML (curve d in Fig. 4(a)). At 0.8 ML, the intensities of the two peaks are almost the same, and the peak at 992.7 eV becomes dominant with the further increase of Zn coverage. As reported, for metallic and oxidized Zn, the Zn L3M45M45 Auger lines are at 993 and 989 eV in KE, respectively [16,26]. Therefore, the result in Fig. 4(a) implies the oxidation of Zn at the interface for initially deposited Zn [9,19]. More evidences can be obtained from x measurements. At low Zn coverage (<0.4 ML), the x value is ~2011 eV, corresponding to oxidized Zn. At the coverage of 0.4–0.8 ML, the x values show the coexistence of

![Fig. 4.](attachment:image-url)
The corresponding XP spectra of Fe 2p core levels are given in Fig. 4(b). The curve a in Fig. 4(b) is from a clean surface of FeO(111). After deposition of 0.8 ML Zn, the characteristic satellite peaks of Fe2+ 2p lines at 716.0 and 730.2 eV obviously become weak. The distance between the Fe 2P1/2 and 2P3/2 doublet lines is 15.2, a 0.3 eV decrease compared with 13.5 eV for the clean FeO(111) surface. At 2.0 ML Zn coverage, the Fe 2p satellite peaks almost disappear, and the distance of Fe 2p doublet lines is further decreased to 12.9 eV. These results strongly suggest a reduction of FeO, a partial reduction of Fe2+, i.e., from FeO to Fe1−xO. Consequently, a thin ZnO layer can be formed on FeO(111) surface. In case of co-deposition of Zn and O2, the thin ZnO layer formed at a thin FeO(111) layer was reported [2]. Since the interfacial interaction between Zn and O-terminated FeO(111) surface can decrease the interfacial energy, an epitaxial ZrO2 film is obtained. Thermodynamically, the growth mode of oxide films relates with the surface free energies of a substrate (γs), the growing film (γf) and their interfacial energy (γi) [1,10]. According to the equilibrium condition of growth, the total energy of the system is given as

\[ \Delta G = \gamma_f + \gamma_i - \gamma_s \]

For \( \Delta G > 0 \), a layer-by-layer growth mode is followed, while for \( \Delta G < 0 \) a three-dimensional structure appears. For \( \gamma_i \), it thermodynamically satisfies the principle of energy minimization and is generally neglectable [27]. Many metal oxides have lower surface free energies than metals, so that most metal oxide films are epitaxially grown on single-crystal metal substrates. Contrarily, most metals are formed as clusters/islands on metal oxide substrates [10]. As a typical example, the Ag clusters are formed on MgO(100), while MgO(100) film is epitaxially grown on Ag(100) because of \( \gamma_{Ag(100)} \) (1.25 J/m²) is higher than \( \gamma_{MgO(100)} \) (0.9 J/m²) [28]. In oxide–oxide system, however, due to the close value of \( \gamma_f \) and \( \gamma_i \), the value of \( \Delta G \) strongly depends on the interfacial interaction between film and substrate surface [2,29]. In our study, the interfacial reactive layer between Zn and O-terminated layer benefits the minimization of \( \gamma_i \) (∼0) [27], which is crucial for the initial nucleation and epitaxial growth of ZnO films on FeO(111) surface. In fact, the value of \( \gamma_i \) of O-terminated ZnO(0001) (1.6 J/m²) [30] is less than that of \( \gamma_i \) of O-terminated FeO(111) (2.0 J/m²) [31], ascribed to the lower energy of FeO(111) surface. In order to minimize the interfacial energy by means of the interfacial interaction between Zn and O-terminated FeO(111) surface, our results prove that ordered iron oxide film of well-oriented structure could be formed on MgO(111) surface by evaporating deposition. The lattice mismatch between ZnO(0001) and FeO(111) is smaller than that between ZnO(0001) and MgO(111) (\( a_0 = 2.98 \) Å), favoring an epitaxial growth of ZnO on FeO. In fact, for ultrathin FeO(111) films its lattice constant can be expanded easily to the values > 3.04 Å with the thickness change of FeO layers due to the lattice strain with the substrates [2,10], which can further reduce the lattice mismatch.

Experimentally, the iron oxides (including FeO(111), Fe3O4(111) and Fe2O3(0001)) can be epitaxially grown on sapphire by controlling the growth rate, oxygen partial pressure and substrate temperature [11,27,32,33], providing the applied perspective. In regard to the lattice mismatch between sapphire and iron oxides, it is thought that the lattice strain plays a dominant role in the epitaxial growth of iron oxide films, and corresponding strain energies are released with the increase of thin film thickness [27,32,33]. In previous study [9], the epitaxial growth of ZnO on a thin Fe3O4(111) buffer layer was reported. In present work we further confirm that the ZnO(0001) can also be grown on FeO(111) surface. These results suggest that ordered iron oxide films, without considering the chemical states of iron, are good candidates as buffer layers for the epitaxial growth of ZnO(0001) on sapphire (0001). These results imply that the development of such binary oxide systems is highly correlated and the study of these systems provides fundamental knowledge for exploring new materials.

5. Conclusion

To sum up, a thin FeO(111) buffer layer has been used to epitaxially grow ZnO(0001) films, and these films have been in situ investigated by various surface analytical techniques. As an effective buffer layer, FeO(111) films not only reduce the lattice mismatch between ZnO(0001) and Al2O3(0001), but also decrease the interfacial energy by means of the interfacial interaction between Zn and O-terminated layer of FeO(111) surface. Our results prove that ordered iron oxide film of FeO(111) is a good candidate as buffer layers for the epitaxial growth of ZnO on sapphire (0001) surface. This study is of help for further understanding the growth mechanism of high-quality ZnO as well as related oxide materials.

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References