

Formation of metastable MgO structures on type-III oxide surfaces: Effect of periodic out-of-plane electric dipole moment of substrates

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ABSTRACT

Metastable structures of MgO overlayer on type-III oxide surfaces were achieved by molecular beam epitaxy. Periodic out-of-plane dipole moment of substrates was revealed to play a dominant role in the formation of metastable oxide structures. Under near-equilibrium epitaxial conditions, this dipole moment was found to drive the over-grown MgO to inherit the out-of-plane substrate lattice, resulting in some new structures with different stacking sequences and bonding configurations from those of thermodynamically stable phase. As typical cases, by adopting the substrate dipole moment along the growth direction, MgO overlayers with metastable wurtzite (WZ) and stacking-fault (SF) structures were formed on α -Al₂O₃(0001) and MgAl₂O₄(111) surfaces, respectively.

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1. Introduction

Heteroepitaxy of low-dimensional systems has attracted extensive attention since it offers an efficient and controllable way to grow artificial structures, such as quantum wells and quantum dots, on highly mismatched substrates [1,2]. Generally, two-dimensional (2D) lattice and symmetry of substrate surface are considered as the most important factors in heteroepitaxy [3]. Most epitaxial growth and theoretical models are thus based on the in-plane lattice matching between film and substrate [4]. Out-of-plane symmetry along the growth direction, whereas, sometimes can also play a vital role in determining the overlayer structure, especially in oxide-on-oxide epitaxy [5]. For example, it has been found that the DyScO₃ substrate, a tetragonal perovskite ferroelectrics oxide, exerts compressive strains on PbTiO₃ epilayer along the out-of-plane polarization direction, resulting in a low-symmetry phase not observed in the bulk material [6].

According to the definitive and widely used classification on ionic crystal surfaces by Tasker [7], the type-III oxide surface is a polar surface, resulting from atomic stacking of alternant layers with oppositely charged ions, and possesses periodic electric dipoles perpendicular to the surface. When this surface is used as a template for epitaxy, the existence of perpendicular dipole moment is expected to prominently influence the bonding configurations of the deposited oxide atoms and then the overlayer structure. However, by far, very little is known about the formation of supported oxide structures under the influence of periodic out-of-plane dipole moment from type-III oxide substrate. As typical type-III surfaces, α -Al₂O₃(0001) and MgAl₂O₄(111) have been extensively used as templates for the heteroepitaxy of semiconductor, magnetic, and superconductor oxides [8–10]. Both surfaces have the same property in terms of alternant stacking with oppositely charged metal and oxygen ion layers. Also, the oxygen sublattice of the substrates can be regarded as the basic framework in respect that the distance d_{O-O} of two neighboring O²⁻ layers approximately is the period of perpendicular electric dipoles. As for sp-bonded MgO, several metastable phases with wurtzite (B4), graphite-like (Bk) and

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stacking faults (SF) structures have been theoretically predicted [11], but not experimentally observed. Therefore, the achievement of metastable MgO phases under the influence of substrate out-of-plane dipole moment is of great interest. In this letter, metastable MgO structures were delicately prepared on α -Al₂O₃(0001) and MgAl₂O₄(111) by radio frequency plasma-assisted molecular beam epitaxy (rf-MBE). *In situ* reflection high-energy electron diffraction (RHEED) and *ex situ* high-resolution transmission electron microscopy (HRTEM) were used to determine the detailed structures of MgO overlayers.

2. Experimental procedure

MgO ultrathin films, with ZnO as cap layer, were grown on α -Al₂O₃(0001) and MgAl₂O₄(111) substrates by radio frequency plasma-assisted MBE. In our experiments, both substrates were degreased, acid-etched and then thermally cleaned at 800 °C in UHV. Prior to growth, the substrate was exposed to oxygen plasma with a radio frequency power of 400 W and a gas flux of 2.0 sccm for 30 min to obtain smooth O-terminated polar surfaces. Afterward, the growth of MgO ultrathin films were controlled deliberately under an O-rich situation, in which defect-free and stoichiometric MgO structure can be obtained. All the growths were designedly carried out by using the so-called near-equilibrium processes [12,13] with very slow growth rate (e.g. 0.02 nm/min) at high substrate temperature (e.g. 600 °C). In these conditions, the effects of substrate-induced out-of-plane dipole moment could be enhanced and the grown MgO overlayers always had different structures from those obtained in off-equilibrium epitaxial conditions. *In situ* RHEED and *ex situ* HRTEM were successfully used to determinate the crystal structures of the metastable MgO ultrathin films. The growth process was

monitored in real-time by RHEED with electron beam energy of 13 KeV. HRTEM experiments were performed with a Philips CM200 field emission gun TEM equipped with the Gatan image filtering (GIF) system, operating at 200 KV.

3. Results and discussion

To probe the structure of MgO overlayer, the epitaxial growth has been monitored by *in situ* RHEED, and the lattice constants can be deduced from corresponding RHEED patterns. On α -Al₂O₃ substrate, at the very beginning of MgO growth, there emerges diffuse streaky patterns, which indicates that the hexagonal MgO is a flat layer. With increase of film thickness, elongated spotty patterns appear, as shown in Fig. 1(a) and (b). It can be established from the observed 2 mm symmetry of diffraction spots in Fig. 1(a) that the MgO overlayer is a wurtzite structure. If film thickness is more than 1 nm, a phase transition from wurtzite to rocksalt structure can be determined from the gradually changed RHEED patterns [14]. Furthermore, the wurtzite MgO is found to inherit the symmetry and lattice constant of the substrate along *c*-direction, as shown in Table 1. As for the lattice constant, the relatively small distance between two neighbor oxygen layers in α -Al₂O₃ lattice, $d_{O-O}^{\text{Al}_2\text{O}_3} = 2.168 \text{ \AA}$, obviously benefits for the formation of the wurtzite MgO with a small $d_{O-O}^{\text{WZ-MgO}}$ of 2.127 Å rather than the rocksalt MgO with a bigger $d_{O-O}^{\text{RS-MgO}}$ of 2.431 Å. Moreover, although there is a relative 30° rotation of the in-plane lattices between MgO and α -Al₂O₃, O²⁻ stacking in wurtzite MgO still takes the ABAB stacking sequence, a natural extension of the O²⁻ hexagonal close packed (HCP) stacking in the substrate.

Under the driving of substrate out-of-plane dipole moment, the resulting *c*-axis uniaxial compressive strain in wurtzite MgO brings an increasing polarity in this structure. Recently, by using LDA total energy calculations, an ideal wurtzite and a relaxed wurtzite MgO have been studied by Lambrecht et al. [15]. In their calculations, the ideal wurtzite MgO has equal Mg–O bond lengths, while in relaxed wurtzite MgO, the neighboring Mg and O layers tend to relax into the same plane to form a hexagonal boron nitride (h-BN) structure. Either of them is nonpolar. Whereas, in our case, the wurtzite MgO with measured $a=3.140 \text{ \AA}$ and $c=4.253 \text{ \AA}$ was thought with more-contorted Mg–O tetrahedrons since the *c/a* ratio of 1.354 deviates far from the ideal value of 1.633. The internal parameter *u* of 0.432 in experimental wurtzite MgO is also quite different from that of either the ideal wurtzite or h-BN MgO. Both the *c/a* ratio and the *u* suggest that the wurtzite MgO observed in our experiment has a very strong polarity. A simple estimate of the magnitude of

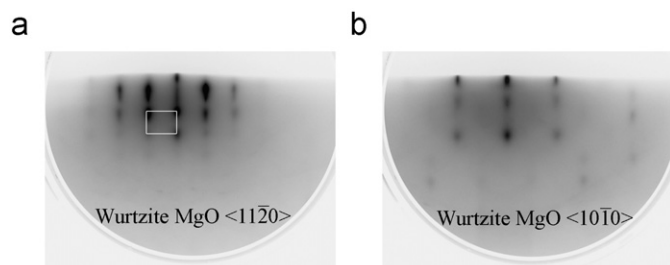


Fig. 1. RHEED patterns of wurtzite MgO overlayer grown on α -Al₂O₃(0001) along (a) MgO $\langle 11\bar{2}0 \rangle$ azimuth and (b) MgO $\langle 10\bar{1}0 \rangle$ azimuth. Pattern in (a) shows the 2 mm symmetry and a rectangle primitive unit cell in diffraction geometry, the same as those of wurtzite ZnO.

Table 1
Lattice parameters of MgO structures and the substrates.

	Ideal wurtzite MgO ^a	Relaxed wurtzite MgO ^a	Experimental wurtzite MgO ^b by RHEED	Experimental SF MgO ^b by HRTEM	Rocksalt MgO ^a	α -Al ₂ O ₃ (0001)	MgAl ₂ O ₄ (111)
<i>a</i> (Å)	3.199	3.413	3.14	2.838	4.211	4.759	8.075
<i>c/a</i>	1.633	1.204	1.354				
<i>c</i>	5.224	4.109	4.253	7.055	$2d_{111}=4.864$	12.911	$3d_{111}=7.112$
<i>u</i>	0.375	0.5	0.432				
O _{in-plane} lattice (Å)	3.199	3.413	3.140	2.838	2.978	2.522	2.862
<i>d</i> _{O-O} (Å)	2.612	2.055	2.127	2.352	2.431	2.168	2.371
O anion stacking	HCP	HCP	HCP	FCC	FCC	HCP	FCC
Volume per molecule (Å ³)	17.8	20.7 ^a	18.2	16.4	18.7		

^a From Ref. [15].

^b From our experiments.

spontaneous electric polarization in our wurtzite MgO is 9.1×10^{-30} C m (2.74 Debye), which is about twelve times than that in wurtzite ZnO (0.73×10^{-30} C m). Remarkably, it is just owing to this strong polarity that metastable wurtzite MgO grown on α -Al₂O₃(0001) could be successfully used as buffer layer for the controlled growth of O-polar ZnO films [14].

When *c*-axis lattice parameter is modulated by substrate perpendicular dipole moment, the wurtzite MgO overlayer always tries to undergo an in-plane relaxation to decrease the strain energy. The in-plane matching between wurtzite MgO and the substrate was determined as MgO[10 $\bar{1}$ 0]//Al₂O₃[11 $\bar{2}$ 0], and they select the domain-matching mode which is a relatively relaxed way since it can freely choose the domain size according to internal strains. Usually, the lattice mismatch between the stable rocksalt MgO(111) and α -Al₂O₃(0001) is 8.3%. However, we found that the obtained wurtzite MgO on α -Al₂O₃ expands this mismatch to 13.9%, indicating that the wurtzite MgO firstly adopts the *c*-axis period of substrate lattice, and then expands the in-plane lattice to minimize the strain energy. The strong polarity of

wurtzite MgO also results from this structure transition caused by the compression in *c*-direction and the in-plane expansion.

Another metastable MgO structure induced by substrate out-of-plane dipole moment has been observed in the MgO/MgAl₂O₄(111) system. Along the MgAl₂O₄[111] direction, O²⁻ sublattice stacks in a face-centred cubic (FCC) way, which is different from that in α -Al₂O₃. At MgO/MgAl₂O₄(111) interface, the SF MgO with a thickness more than 10 nm is identified by HRTEM, as shown in Fig. 2, where the image of the interface was taken along the MgAl₂O₄[10 $\bar{1}$] zone axis. Four relatively large areas are chosen in the image for fast Fourier transform (FFT). Area 1 is in the region of wurtzite ZnO cap layer, and areas 2–4 are selected in MgO region. In the right panels (2–4) of Fig. 2, MgO FFT images clearly show the 2mm symmetry. It is well known that the [10 $\bar{1}$] FFT pattern of a perfect cubic structure will show the two-fold instead of 2mm symmetry. Thus, the grown MgO on the MgAl₂O₄(111) surface does not take the stable cubic structure. Meanwhile, although the FFT images of MgO interfacial layer have the same symmetry with that of the wurtzite structure, this MgO phase cannot yet be identified as the wurtzite because some anomalous stacking orders (SFs) can be clearly seen in the HRTEM image.

Stacking-faults (SFs), as the main extended defects of the strained interface, can lead to the formation of MgO with some new structures (SF structures), which have been theoretically discussed in Ref. [11]. In our case, three kinds of SF structures with stacking orders of ABC, ABA, and ABAC are observed, as shown in Fig. 3(a, c, e). In SF structure, the basic stacking unit is the hexagonal Mg–O bilayer. It is notable that in these three SFs, MgO stacking period along *c*-axis always keeps a close value to that in MgAl₂O₄[111] direction, which can be seen from the comparison of *d*₀₋₀ between SF MgO and the substrate. By the HRTEM intensity profiling of three stacking modes in SF MgO, shown in Fig. 3(b, d, f), the identical periodicity of about 7.055 Å is determined. In ABC stacking MgO presented in Fig. 3(a) and (b), the A–A interlayer distance keeps 7.055 Å, while the B and C layers incline to leave their original FCC stacking positions and approach to each other under the out-of-plane compression. In this way, the perfect FCC stacking becomes partly compacted. This SF structure can be thought to be constructed repeatedly by two distorted hexagonal layers (BC) and an undistorted layer A. Similarly, the other SF ABA (or ABAC), as presented in Fig. 3(c) (or Fig. 3(e)), can also be considered to be constructed from two (three) compressed layers BA (BAC) and the undistorted layer A.

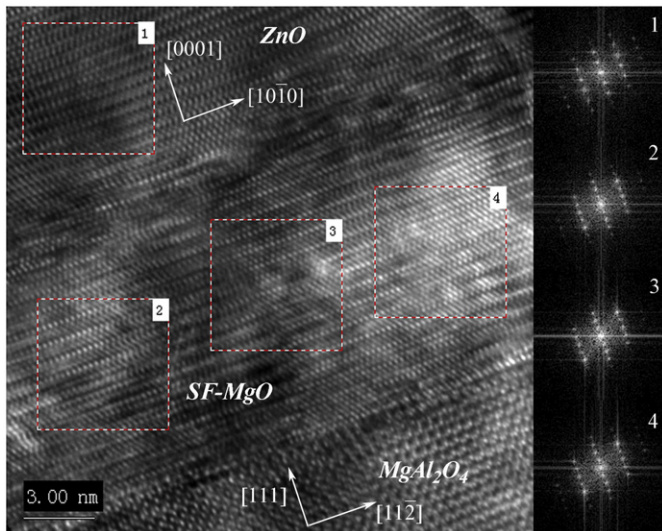


Fig. 2. HRTEM image of SF MgO on the MgAl₂O₄(111) surface. The right panels are FFT images of (1) wurtzite ZnO cap layer and (2–3) SF MgO regions. All FFT images exhibit the 2mm symmetry.

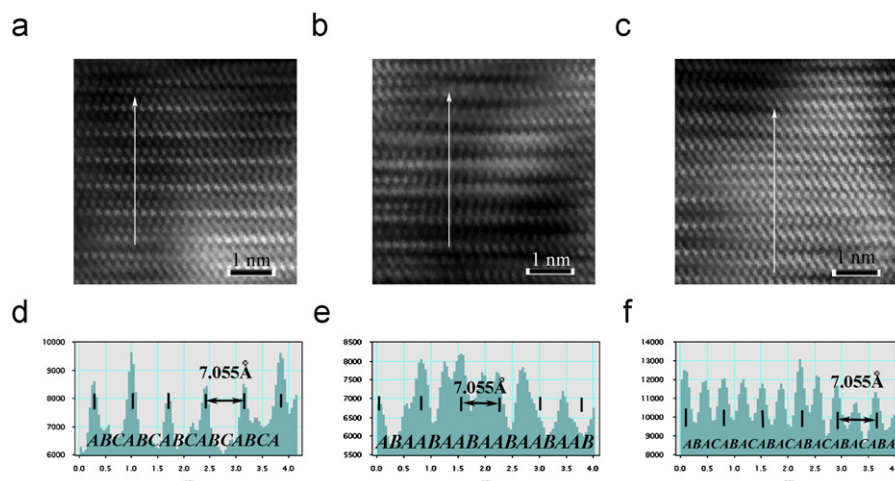


Fig. 3. HRTEM images of SF MgO with various stacking sequences and their intensity profiles along the growth direction. (a) and (b) ABC stacking, (c) and (d) ABA stacking, and (e) and (f) ABAC stacking.

These can be equally regarded as the wurtzite-like structures with AXAX stacking, where A is the layer with fixed stacking period (7.055 Å), while X consists of two or three compressed layers. Only in this stacking manner, can the SF structure synchronously satisfy both the “ABC” stacking order and the 2mm symmetry in FFT images.

Likewise, the formation of SF MgO can be attributed to the substrate perpendicular dipole moment. One can see from Table 1 that the period $d_{0-0}^{\text{SF-MgO}}$ in SF MgO has the close value to that in MgAl₂O₄. The in-plane lattice of SF MgO is overlapped on substrate surface in the lattice-matching mode with a relationship of MgO[10 $\bar{1}$ 0]//MgAl₂O₄[11 $\bar{2}$]. Remarkably, the in-plane lattice parameter of SF MgO is as small as 2.83 Å, almost the same as that of MgAl₂O₄ substrate. This means the SF MgO can still adopt the c-axis lattice parameter under the influence of substrate out-of-plane dipole moment, even in the lattice-matching situation with great in-plane compressive strain. The great strain energy stored in the structure will result in the final formation of the observed SF MgO with regular SFs.

4. Conclusion

In summary, a novel epitaxy mode for MgO grown on type-III polar oxide surfaces was investigated. The periodic out-of-plane electric dipole moment from the substrate along the growth direction was revealed to play a key role in formation of metastable structures of oxide overlayer. As cases, two metastable MgO interfacial structures, i.e., the wurtzite MgO with strong polarity and the SF MgO structure, have been achieved on

α -Al₂O₃(0001) and MgAl₂O₄(111) surfaces under the influence of substrate perpendicular dipole moment.

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