Layer-by-layer epitaxial growth of polar MgO(111) thin films

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We have observed layer-by-layer epitaxial growth mode of MgO (111) films on yttrium stabilized zirconia (111) substrates with NiO buffer layers by pulsed laser deposition despite a strong electrostatic instability of the [111] polar growth direction. Layer-by-layer growth has been realized up to ~10 MgO layers. For thicker films with 10–500 MgO layers, although clear step and terrace structures disappear, the root mean square surface roughness remains as small as ~0.2 nm with high crystalline quality comparable to single-crystals. MgO (111) films with the atomically flat surface thus obtained can be a platform to study polar surfaces and interfaces of simple binary oxides.

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The physical properties of surfaces and interfaces of ionic materials can strongly be modified when controlled on an atomic scale. While such deviation is a severe obstruction to overcome for further miniaturization of electronic devices, it would strongly motivate one to study the surfaces and interfaces of these materials to explore new physical properties realized only on an atomic scale. Among various surfaces and interfaces of ionic materials, atomically controlled polar surfaces and interfaces, which are not formed in conventional elementary metals and semiconductors, have been intensively studied these years.[1] Unusual electronic states formed at such interfaces have attracted many researchers' attention from the viewpoints of low dimensional solid-state physics and of electronic device applications.[2] One of the simplest polar structures is polar (111) film of metal monoxides with rocksalt structure, where oppositely charged metal and oxygen atom layers alternately pile up along the [111] direction. As the thin film with rocksalt structure grows along the [111] direction, the corresponding dipole moments also pile up, which gives a diverging electrostatic potential, making rocksalt (111) surface highly unstable.

MgO is a typical simple oxide with rock salt structure having a large band gap of 7.8 eV (Ref. 3) and its polar (111) surfaces have intensively been studied both theoretically[4–7] and experimentally.[8–12] Due to its large band gap and strong ionic character, an atomically flat MgO (111) surface should be quite unstable compared with other metal monoxide (111) surface with rocksalt structure. Indeed it has not been succeeded in preparing an atomically flat (111) surface by polishing, annealing or cleaving MgO crystals[13] and the only available method would be layer-by-layer growth utilizing a highly nonequilibrium technique. So far, it has been found that MgO (111) films with relatively flat surface grow on GaN (0001),[9] 6*H*-SiC (0001) (Refs. 10 and 11) and α-Al_2O_3 (0001) (Ref. 12) substrates without a significant surface reconstruction. However, the formation of an atomically flat (111) surface has not been confirmed except for MgO (111)/Ag (111), where the in-plane lattice constant largely deviates from the value of rocksalt MgO.[8] Relaxation of the electrostatic instability of MgO (111) films accompanied by an increase in in-plane lattice constant has theoretically been suggested.[5,6] Therefore, in order to study the instability of polar films, it is quite challenging to prepare high quality MgO (111) thin films (i) with the lattice constant similar to the bulk rocksalt value and (ii) with atomically flat surface. It should be noted that the coexistence of Mg plane and O plane at the top (111) surface significantly relax the polar instability even if the surface roughness is subnanometer scale. Here we report the first layer-by-layer growth of unreconstructed rocksalt MgO (111) thin films using atomically flat single-crystalline NiO (111) buffer layers. Reflection high energy electron diffraction (RHEED) intensity oscillation has been observed up to ~10 MgO layer and the root mean square roughness (R_{RMS}) of film surface has been as small as 0.2 nm even at 500 MgO layers.

NiO buffer and MgO films were grown by pulsed laser deposition using KrF excimer laser (wavelength is 248 nm, pulse duration ~20 ns) with a MgO single-crystal target (4N purity) and a NiO sintered disk (3N purity). 2–150 nm-thick epitaxial NiO (111) buffer films were grown on yttrium stabilized zirconia (YSZ) (111) substrates at room temperature (RT) and at the oxygen partial pressure $(Po_2)=1\times10^{-3}$ Pa with a laser power density of ~1.5 J cm^{-2}, giving a growth rate of ~2 nm/min. After NiO film deposition, two NiO/YSZ samples were stacked with the film surfaces of samples attached to each other and were annealed in air at 1300 °C for 1 h in an alumina crucible to form single-crystalline NiO (111) films.[14,15] MgO thin films were then deposited on the NiO buffer films thus fabricated and also on commercial NiO (111) single-crystal substrates for comparison. The substrate temperature during the growth (T_G) of MgO films was varied from 500 °C to 850 °C and Po_2 from 10^{-4} to 5.0 Pa with a laser power density fixed to ~3.5 J·cm^{-2}. RHEED intensity oscillations were *in-situ* monitored with the electron beam incident along the $[11\bar{2}]_{\mathrm{MgO}}$ direction during MgO growth. A high resolution x-ray diffraction (HR-XRD) was used to determine epitaxial relationships, lattice constants of the films by reciprocal space maps (RSMs), and film thicknesses by glancing incident x-ray reflectivity (GIXRR). Film surface morphologies were studied by atomic force microscopy (AFM) in ambient atmosphere at RT.

Figures 1(a)–1(c) show atomic force microscopy (AFM) images and cross sections of 1300 °C-annealed commercial NiO substrate, 20 nm-thick NiO film on YSZ (111) and 5 MgO (111) layer film on YSZ (111) with the 20 nm-thick

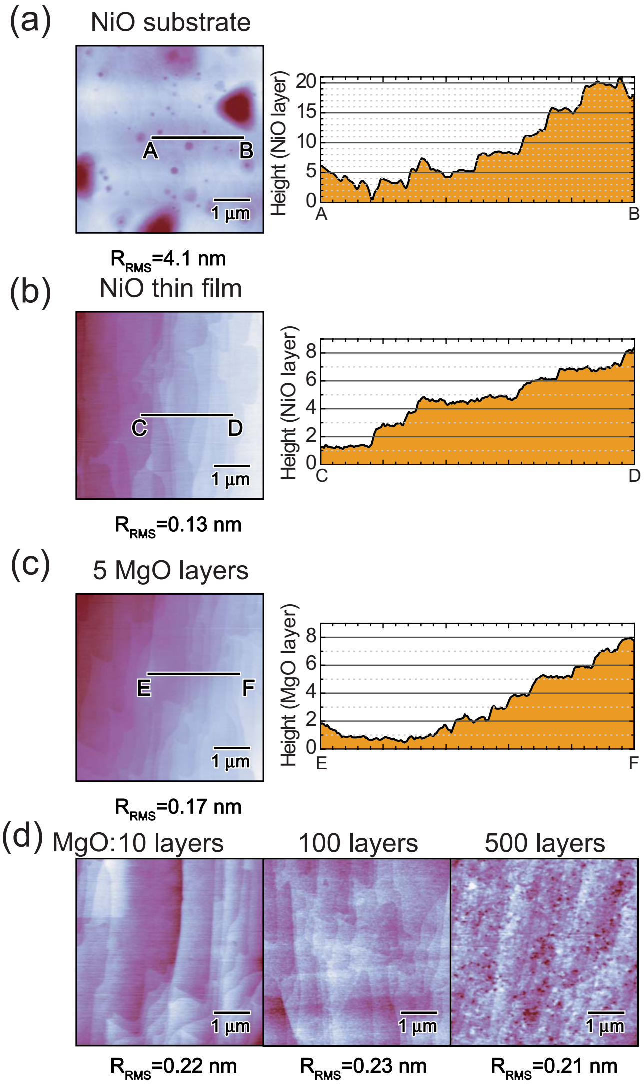

FIG. 1. (Color online) AFM images and cross sections (AB, CD and EF) of (a) NiO (111) single-crystal substrate annealed at 1300 °C, (b) 20 nm-thick NiO (111) film grown on a YSZ (111) substrate annealed at 1300 °C and 5 MgO (111) layers grown on a YSZ (111) substrate with the 20 nm-thick NiO (111) buffer layer. (d) AFM images of MgO (111) thin films with various thicknesses grown on a YSZ (111) substrate with the NiO (111) buffer layer.

NiO buffer layer. Atomically flat NiO (111) surface was realized at the film thickness of $\sim$20 nm and annealing temperature of 1300 °C and single NiO unit layer steps (1 Ni-O layer corresponding to 2.41 Å) were dominant although step bunching was also present as visible in Fig. 1(b). NiO film thickness was critical to form an atomically flat surface: NiO films were distorted to the YSZ substrate lattice for 2–10 nm-thick films while step bunching was significant for >100 nm-thick films. HR-XRD measurements have revealed that NiO was grown epitaxially with the relationship of [111] NiO‖[111] YSZ and [1$\bar{1}$0] NiO‖[1$\bar{1}$0] YSZ (data not shown). For comparison we annealed a commercial NiO (111) substrate at 1300 °C in air, the temperature and atmosphere used to prepare an atomically flat surface for NiO (111) film on YSZ (111) substrate and found that many pits

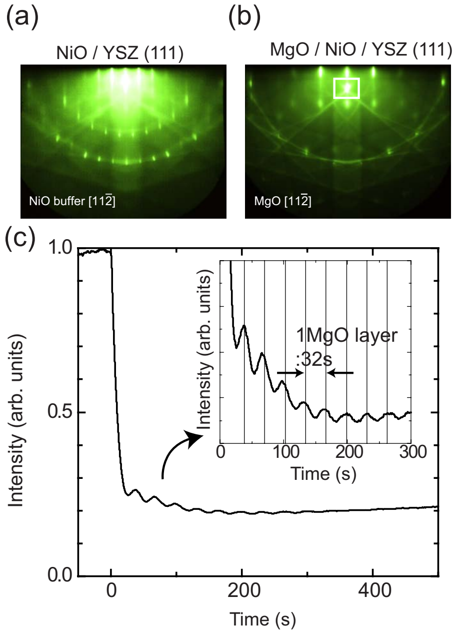

FIG. 2. (Color online) RHEED images of (a) NiO (111) /YSZ (111) and (b) 100 MgO (111) layer film grown on NiO/YSZ (111). Electrons with 30 keV was incident along the [11$\bar{2}$] azimuth of NiO or MgO. (c) A RHEED intensity oscillation of the direct diffraction spot indicated by a rectangle in (b) during the MgO heteroepitaxial growth. Inset shows the enlarged signal of the RHEED intensity oscillation.

were present as shown in Fig. 1(a). Further annealing of the NiO substrate in air at 900–1600 °C has given the surface with step and terrace structure; however, 1–2 μm wide hexagonal or triangle pits were always present and they became larger with increasing annealing temperature. Figure 1(c) shows AFM image of 5 MgO (111) layer film grown at T_G =600 °C and $Po_2=1\times10^{-3}$ Pa on YSZ (111) substrate with the NiO (111) buffer layer as well as the cross sectional profile, showing that an atomically flat MgO (111) surface with single MgO unit layer steps (1 Mg-O layer corresponding to 2.43 Å) was formed. AFM images for thicker MgO (111) films are shown in Fig. 1(d): For the films up to 10 MgO layers, the film surface shows a step and terrace structure inherited from the NiO buffer layer surface. For further thicker films with 100–500 MgO layers, step and terrace structures have gradually disappeared. Here, surface roughness of polar MgO (111) films is expected to increase with increasing film thickness to suppress the correspondingly increasing polar electrostatic instability, which has been observed in MgO(111)/α-Al$_2$O$_3$(0001).[12] In the present case of MgO (111)/NiO (111)/YSZ (111) structure, R_{RMS} of film surface estimated by 5×5 μm^2 AFM scan was strikingly as small as $\sim$0.2 nm even at 500 MgO layers, which was very small compared with the values for MgO (111) films grown on GaN (0001),[9] 6H-SiC (0001) (Refs. 10 and 11) and α-Al$_2$O$_3$ (0001).[12]

Figure 2(a) shows a RHEED image of the atomically flat 20 nm-thick NiO (111) film, showing $p(2\times2)$ surface reconstruction.[16–18] Clear diffraction with Kikuchi lines indicates high film crystallinity and an atomically smooth surface, in accordance with AFM and HR-XRD measurements. Two terminal resistance measurements in an ambient atmosphere at RT have shown that these NiO films are completely insulating ($<10^{-10}$ S cm^{-1}), which is comparable to a reported value ($\sim 10^{-10}$ S cm^{-1}) measured for a nearly-stoichiometric high quality NiO single crystal.[19] Figure 2(c) shows RHEED intensity of the specular diffraction as indicated by a rectangle in Fig. 2(b) during the MgO growth at $T_G = 600$ °C and at $Po_2 = 1 \times 10^{-3}$ Pa on NiO (111)/YSZ (111). Immediately after MgO deposition started, the RHEED intensity was drastically reduced and then the intensity oscillated up to ~9 periods, consistent with a surviving step and terrace structure at 10 MgO (111) layers observed by AFM [Fig. 1(d)].[20] GIXRR measurements have shown that the RHEED oscillation interval (~32 s) in Fig. 2(c) corresponds to one MgO layer with the rocksalt structure along the [111] direction. Therefore, a polar MgO (111) film has grown in a layer-by-layer mode on a YSZ (111) substrate with the atomically flat NiO (111) buffer layer. RHEED intensity oscillation was observed in a wide growth condition window: $T_G = 500-800$ °C ($Po_2 = 1 \times 10^{-3}$ Pa) and $Po_2 = 10^{-4} - 10^{0}$ Pa ($T_G = 600$ °C). In the case of MgO growth on commercial NiO (111) substrates, no RHEED intensity oscillation was observed due to the large surface roughness of substrates. RHEED oscillation was also absent for MgO growth on as-deposited NiO (111) buffer layers on α-Al_2O_3(0001) substrates: a very high crystallinity of post-annealed NiO (111) films on YSZ (111), which is available only owing to the absence of intermixing between NiO and YSZ up to 1300 °C is critical for the layer-by-layer growth of MgO (111) film. Figure 2(b) shows a typical RHEED image of 100 MgO layer film deposited on YSZ (111) substrate with the 20 nm-thick NiO buffer layer. Kikuchi lines have clearly been observed, which implies high film crystallinity and ultra smooth surfaces inherited from the NiO buffer layers. During the MgO deposition, only an unconstricted diffraction was observed by RHEED measurements with the electron beam incident along both the $[1\bar{1}0]_{\mathrm{MgO}}$ and $[11\bar{2}]_{\mathrm{MgO}}$ azimuth. During the MgO deposition, a deviation of in-plane lattice constant of the MgO films from that of the NiO buffer layers was less than 2% according to the streak-to-streak distance of the RHEED image. As already described, for MgO films grown on Ag (111) the in-plane lattice constant is considerably enlarged,[8] which can effectively relax the polar instability. It is quite striking that the present MgO (111) film, having an atomically flat surface, does not show a significant change in the lattice constant, surface roughening or reconstruction.

We performed HR-XRD measurements for further investigation of the lattice constant of MgO/NiO/YSZ (111) multilayer structures. Figure 3 shows a typical RSM around asymmetric 402_{NiO} diffraction of 10 MgO (111) layer film. Lattice constants and stress-relaxation rates ($\Delta d/d_0$) for 10–500 MgO layer films determined by the 402 diffraction of MgO and NiO were summarized in Table I. Out-of-plane and in-plane lattice constants of 20 nm-thick NiO buffer layer were $d_{111} = 2.405$ Å and $d_{1\bar{1}0} = 2.965$ Å, respectively, whose $\Delta d/d_0$ compared to the bulk NiO (JCPDS: 47–1049) are −0.4% and +0.3% due to a lattice mismatch to YSZ substrate. The full width at half maximums (FWHMs) of out-of-plane and in-plane rocking curves were 0.03 and 0.30 degree (data not shown), indicating high crystallinity comparable to commercial NiO substrates (0.15 and 0.19 degree, respectively). As for 10 MgO layer film grown on YSZ substrate with the 20 nm-thick NiO buffer layer, the out-of-plane and in-plane lattice constants were $d_{111} = 2.432$ Å and $d_{1\bar{1}0} = 2.965$ Å, respectively, whose $\Delta d/d_0$ were as small as 0.0% and −0.3% compared to the bulk MgO (JCPDS: 45–0946). As the MgO thickness increased up to 100–500 MgO layers, the out-of-plane lattice constant was slightly expanded to 2.436–2.437 Å ($\Delta d/d_0 = +0.2\%$) while the in-plane one remained 2.965 Å, pinned to the value of the NiO buffer layers, consistent with the *in situ* RHEED observation. As already described, in-plane lattice constant would expand while out of plane lattice constant would shrink to suppress the electrostatic instability of polar film by reducing the distance between two oppositely charged atomic layers. A slightly shrinking in-plane lattice constant and a slightly expanding out-of-plane lattice constant in the present MgO (111) film are quite remarkable. For 500 MgO layer film, the FWHMs of out-of-plane and in-plane rocking curves were still as small as 0.03 and 0.29 degree, respectively, which were almost the same as those of NiO buffer layer, indicating that crystalline quality of MgO (111) films is as high as single-crystal quality NiO film.

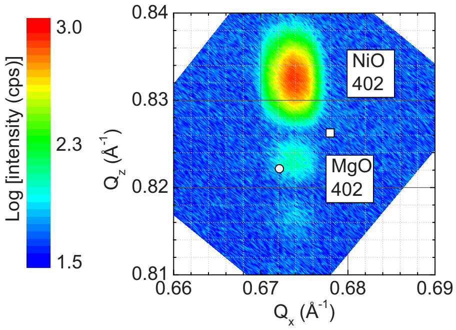

FIG. 3. (Color online) A RSM of 10 MgO (111) layer film grown on NiO/YSZ (111) near 402_{MgO} and 402_{NiO} diffractions. The circle and square indicate the bulk values of MgO and NiO, respectively.

TABLE I. Out-of-plane and in-plane lattice constants and stress relaxation rates of MgO (111) films with various thicknesses and 20 nm-thick NiO (111) buffer layer compared with their bulk values. Lattice constants were determined by asymmetric 402 diffraction.

	Out-of-plane		In-plane	
	d_{111} (Å)	d/d_0 (%)	$d_{1\bar{1}0}$ (Å)	d/d_0 (%)
MgO (45–0946)	2.432		2.978	
MgO 10 layers	2.432	0.0	2.965	−0.4
MgO 100 layers	2.437	+0.2	2.965	−0.4
MgO 500 layers	2.436	+0.2	2.965	−0.4
NiO (47–1049)	2.412		2.954	
NiO buffer layer	2.405	−0.3	2.965	+0.4

A possible stabilizing mechanism for such MgO (111) films with an atomically flat surface and with unchanged lattice constants would be the effect of NiO [111] dipole moment, which is similar to MgO [111] dipole moment, at the interface between the film and buffer layer. The role of such continuity of dipole moment which is perpendicular to the interface has been suggested for low-energy growth of nonbulk MgO phases on α-Al_2O_3 (0001) and on $MgAl_2O_4$ (111) substrates.[21] Here, considering a charge degree of freedom for transition metal and less ionic character of Ni than Mg, the polar instability of NiO (111) film would be considerably smaller than that of MgO (111) film. The present observation of MgO (111) film growth on NiO (111) buffer layer demonstrates a possibility of fabricating highly polar structure using less polar template, and would be applied to a variety of polar interfaces. For the (111) surface of bulk MgO crystal it has been reported that hydrogen termination plays a dominant role to stabilize the unreconstructed (111) polar surface.[22] It should be clarified in future the effect of such surface termination in the present film with the atomically flat surface.

In summary, we succeeded in controlling layer-by-layer growth of polar MgO (111) films by using YSZ (111) substrates with atomically flat NiO (111) buffer layers. The key was to prepare high crystalline quality NiO films comparable to single-crystals having a step and terrace surface structure with the step height of one Ni-O layer. Layer-by-layer growth was present up to ~10 MgO (111) layers, confirmed by RHEED intensity oscillation and by AFM measurements. Crystalline quality of the MgO (111) films thus grown was as high as that of single-crystalline NiO buffer films. Although three dimensional growth was dominant for further deposition, the surface roughness remained as small as R_{RMS} ~ 0.2 nm, which was remarkably small considering the strongly polar character of MgO (111) film. The atomically flat (111) surface of MgO (111) film thus prepared will not only be quite valuable to study the polar oxide surface but also open up a possibility of polar interface engineering using simple metal monoxides with rocksalt structure, where Mott insulators (FeO and CoO) as well as correlated metals (TiO and VO) are available.

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