Epitaxial growth of CaO films on MgO(001) surface: Strain relaxation at the CaO/MgO heterointerface

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The epitaxial growth of CaO films on mechanical-damage-free MgO(001) surface using low-temperature buffer technique has been carefully investigated. The strain is effectively relaxed in the CaO/MgO interfacial layers by lattice distortion and misfit dislocations as confirmed by transmission electron microscopy, which facilitates the subsequent growth of smooth CaO film at high temperature. The strain relaxation mechanism of the heterointerface is discussed in detail.
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Heteroepitaxy of CaO on MgO is of special scientific and technical interest. As typical ionic crystals, CaO and MgO share the same rocksalt (RS) structures and have a big lattice mismatch of ~14%. They are almost immiscible[1] that the interdiffusion between them could be neglectable, which would facilitate a sharp interface. Based on these above mentioned properties, they are ideal materials for exploring strain relaxation in heteroepitaxy, which plays a significant role in buffer and/or barrier-layer applications.[2] Besides, CaO is a well-known chemical reactive material, already being used in many industry process and showing its exciting potentials in catalytical chemistry[3] and surface science research.[4] According to recent theoretical prediction, CaO can even exhibit extraordinary ferromagnetic properties.[5] While compared with MgO, it is less explored. To better understand the basic physics and chemistry and further explore possible applications of this material, therefore, it is necessary to prepare CaO single crystals, especially crystalline surfaces.

Only one previous work has been done to grow CaO film on MgO. Using chemical solution deposition method, Langjahr *et al.* prepared polycrystalline CaO films on MgO(001) substrates and carefully discussed the strain relaxation mechanism in such a large lattice mismatched system using near-coincidence site lattice (NCSL) model.[6] In this work, we demonstrate that by a low-temperature (LT) CaO buffer technique, single crystalline CaO films with smooth surface can be prepared on rough MgO(001) substrate despite the lattice mismatch up to 14% using molecular beam epitaxy (MBE). Before the growth of CaO buffer, the substrate surface of the chemically etched MgO(001) is improved by using a homoepitaxial MgO layer, resulting in an excellent template for CaO epitaxy. It is revealed that a LT CaO buffer is very effective on compromising the huge lattice mismatch. Different from the work of Langjahr *et al.*,[6] the strain relaxation mechanism at the heterointerface is discussed in terms of dislocation kinetics.

The films were prepared by a set of radio frequency plasma-assisted MBE (rf MBE) system which has been successfully used to grow ZnO on different substrates.[7] After being degreased in trichloroethylene and methanol, the MgO substrates were chemically etched for 30 s in hot solution of 98% H_3PO_4 at 80 °C to remove the surface contamination and the damaged surface layers by mechanical polishing.[8] Before growth, the substrate was thermally cleaned at 650 °C for 30 min, followed by oxygen radicals pretreatment at 650 °C for 30 min. To improve the MgO(001) surface quality after chemical etching, a homoepitaxial MgO layer was grown at 650 °C for 30 min. Then a CaO buffer layer was grown at substrate temperature of 400 °C prior to the deposition of CaO epilayer at 600 °C. Mg and Ca atoms were evaporated from standard *K* cells with pyrolytic BN (PBN) crucibles. The oxygen radicals were supplied by the rf-plasma source (model 4.5ALO, SVTA), and the flow rate of oxygen was controlled by a mass flow controller. Growth temperature was monitored by a W/Re thermal couple. During deposition, the beam equivalent pressure (BEP) of Mg and Ca was controlled at the level of 10^{-8} mbar, and the oxygen pressure was about 10^{-5} mbar to ensure an oxygen-rich growth condition. The reflection high-energy electron diffraction (RHEED) was used to *in situ* monitor the evolution of surface morphology and crystallinity. The interfaces and crystal lattice structures were characterized by using high-resolution transmission electron microscopy (HRTEM). In addition, x-ray diffraction (XRD) θ-2θ and ω rocking scans and atomic force microscope (AFM) were performed to determine the crystal and surface qualities of the as-deposited films, respectively.

Although the commercially available polished MgO(001) substrates have atomically smooth surfaces [root mean square (rms) roughness <1 nm in a scale of 2

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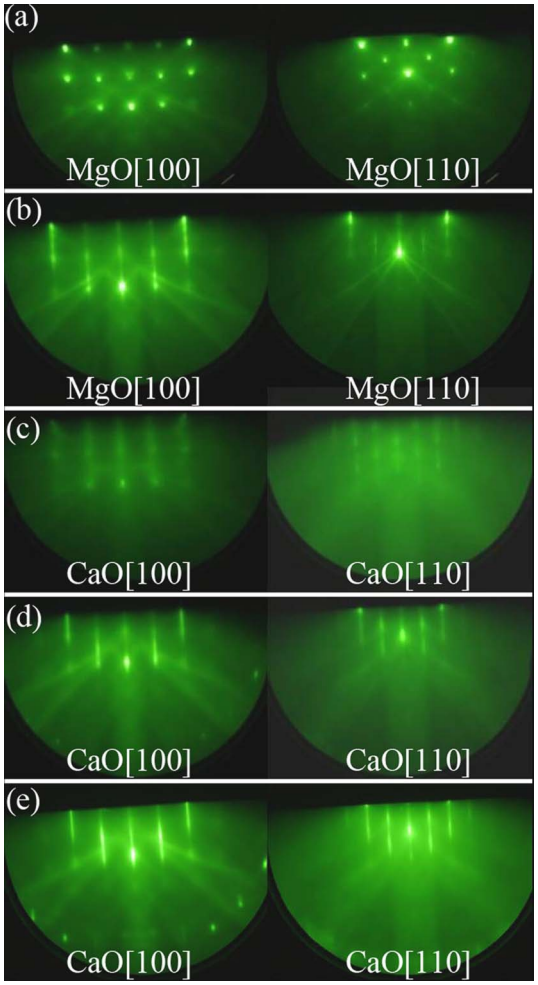

FIG. 1. (Color online) RHEED patterns taken during growth of a CaO film. The patterns are observed on ⟨100⟩ and ⟨110⟩ azimuths of the MgO substrate; (a) the MgO substrate after chemical polishing showing a spotty pattern, (b) the homoepitaxial MgO layer, (c) the nucleation of a CaO layer after several seconds of growth, (d) as-grown LT CaO buffer, and (e) as-grown HT CaO epilayer.

$\times 2\ \mu m^2$, characterized by AFM], their RHEED patterns are dark and obscure (not shown here), which indicates a poor surface crystallinity not suitable for epitaxial growth. Hence, the chemical etching process mentioned before is necessary to avoid the possible influence of the damaged layers on the subsequent growth, though the substrate surface becomes rougher than the unetched one. The evolution of RHEED patterns on ⟨100⟩ and ⟨110⟩ azimuths during the growth of a CaO sample is shown in Fig. 1. After the thermal cleaning of the MgO(001) substrate, clear spotty patterns are observed [Fig. 1(a)], implying the successful removal of the upper layers. In the following homoepitaxial growth at 650 °C, such pattern evolves slowly to sharp streaks with clear Kikuchi lines [Fig. 1(b)], indicating a remarkable improvement of the surface quality. However, the substrate is still featured with rough surface morphology, as confirmed by *ex situ* AFM (rms roughness: 4.2 nm, in a scale of $2\times 2\ \mu m^2$) in another experiment (not shown here). On such surface, the two-step heteroepitaxial growth of CaO is carried out. In Fig. 1(c), after several seconds' growth, the persisting streaky pattern of MgO fades away and a set of new streaks appears

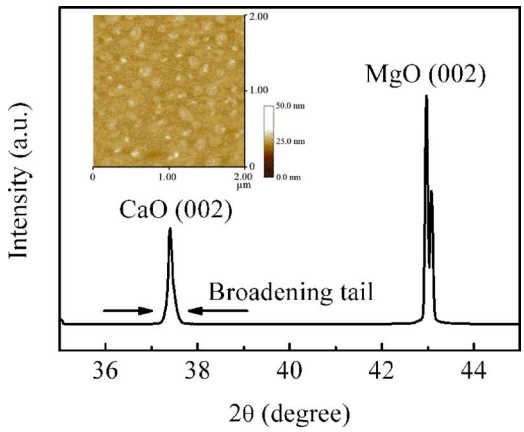

FIG. 2. (Color online) XRD (θ-2θ scan) from the (002) peaks of CaO and MgO. The inset shows the AFM image of an as-deposited CaO surface (rms roughness: 1.2 nm, in a scale of $2\times 2\ \mu m^2$).

faint. This implies the initial nucleation process of the CaO film on the MgO(001). Further LT buffer growth of CaO at 400 °C slowly leads to sharp streaky pattern with clear Kikuchi lines [Fig. 1(d)]. The high-temperature (HT) epitaxial CaO layer is so smooth that very sharp and clear RHEED patterns with high-order diffraction spots are observed during the whole depositing process [Fig. 1(e)]. No rotation domains are observed by RHEED, and the in-plane orientation shows that CaO(001) lattice overlaps on that of MgO(001), i.e., cube on cube.

Quality of the CaO films was further examined by *ex situ* XRD and AFM. Figure 2 shows the XRD θ-2θ scan curve of the CaO film. Two peaks are observed at 2θ=37.4°, 43.0°, which correspond to the diffractions from CaO(002) and MgO(002), respectively. The broadening tail of the CaO(002) peak indicates the residual strain in the film. The XRD ω rocking curve of CaO(002) (not shown here) gives a full width at half maximum (FWHM) value of 0.5312° (the FWHM of MgO substrate is 0.26° as a reference). The inset of AFM image in Fig. 2 shows the surface morphology of the film. In a scale of $2\times 2\ \mu m^2$, the rms roughness is 1.2 nm. These results indicate the prominent effect of the LT CaO buffer layer on improvement of the quality of CaO epilayer.

HRTEM observation was carried out to understand the role of the CaO buffer in atomistic details. The CaO/MgO interfacial structure is shown in Fig. 3. It can be seen that the CaO buffer layer and the MgO substrate are separated by a distinct interfacial region in a range of a few nanometers (indicated by the dashed rectangle). The homoepitaxial MgO layer shows a good lattice arrangement with few dislocations. Compared with the MgO lattice, the CaO counterpart has bigger lattice spacing and is featured with distorted lattice, which explicitly indicates the residual strain existing in the CaO buffer layer as the XRD result shows. The severe lattice distortion and high dislocation density are observed in the interfacial layers, which makes it hard to mark off a distinguished boundary between CaO layer and MgO substrate because the lattice constants in the region are undistinguishable. Most of the misfit dislocations in the interfacial layers are featured with their Burger's vectors perpendicular to the interface (labeled inside the dashed rectangle). To-

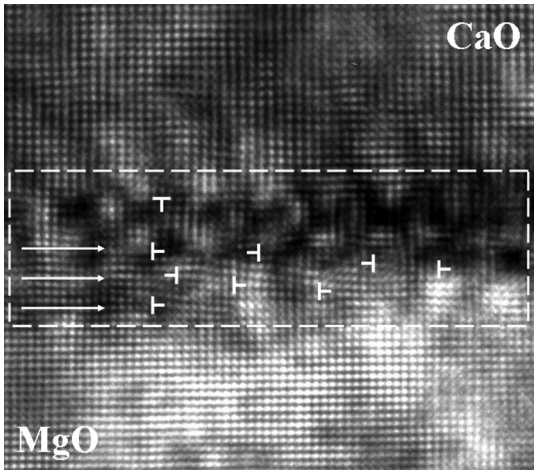

FIG. 3. Cross-sectional HRTEM image of the interfacial structure between CaO buffer layer and MgO substrate.

gether with lattice distortion in the upper CaO layers, these defects explicitly relax the epitaxial strain introduced by the large lattice mismatched CaO/MgO interface. It is worth mentioning that most of the dislocations observed in the CaO/MgO interfacial region are buried under the upper CaO layer, and the degree of lattice distortion decreases as the film thickness increases.

In an ideal situation where heteroepitaxy with large lattice mismatch happens on a "flat" surface, the misfit dislocations will locate at the interface with their Burger's vectors lying in the interfacial plane, such as the well-known domain matched epitaxy (DME).[9] While, strain relaxation, in fact, is kinetically limited due to the competing between relaxation mechanisms of surface "roughening" and misfit dislocations.[10] In our experiment, both mechanisms represented by wave-form-like lattice distortion and the dense dislocations distributing at the heterointerface, respectively, are observed. The perpendicular-to-interface direction of the Burger's vectors indicates the unique relaxation mechanism of the strained CaO film on rough MgO(001) substrate. In the view of dislocation kinetics, when energetically favored, misfit dislocations can only be introduced into the interface by slip of preexisting dislocations generated at the film surface that penetrate the overgrowth and substrate.[11] The energetic barrier for edge dislocations to slip in flat heterointerfacial plane is very low. Compared with slip motion, climb motion of dislocations is even harder in crystals because the latter breaks more bonds than the former does.[12] Supposing a simple situation where a misfit dislocation generated at the film surface moves along a rough interface in the slip plane [i.e., RS(001)], it will inevitably experience a process of climbing up or down (when meeting an island or a pit at the rough interface, respectively), which is rather energetically unfavorable. While in the perpendicular direction (RS[001]), since only slip mechanism works, kinetics of dislocations is quite more energetically favorable than in the rough interface. As a result, strain relaxation by misfit dislocations is much easier in perpendicular direction than that in growth plane. Besides such dislocation configuration mentioned above, it needs to be pointed out that an alternate configuration of misfit dislocations in the growth direction characterized with inverse Burger's vector directions (indicated by arrows in the dashed rectangle, Fig. 3) also compensates the tilting lattice distortion introduced by the dislocations in the interfacial layers as film thickness increases. Although residual strain still remains in the upper CaO buffer layers, the subsequent CaO epilayer has a very smooth surface as confirmed by *in situ* RHEED and *ex situ* AFM, and is qualified for various research and application purposes. Considering there are a lot of important RS oxides (such as SrO, BaO, TiO, CoO, NiO, etc.) with physical properties analogous to MgO and CaO, the relaxation mechanism studied in this work could be a good reference for heteroepitaxy of these materials.

In summary, using LT buffer technique, we have prepared CaO epitaxial films on large lattice mismatched MgO(001) substrate. An interfacial region with unique misfit dislocation configuration and severe lattice distortion between CaO and MgO is observed by HRTEM. The unique strain relaxation mechanism and interfacial dislocation configuration are attributed to the dislocation kinetics which drives the misfit dislocations slipping perpendicular to the interface.

ACKNOWLEDGMENTS

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