Structure stability of epitaxial MgO-CaO solid-solution films: effect of diffusion

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The nonequilibrium epitaxial growth process of $Mg_xCa_{1-x}O$ solid-solution films at 600°C is carefully investigated. No obvious phase separation is observed until annealing at 800°C despite a large miscibility gap. The solid-solution film is featured with disorder alloy as confirmed by transmission electron microscopy (TEM). Spinodal decomposition caused by uprising diffusion happens after short-time annealing which explicitly indicates the structure stability of the metastable solid-solution films does result from diffusion quenching. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2732411]

Rock salt (RS) compounds such as alkali halides and oxides have long been considered as the ideal systems for ionic crystals epitaxial studies.[1] Superior to the halides, the oxide counterparts are commonly wide-gap insulators with high dielectric constants and high melting points. They are sufficiently tough and unreactive, which would benefit a heteroepitaxy with sharp interface. In that case, they are excellent for various applications such as dielectric layers,[2] buffer layers,[3] tunnel barriers,[4] optical windows,[5] etc. To enlarge their application in band gap engineering and explore chemistry and physics, it is naturally necessary to mix different oxides into one single phase. Unfortunately, the solubility between RS oxides is so limited by their large positive mixing enthalpy that it is hard to prepare such solid solutions under thermodynamic equilibrium.[6]

Efforts have been made on mixing RS oxides, typically focusing on a MgO-CaO system due to its simplicity. Using molecular-beam epitaxy (MBE) under thermodynamic nonequilibrium conditions, Talvacchio *et al.* tried to grow $Mg_{0.73}Ca_{0.27}O$ as lattice matched barriers for NbN Josephon junctions.[7] In Hellman and Hartford's further work, full composition range of MgO-CaO solid-solution films were prepared on (100) MgO substrates.[8] Iedema *et al.* showed the atomic-scale mixing above 1100 K and nonlinear chemical properties of the single phase MgO-CaO films.[9] In addition to such foregoing scientific exploring, more recently, $Mg_xCa_{1-x}O$ has been applied in different fields and shown its unique potentials as low firing voltage protective layers for plasma display panels (PDPs),[10] surface passivation layers for AlGaN/GaN high electron mobility transistors (HEMTs),[11] or as lattice and valence-matched dielectric layers for ZnO,[12] a kind of promising optoelectronic semiconductor material. Driven by the technical and scientific interests in the mixing of the immiscible oxides, a further understanding of the structure, especially the structure stability of the solid solutions is necessary. In this work, the epitaxial growth property of the MgO-CaO solid solutions on CaO(001) surface at high temperature was investigated, and the microstructures of the solid-solution films were characterized with high-resolution transmission electron microscopy (HRTEM). The spinodal lines of the crystal lattice formed after a short-time annealing were observed, which evidently testified the metastable nature of such solid solutions. The structure stability of such metastable films was discussed in detail.

The films were prepared by a radio frequency plasma-assisted MBE (rf MBE) system which has been successfully used to grow MgO films on sapphire substrates.[13] The RS(001) surface was chosen to avoid the influence of the crystal polarity on the epitaxial growth. To directly compare the lattice structures between CaO, MgO, and the solid solutions, a CaO(001) layer was deposited on the MgO(001) substrates. Then the solid-solution films were grown on such substrates by simultaneously evaporating Mg and Ca atoms 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 surface morphology evolution and crystallinity. X-ray diffraction (XRD) θ-2θ scan was performed to determine the lattice constants of the solid-solution films. The interfaces and crystal lattice

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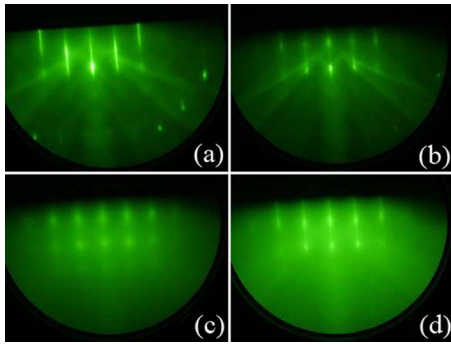b)Electronic mail: zezhang@bjut.edu.cn

FIG. 1. (Color online) RHEED patterns taken during growth of a $Mg_{0.7}Ca_{0.3}O$ film. The patterns are observed along a $\langle 100 \rangle$ azimuth of the CaO substrate; (a) the CaO substrate, (b) constrained $Mg_{0.7}Ca_{0.3}O$ lattice on CaO, (c) after 10 min of growth, constrained lattice relaxed, (d) at the end of the growth.

FIG. 2. (a) XRD (theta-2 theta scan) from the (002) peaks of CaO, $Mg_{0.7}Ca_{0.3}O$ and MgO, (b) Low magnification of cross-sectional TEM image of the films, (c) corresponding selected area electron diffraction patterns from $Mg_{0.7}Ca_{0.3}O$, CaO, and MgO denoted by (3), (2), and (1), respectively in (b).

structures were characterized by using HRTEM. In addition, energy dispersive x-ray spectrometry (EDX) and x-ray photoelectron spectrometry (XPS) were used to determine the film composition. Before the XPS measurement, the films were transferred into the analyzing chamber right after the growth, and the Argon ion bombardment was adopted to remove the surface contaminations. As to the EDX measurement, random data acquisition, and linear scan along the growth direction of the epitaxial films were both used with a focused electron beam whose spot diameter was 10 nm.

A high growth temperature of 600 °C was chosen for a better understanding of the epitaxial metastabilities in the case that ions diffusion mobilities both on the surface and in the bulk are greatly enhanced. The evolution of RHEED patterns during the growth of an $Mg_{0.7}Ca_{0.3}O$ sample is shown in Fig. 1. After the thermal cleaning of the MgO(001) substrate, spotty patterns were observed (not shown here) and a two-step method was used to deposit CaO film on the substrate. Figure 1(a) is the streaky pattern of the CaO(001) surface before deposition of the solid-solution film. The well-defined Kikuchi lines indicate the high quality of the CaO layer. In Fig. 1(b), after several seconds' growth, the RHEED pattern appears weak and somewhat spotty while remaining the same space between these streaky lines as that of CaO(001). This implies the existence of a pseudomorphic $Mg_{0.7}Ca_{0.3}O$ layer on the CaO(001). Such patterns retain for several minutes, and then break into dim spots, which can be attributed to the relaxation of the $Mg_{0.7}Ca_{0.3}O$ layer and its surface roughening [Fig. 1(c)]. During the subsequent growth, the RHEED patterns evolve very slowly to sharper streaks and spots [Fig. 1(d)]. Neither rotation domains nor obvious phase separation near the surface are observed by RHEED.

The films were carefully checked under an optical microscope with a magnification of 40 right after growth. They were smooth and transparent without any visible cracks and precipitates despite the large lattice mismatch between the solid-solution films and the substrates. EDX random data acquisition and linear scan (not shown here) both demonstrate good composition uniformity inside the $Mg_xCa_{1-x}O$ films and the results are consistent with the XPS measurements (not shown here), which indicates no segregations of

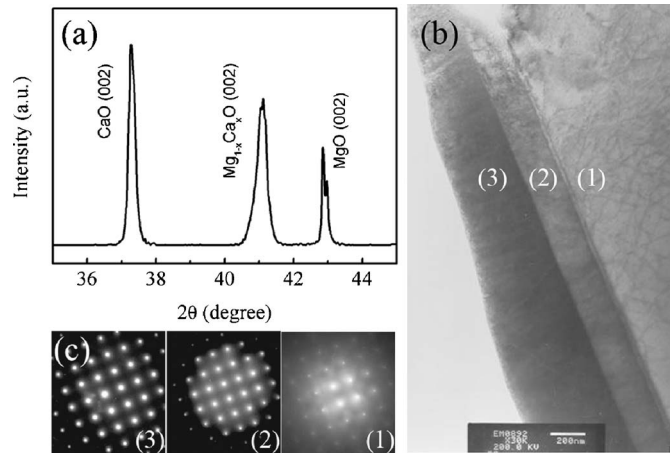Mg or Ca happening on the surface and inside the bulk even at such high growth temperature. XRD and TEM were used to testify the structure nature of the as-grown $Mg_xCa_{1-x}O$ films. Typical XRD and TEM images of an $Mg_{0.7}Ca_{0.3}O$ film are shown in Fig. 2. In Fig. 2(a), the new peak locating at 41.11° between CaO(002) (37.26°) and MgO(002) (42.85°) explicitly indicates the formation of a new RS-structure lattice. Data from a low magnification cross-sectional TEM image of a $Mg_{0.7}Ca_{0.3}O$ film are shown in Fig. 2(b). It can be seen that there are three distinct regions which represent the epitaxial layer sequences of MgO, CaO, and $Mg_xCa_{1-x}O$, respectively. A careful comparison of the electron diffraction patterns reveals that there are no satellite spots in Fig. 2(c). The intensity distribution of diffraction spots between MgO, CaO, and $Mg_xCa_{1-x}O$ is homogeneous, indicating that they share the analogous structure factors. In other words, the Ca^{2+} and Mg^{2+} ions randomly locate at the cation sites in the RS lattice and form the homogeneous solid solution. This is quite the same as the case of the mixed alkali halides epitaxy, where ordered compounds cannot be obtained directly by MBE and it is found that the larger bonding energy makes the ordering process impossible to occur.[14] The differences between the lattice spacings of MgO, $Mg_xCa_{1-x}O$, and CaO deduced from the electron diffraction patterns are quite similar to those deduced from x-ray diffraction results. Considering the growth temperature and source fluxes were fixed during the whole epitaxial process, the growth rate is calculated as ~0.12 Å/s by measuring the thickness of the film (~430 nm) and growth time (~10 h).

To understand the structure stability nature of the solid-solution films grown by MBE, the $Mg_{0.7}Ca_{0.3}O$ sample was annealed at 800 °C in an oxygen radicals ambient (10^{-5} mbar). The sample is not cooled down slowly to room temperature until two sets of RHEED patterns appear [Figs. 3(a) and 3(b), indicated by arrows] after a 5 min annealing which means a breakdown of long-range ordering. The HRTEM characterization of the lattice structure is shown in Fig. 3(c). Misfit dislocations (indicated by arrows inside the dashed rectangle) are the main defects abounding at the het-
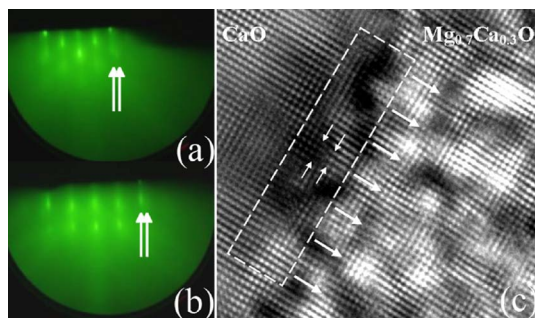
FIG. 3. (Color online) (a) and (b) RHEED patterns of phase separation of a $Mg_{0.7}Ca_{0.3}O$ film along $\langle 110 \rangle$ and $\langle 100 \rangle$ azimuth respectively, (c) HRTEM image of the interface between CaO and $Mg_{0.7}Ca_{0.3}O$.

erointerface which displays a weak lattice coherence of the CaO substrate and the $Mg_xCa_{1-x}O$ film. In the solid-solution region, lattice spinodal lines (indicated by arrows array) are observed indicating explicitly uprising diffusion which causes unmixing of the solid solutions. It is worth mentioning here that because the whole annealing process is very short, the unmixing kinetics can be quenched. Therefore, the lattice structure can be maintained after the spinodal decomposition. The chemical compositions of the precipitates separating from the $Mg_{0.7}Ca_{0.3}O$ solid solutions are $Mg_{0.53}Ca_{0.47}O$ and $Mg_{0.12}Ca_{0.88}O$ corresponding to the minimal and maximal lattice spacing respectively in the spinodal region, which are calculated by Vegard's law using the CaO lattice spacing as a reference. Although dislocations are still observed somewhere, most of the crystal lattices between different phases are coherent implying a coherent spinodal decomposition at its initial stages.

Both MgO and CaO have a very high melting point, i.e., very strong bonding of the cations at the lattice sites. Their equilibrium solubility in each other is very limited suggesting a very weak diffusing ability into each other. The structure stability of the epitaxial MgO-CaO solid-solution films was accounted theoretically in terms of epitaxial quenching by Hellman *et al.*[8] In this view, the structure stability during the high temperature epitaxial process can be described as follows: at the first stage of growth, in addition to epitaxial quenching mechanism, the solid-solution film is also epitaxially stabilized[15] by the constraint of the CaO substrate until relaxation happens at the heterointerface. Even without the additional constraint of the substrate, the diffusion of cations is still very limited due to the strong bonding at the RS lattice sites which protects the long-range ordering lattice arrangement. Considering that the high quality homoepitaxy of MgO can occur at 1/20 of its melting point,[16] it is worth mentioning that the surface mobility of the solid-solution film is evidently reduced by alloy disorder that leads to a poor surface morphology even at a high growth temperature

of 600 °C. It is well known that diffusion depends exponentially on the temperature, so does the unmixing kinetics of the solid solution. It may explain the obvious lattice structure distortion when temperature rises from 600 °C to 800 °C. Since the diffusion can be effectively quenched even at a temperature as high as 600 °C, the MgO-CaO solid-solution films prepared by nonequilibrium method such as the MBE can have ultrastrong structure stability at common temperature and will have an exciting future in heterostructure engineering.

In summary, we explored the nonequilibrium epitaxial growth process of $Mg_xCa_{1-x}O$ solid-solution films at 600 °C by RHEED. No obvious phase separation was observed until annealing at 800 °C despite a large miscibility gap. Compositions of the films were measured by XPS and EDX. The structure nature of the films was examined by XRD and TEM. Spinodal decomposition caused by uprising diffusion was observed by HRTEM which indicates the structure stability of the metastable solid-solution films is the result of diffusion quenching.

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