Atomistic Crystal Growth Simulation of Metal Oxide Materials

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We developed a new crystal growth molecular dynamics code MOMODY to simulate epitaxial growth processes of metal oxide surfaces. In this methodology, various metal oxide molecules are deposited over substrate surfaces one by one in regular time intervals with definite velocity. It enables us (1) to clarify the crystal growth mechanism of homo- and hetero-epitaxial growth, (2) to elucidate the hetero-interface structures of metal oxides, (3) to predict new metal oxide structures including quantum dots and superlattices, (4) to design buffer layers for hetero-interfaces, and (5) to optimize various experimental conditions for crystal growth. In the present paper, we reviewed the application of our MOMODY code to the crystal growth processes of various metal oxide systems and discussed its effectivity.

Key words: Crystal Growth Simulation, Molecular Dynamics, Metal Oxide Materials, Epitaxial Growth

1. INTRODUCTION

Artificial construction of atomically defined metal oxide layers is important in making electronics devices including light-emitting materials, high temperature superconducting oxide films, and magnetic devices as well as other advanced materials such as metal oxide catalysts. Hence, atomistic understanding of the layer-by-layer epitaxial growth process of metal oxide surfaces is desired to fabricate atomically controlled structure, which exhibits unexplored and interesting physical properties. Although a lot of information has been accumulated by the epitaxial growth experiments, theoretical approaches would be also desirable for the atomistic understanding and control of the epitaxial growth processes of metal oxide thin films.

Among various theoretical approaches, molecular dynamics (MD) is a best approach for the crystal growth simulation [1,2]. However, no MD studies were so far devoted to the simulation of the epitaxial growth processes of metal oxide surfaces. Hence, we developed a new crystal growth molecular dynamics (MD) code MOMODY [3,4] to simulate the epitaxial growth process of metal oxide materials. It enables us (1) to clarify the crystal growth mechanism of homo- and hetero-epitaxial growth, (2) to elucidate the hetero-interface structures of metal oxides, (3) to predict new metal oxide structures including quantum dots and superlattices, (4) to design buffer layers for herero-interfaces, and (5) to optimize various experimental conditions for crystal growth. Hence, in the present paper, we reviewed the application of our MOMODY code to the crystal growth processes of various metal oxide systems and discussed its effectivity.

2. DEVELOPMENT OF ATOMISTIC CRYSTAL GROWTH SIMULATOR [3,4]

We developed a new crystal growth MD simulation code MOMODY. The total number of species

in the system is not fixed but increases with time. Fig. 1 shows the model system of the crystal growth simulations: the top corresponds to the source of emitting metal oxide molecules and the substrate lies at the bottom. In this program, the number of metal oxide molecules deposited over the substrate surface is increased one by one. The metal oxide molecules are shot to the surface in regular time intervals with definite velocity. Since the emitting molecules, the substrates, the temperature of substrate, the number of emitting molecules, the emitting rates of molecules, and the time interval of the emission are variable parameters. various experimental conditions are expected to be optimized by our new crystal growth simulator.

3. EPITAXIAL GROWTH PROCESS OF SrO LAYER ON $SrTiO_3(001)$ [5]
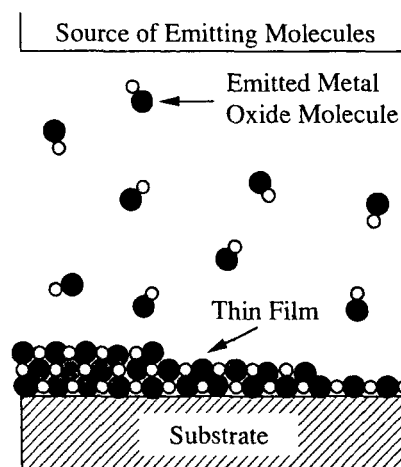
$SrTiO_3$ has attracted much attention among metal

Fig. 1 Model system for simulating the epitaxial growth process of metal oxide surfaces.

oxide crystals, due to its significance as a lattice-matched substrate, which is suitable for the epitaxial growth of high-Tc superconducting films. Hence, the crystal growth process on the $SrTiO_3(001)$ surface has been well investigated by various experimental techniques. However, atomistic understanding of the epitaxial growth mechanism on the $SrTiO_3(001)$ was not established still, both experimentally and theoretically. Hence, we applied our crystal growth simulator to investigate the homoepitaxial growth process on the $SrTiO_3(001)$ surface.

Since the $SrTiO_3$ crystal has a structure stacked alternately by nonpolar SrO and TiO_2 atomic planes, two different surface terminations with either SrO or TiO_2 at the (001) top layer are possible. Kawasaki et al. [6] have succeeded in fabricating an atomically flat and smooth $SrTiO_3(001)$ surface completely terminated by TiO_2 atomic plane by the treatment with pH-controlled NH_4F-HF solution. In order to make a straight comparison with the experimental results, we employed the $SrTiO_3(001)$ surface model terminated by TiO_2 atomic plane as a substrate for the present simulations.

The simulation was performed at 300 K and SrO molecules are continuously deposited over the $SrTiO_3(001)$ surface. After the migration of SrO molecules on the $SrTiO_3(001)$ surface, a two-dimensional and epitaxial growth of the SrO thin layer was observed. Moreover, the deposited SrO molecules retained the perovskite structure and the (001) oriented configuration during the MD simulations. However, some defects were observed in the SrO layers and the complete layer-by-layer homoepitaxial growth of SrO thin films without defects was not obtained at a low temperature of 300 K.

We also simulated the deposition process of SrO molecules on the $SrTiO_3(001)$ at 713 K (Fig. 2). Even at this high temperature, the SrO layer grew epitaxially retaining the perovskite structure and (001) oriented configuration. Furthermore, the formation of a single two-dimensional uniform and flat SrO layer without any defects was observed at 50000 time step, which is significantly different from the results at 300 K. Thus,
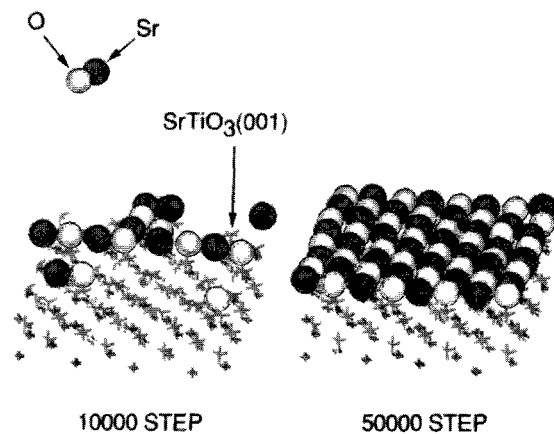
high temperature was found to lead to the complete epitaxial growth of the SrO layer on the $SrTiO_3(001)$ surface. We also found that the increase in the diffusivity of the deposited SrO molecules with increasing temperature is responsible for a complete layer-by-layer homoepitaxial growth.

Experimentally, Kawasaki et al. [7] applied laser MBE technique to fabricate the SrO layer on the atomically flat $SrTiO_3(001)$ surface terminated by TiO_2 atomic plane obtained by the NH_4F-HF treatment [6] and they achieved the epitaxial and two-dimensional growth of single SrO layer at 713 K, which is in good agreement with our simulation results. Moreover, they confirmed the atomically flatness of the grown SrO layer on the $SrTiO_3(001)$ surface by using the atomic force microscopy (AFM) technique. The preferability of high substrate temperature for the complete layer-by-layer homoepitaxial growth of the $SrTiO_3(001)$ surface was also observed experimentally.

4. HOMOEPITAXIAL GROWTH PROCESS OF SMOOTH ZnO(0001) [8]

Recently, Kawasaki et al. constructed ZnO quantum dots on an α-$Al_2O_3(0001)$ surface by using laser molecular-beam epitaxy techniques and observed an ultraviolet laser emission of the above material as pumped by a yttrium aluminum garnet (YAG) laser at a room temperature [9,10]. After their reports, the studies on ZnO-based ultraviolet laser-emitting materials are rapidly stimulated. Especially, the optical properties of the ZnO quantum dots were very sensitive to their crystal quality, orientation, and size. Hence, in order to control these factors, it is crucially important to understand the epitaxial growth process of ZnO quantum dots on an atomic scale. Hence, we applied our crystal growth simulator to the homoepitaxial growth process of ZnO(0001) surface.

Since ZnO crystal has a wurtzite structure, two different surface terminations by either Zn or O atomic plane at the (0001) surface are possible. Kawasaki et al. clarified that ZnO quantum dots on α-$Al_2O_3(0001)$ surface is terminated by O atomic plane by using coaxial impact collision ion scattering spectroscopy (CAICISS)

Fig. 2   Epitaxial growth process of SrO layer on $SrTiO_3(001)$ surface terminated by TiO_2 atomic plane at 713 K.
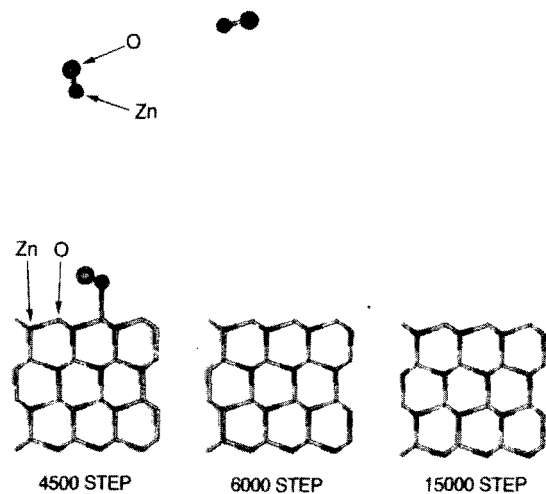

Fig. 3   Homoepitaxial growth process of smooth ZnO(0001) at 700 K.

measurements [11], and hence we employed a ZnO(0001) surface model terminated by O atomic plane to be compared with experiments.

Fig. 3 shows the homoepitaxial growth process on the ZnO(0001) surface terminated by O atomic plane at 700 K. One ZnO molecule stuck on the ZnO(0001) surface at 4500 step. The Zn atom of the deposited ZnO molecule is bonded to an O atom of the surface, indicating that the adsorbed ZnO molecule can form bonds with the surface through only single coordination. It is due to the fact that the topmost surface consists of only O atomic species and Zn atoms are not exposed at the surface. However, the adsorbed ZnO molecule was readily evaporated from the surface at 6000 step. We suggest that the small interaction resulting from single coordination favors the release of the adsorbed ZnO molecule from the surface at a high temperature of 700 K (Fig. 3). Although another ZnO molecule stuck to the surface again at 7500 step, it was also readily evaporated from the surface. Similar processes were repeated on the surface, and hence finally no ZnO molecule adhered to the smooth ZnO(0001) surface at 15000 step. It indicates that ZnO thin films or quantum dots rarely grow from the smooth ZnO(0001) surface.

5. HOMOEPITAXIAL GORWTH PROCESS OF ZnO(0001) WITH SURFACE STEP [8]

We also simulated the continuous deposition process of ZnO molecules on ZnO(0001) with a surface step at 700 K (Fig. 4). Suprisingly the ZnO epitaxial film was smoothly constructed at 15000 step, in contrast to the process on the smooth ZnO(0001) surface. It indicates that the crystal growth readily starts at the surface step, which is not realized at the smooth surface. Moreover, the deposited ZnO molecule kept a wurtzite structure and (0001) oriented configuration on the surface. The detiled mechanism of the above process is discussed below.

First, one ZnO molecule stuck to the surface step at 4500 time step. Here, the Zn atom of the deposited ZnO molecule is bonded to an O atom of the surface, while the O atom of the deposited ZnO molecule is bonded to a Zn atom of the surface. Namely the deposited ZnO molecule forms bonds to the surface
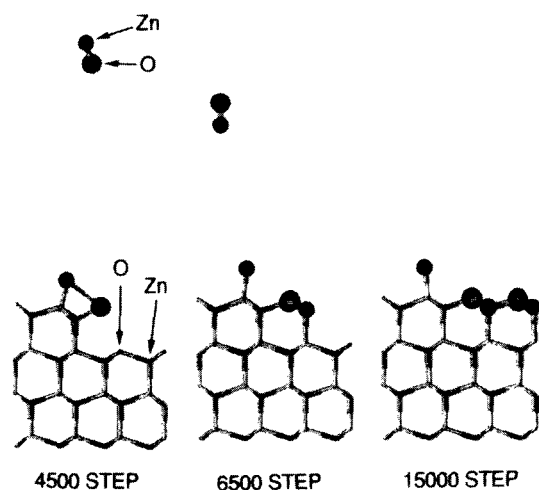

Fig. 4 Homoepitaxial growth process of ZnO(0001) with a surface step at 700 K.

through double coordination, which is much different from the process on the smooth ZnO(0001) surface. It is due to the fact that both Zn and O atoms are exposed at the surface step, which is not realized at the smooth surface. A second deposited ZnO molecule adhered to the surface step at 6500 step and a six-membered ring was formed at the surface step. This result indicates that the first adsorbed ZnO molecule at the surface step plays a role of nucleation center.

The similar processes repeated many times and finally the first ZnO layer was completely constructed at 15000 step. We should note that the deposited second ZnO molecule formed three six-membered rings at the same time, which greatly stabilized the second deposited ZnO molecule. It may also be another reason, justifying that the epitaxial growth smoothly starts from the surface step. Experimentally, Kawasaki et al. revealed [12] that ZnO quantum dots are formed in a spiral growth mode on α-Al$_2$O$_3$(0001) surface. Since a spiral growth is realized by the step flow growth with screw dislocation, our MD simulations support their experiments.

6. COMPARISON OF HOMOEPITAXIAL GROWTH PROCESS OF SrTiO$_3$(001) AND ZnO(0001)

The homoepitaxial growth mechanism of the ZnO(0001) is completely different from that of the SrTiO$_3$(001) surface. SrO thin film grows epitaxially on the smooth SrTiO$_3$(001) surface terminated by TiO$_2$ atomic plane, keeping perovskite structure and (001) oriented configuration during the MD simulation. Moreover, surface steps do not greatly affect the growth process of the SrTiO$_3$(001) at 713 K. This difference is clearly interpreted from the surface structure of the SrTiO$_3$(001). Since SrTiO$_3$ crystal has a perovskite structure and both Ti and O atoms are exposed at the (001) surface terminated by TiO$_2$ atomic plane, the adsorbed SrO molecules are stabilized through more than two coordinations even on the smooth SrTiO$_3$(001) surface. This adsorption structure cannot be realized in the deposition process of ZnO molecules on the smooth ZnO(0001) surface, as mentioned before. Consequently, the surface morphology of the metal oxide surfaces is found to have a major influence on the epitaxial growth processes.

7. CHEMICAL VAPOR DEPOSITION PROCESS ON ZSM-5(010) SURFACE [13]

Zeolites have been widely applied to catalysts, adsorbents, molecular sieves, and so on. A discovery of novel zeolite framework structure has given great impacts on industry, engineering, and science. Especially, the development of Y-type zeolite enabled us to industrialize the catalytic cracking process, while the development of ZSM-5 enabled us to industrialize the methanol to gasoline process, isomerization of xylene, and many other processes. Although a lot of studies on the effects of zeolite structures, exchanged cations, and framework cations on the catalytic activity have been carried out, a significantly lower number of researches on the development of novel zeolite framework structure has been performed despite their intense demand, because of its difficulties and long time consumption.

Hence, in order to realize the theoretical design of novel zeolite structure, we performed a crystal growth simulation of zeolite surfaces.

In the above crystal growth MD simulations, metal oxide molecules are continuously deposited on the substrates and the deposited molecules stack on the substrate without surface chemical reactions. However, the above simulation methodology is not sufficient for the simulation of the zeolite synthesis process, since the surface of zeolites is normally terminated by silanol groups (HO-[zeolite]) and the simulations on the surface chemical reaction processes such as $Si(OH)_4$ + HO-[zeolite] -> $Si(OH)_3$-O-[zeolite]+ H_2O are required. The treatment of the above surface chemical reactions is crucial for the MD simulations and has prohibited the simulation of the synthesis process of zeolites. In the present study, we determined novel force field, which can reproduce the surface chemical reactions on zeolites and applied our MD simulation code to the chemical vapor deposition (CVD) process on the ZSM-5(010) surface. The details of the novel force field for zeolite synthesis simulations are described in the reference [13].

Totally 12 $Si(OH)_4$ molecules were placed on the ZSM-5(010) surface as a CVD source. Fig. 4 shows the CVD process of $Si(OH)_4$ molecules on the ZSM-5(010) surface at 1500 K. The formation and evaporation of H_2O molecules over the ZSM-5(010) surface was observed. It indicates that the surface chemical reactions such as $Si(OH)_4$ +HO-[ZSM-5] -> $Si(OH)_3$-O-[ZSM-5] and others take place. Attention was given to the Si atoms represented by spheres on the ZSM-5(010) surface at 30000 step, which originally come from the $Si(OH)_4$ molecules. All the above Si atoms connected to the ZSM-5(010) surface or other $Si(OH)_4$ molecules, indicating the formation of new Si-O-Si bonds. It also shows the surface chemical reactions take place on the ZSM-5(010) surface.

Moreover, the constructed SiO_2 layer was not amorphous, but inherited the ZSM-5 structure, keeping ten-membered ring and (010) oriented configuration. These results indicate that the epitaxial growth of ZSM-5(010) is realized in the CVD crystal growth simulation. Finally, we confirmed that the crystal growth
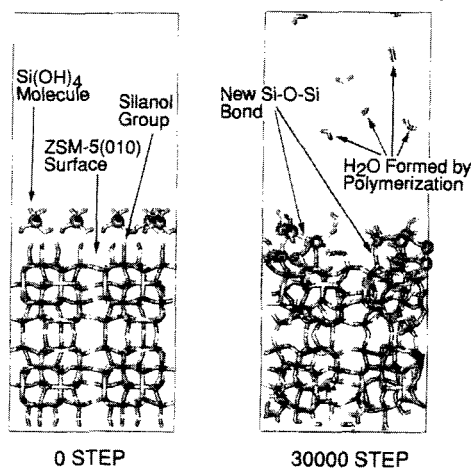

0 STEP   30000 STEP

Fig. 5   Chemical vapor deposition process of $Si(OH)_4$ molecules on ZSM-5(010) surface at 1500 K.

process including the surface chemical reactions can be also reproduced by the MD simulations.

8. CONCLUSION

In addition to the above results, we have also applied our crystal growth simulation code MOMODY to the homoepitaxial growth process of MgO(001) [3], heteroepitaxial growth of BaO layers on $SrTiO_3(001)$ [14], and so on. We also succeeded to design the buffer layers for the $YBa_2Cu_3O_{7-x}/SrTiO_3(001)$ interface [15] by using the above simulation code.

Finally, we confirmed that our crystal growth simulator MOMODY is very effective tool to design the atomistic structures of metal oxides, including superlattices, quantum dots, buffer layers and so on. We expect that our crystal growth simulator MOMODY will contribute to the science and technology of metal oxide electronics materials.

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