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# Layer-by-layer homoepitaxial growth process of MgO(001) as investigated by molecular dynamics, density functional theory, and computer graphics

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We applied molecular dynamics, density functional theory, and computer graphics techniques to the investigation of the homoepitaxial growth process of the MgO(001) surface. MgO molecules are deposited over the MgO(001) plane one by one at regular time intervals with definite velocities. Any deposited MgO molecule migrated on the surface, and later a two-dimensional and epitaxial growth of MgO thin layer was observed at 300 K which is in agreement with the experimental result. However, some defects were constructed in the grown film at low temperature of 300 K, which is in remarkable contrast to that at 1000 K. In the latter case, a single flat and smooth MgO layer without defects was formed, which also agreed with the experimental result. Self-diffusion coefficients and activation energy for the surface diffusion of the deposited MgO molecule on the MgO(001) plane were discussed to clarify the temperature-dependency of the epitaxial growth process. © 1997 American Institute of Physics. [S0021-9606(97)50735-5]

## I. INTRODUCTION

Artificial construction of atomically defined metal oxide layers is important in making electronic devices including high temperature superconducting oxide films, magnetic and optical devices as well as other advanced materials such as supported metal oxide catalysts.<sup>1-8</sup> Hence, the atomistic understanding of the layer-by-layer epitaxial growth process of metal oxide surfaces is desired to fabricate atomically controlled structure that exhibits unexplored and interesting physical properties.

MgO thin film fabrication has attracted much attention, due to its significance as high temperature material, wide-gap insulator, unreactive substrate, secondary electron emission material, model catalyst, and other interesting materials. Hence, the epitaxial growth of MgO thin films on various substrates, such as MgO,<sup>9-11</sup> silicon,<sup>12</sup> quartz,<sup>13</sup> sapphire,<sup>14</sup> GaAs,<sup>15</sup> TiO<sub>2</sub>,<sup>16</sup> etc., has been well investigated by using various experimental techniques, such as molecular beam epitaxy (MBE), chemical vapor deposition (CVD), sputtering, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), transmission electron microscopy (TEM), atomic force microscope (AFM) etc. Recently, MgO thin film has been actively studied as a buffer layer of high T<sub>c</sub> superconducting films. Since a MgO buffer should be atomically flat, smooth and dense to enhance the growth of superconducting oxides such as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>,<sup>17-19</sup> the studies

on the atomistic control of the surface, interface and growth process of MgO were rapidly stimulated. Although important information has been obtained from the epitaxial growth experiments, theoretical approaches, such as molecular dynamics (MD), quantum chemistry, Monte Carlo simulation, and computer graphics (CG) would be also desirable for the atomistic understanding of the epitaxial growth process of MgO thin films and fabricating thin MgO films with atomically flat surface and interface.

Many MD simulations have been performed on bulk properties of inorganic materials, such as metal oxides, glasses, and zeolites.<sup>20-23</sup> Moreover, the MD technique was also applied to simulate the continuous deposition process of monoatomic species on surface. In 1985, Schneider *et al.*<sup>24</sup> developed the first MD algorithm to simulate the vapor-phase crystal growth process and applied it to a Lennard-Jones system. Later, the growth process of silicon films was actively studied by means of epitaxial growth MD simulators.<sup>25-29</sup> In 1991, Luedtke and Landman employed an embedded-atom MD method to investigate the continuous deposition process of metals on metal surfaces.<sup>30</sup> In 1992 Athanasopoulos and Garofalini studied the continuous deposition process of Pt particles on silica surface.<sup>31</sup> We also investigated the formation mechanism of ultrafine Au and Pd particles on the MgO(001) plane.<sup>32-37</sup>

Although the MD simulation of the epitaxial growth process of metal oxide surfaces is essential for the design and fabrication of the atomically defined metal oxide layers, no studies were devoted to the simulation of the epitaxial growth process of metal oxide surfaces except our previous work.<sup>38</sup> In that paper, we studied the deposition process of single Ti<sup>4+</sup>, TiO<sup>2+</sup>, TiO<sub>2</sub> and Sr<sub>4</sub>Ti<sub>4</sub>O<sub>12</sub> on the SrTiO<sub>3</sub>(001)

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surface. However, in order to clarify the whole and complete process of epitaxial growth of the metal oxide surface, MD simulation has to be applied to the continuous deposition of metal oxide molecules and to the formation of the metal oxide layer. Hence, in the present study we continuously deposited MgO molecules over the MgO(001) surface one by one at regular time intervals with a definite velocity and investigated the whole epitaxial growth process of the MgO(001) surface. Moreover, the effect of the substrate temperature on the structure of the formed MgO layer was discussed.

## II. METHOD

### A. First principle calculations

Quantum chemical calculations based on the density functional theory (DFT) (Ref. 39) were performed to determine the atomic charges on Mg and O atoms required for the MD potential parameters of the MgO system using the DMol (Ref. 40) software package of MSI. All calculations were carried out with double numerical basis sets with polarization functions.<sup>41</sup> The Becke-Lee-Yang-Parr nonlocal correlation functional was used for exchange correlation energy terms in the total energy expression.<sup>42,43</sup> The calculations were performed on a Silicon Graphics IRIS-Indy workstation. The visualization was made with Insight II software of MSI (Ref. 44) on a Silicon Graphics IRIS-Indigo2 workstation.

### B. Molecular dynamics simulations

For the present MD calculations, we modified the MD simulation code MXDORTO developed by Kawamura<sup>45</sup> to investigate the continuous deposition process of metal oxide molecules and whole epitaxial growth process of metal oxide surfaces. Our modifications concern the total number of species in the system which is not fixed but increases with time. Fig. 1 shows the model system of these MD simulations: the top corresponds to the source of emitting metal oxide molecules and in the bottom lies the substrate. Metal oxide molecules, which emerge randomly from any point of the emitting source of MgO molecules, are emitted one by one at regular time intervals of 1000 time steps with a constant velocity of 900 m/s. The distance between the MgO(001) plane and the emitting source of MgO molecules is 15 Å, the temperature of MgO substrate is fixed at either 300 K or 1000 K, and the total number of emitted MgO molecule is 32.

The Verlet algorithm<sup>46</sup> was used for the calculation of atomic motions, while the Ewald method<sup>47</sup> was applied for the calculation of electrostatic interactions. The temperature was controlled by means of scaling the atom velocities under periodic boundary conditions, according to previous works on the deposition process.<sup>24,25,28,30–38</sup> Only the substrate temperature was controlled such that the energy released from deposited MgO molecules is correctly reproduced from the deposition event. The calculations were performed for 50 000 steps with a time step of  $2.0 \times 10^{-15}$  s. The two-body,

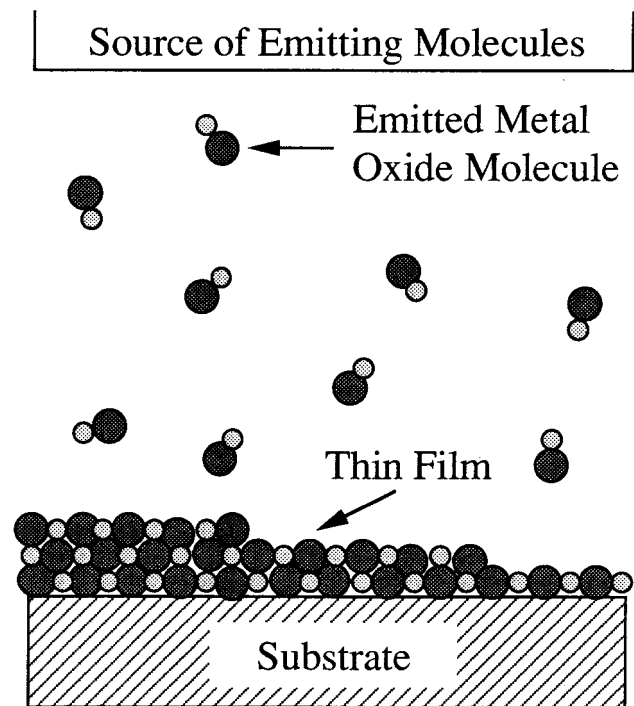


FIG. 1. Model system for simulating the epitaxial growth process of metal oxide surfaces.

central force interatomic potential, as shown in Eq. (1), was used for all calculations. In Eq. (1), the first and second terms refer to Coulomb and exchange repulsion interactions, respectively,

$$u(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \times \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right), \quad (1)$$

where  $Z_i$  is the atomic charge,  $e$  the elementary electric charge,  $r_{ij}$  the interatomic distance, and  $f_0$  ( $= 6.9511 \times 10^{-11}$  N) a constant for unit adaptations. The parameters  $a$  and  $b$  in the exchange repulsion interaction represent the size and stiffness, respectively.

Calculations were performed on Hewlett Packard Apollo 9000 Model 710 workstation. Dynamic features in the homoepitaxial growth process were investigated by using CG visualization with the MOMOVIE code and RYUGA (Ref. 48) code developed in our laboratory on the OMRON LUNA-88K workstation and Hewlett Packard Apollo 9000 Model 715/33 workstation, respectively.

## III. RESULTS AND DISCUSSION

### A. Determination of potential parameters

Accurate potential parameters for MgO are required to simulate the homoepitaxial growth process of MgO quantitatively. In the present study we performed DFT calculations to determine atomic charges on Mg and O atoms. Fig. 2 shows Mg<sub>4</sub>O<sub>4</sub> and Mg<sub>6</sub>O<sub>6</sub> cluster models for DFT calculations. Their geometries are fixed and correspond to that of similar fragments of the bulk MgO.<sup>49</sup> The sketched charges on various atoms were derived from the Mulliken population

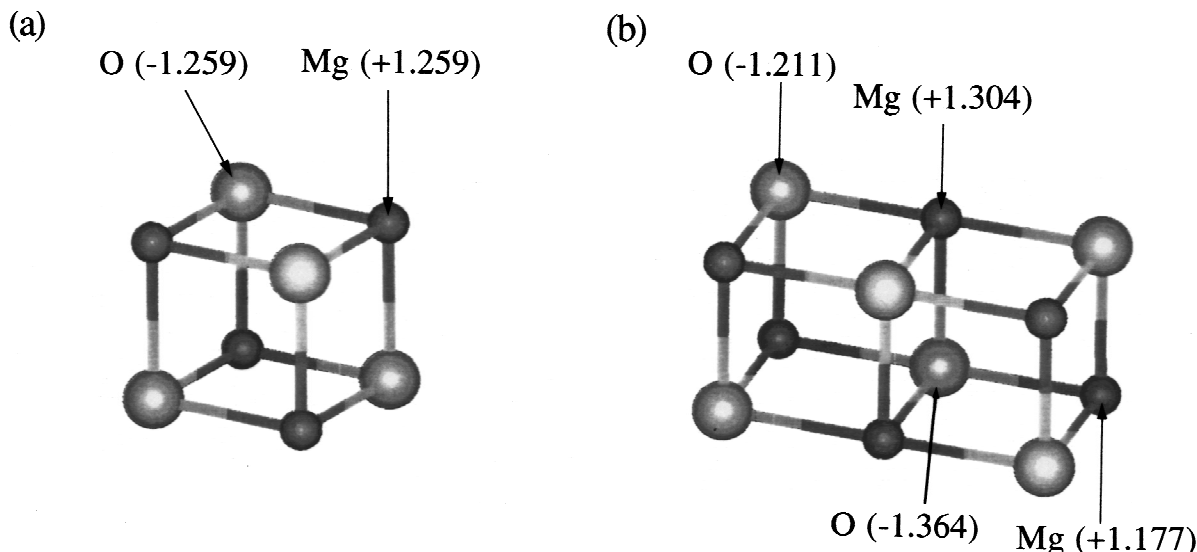


FIG. 2. Model clusters of (a)  $\text{Mg}_4\text{O}_4$  and (b)  $\text{Mg}_6\text{O}_6$ , and the charges on Mg and O atoms. Calculated binding energies of the  $\text{Mg}_4\text{O}_4$  and  $\text{Mg}_6\text{O}_6$  clusters are 583.5 and 952.8 kcal/mol, respectively.

analysis. The charges on Mg atoms vary from +1.177 to +1.304, while those on O atoms vary from  $-1.211$  to  $-1.364$ . We have also calculated larger clusters, such as  $\text{Mg}_8\text{O}_8$  and  $\text{Mg}_9\text{O}_9$ , and we found that atomic charges on Mg and O atoms do not significantly change with the cluster size. Therefore, for our MD simulation we have chosen the charges on Mg and O atoms to be +1.2 and  $-1.2$ , respectively.

Using these charges, we optimized a and b parameters of Eq. (1) by using MD simulations, such that the lattice constant, the expansion coefficient, the melting point of the bulk MgO etc. were reproduced. The determined potential parameters of Mg and O atoms are presented in Table I and the potential curve of the Mg-O interaction is shown in Fig. 3. The calculated lattice constant of bulk MgO is  $4.212 \text{ \AA} \pm 0.006 \text{ \AA}$  at 294 K, which is in good agreement with the experimental value of  $4.211 \text{ \AA}$ .<sup>49</sup> The trajectories of Mg and O atoms during 10 000 time steps of MD simulation were markedly close to the average positions of the ions determined by X-ray crystal structure analysis.<sup>49</sup> Moreover, the mean square displacements (MSD) of Mg and O atoms from the positions determined by the X-ray analysis were  $0.011 \text{ \AA}^2$  and  $0.010 \text{ \AA}^2$ , respectively. These MSD values are not significant in comparison with the temperature factor in X-ray crystal structure analysis.

We also calculated the bond length of a diatomic MgO molecule, the MD value of  $1.82 \text{ \AA}$  is very close to the experimental value of  $1.76 \text{ \AA}$  and the DFT value of  $1.80 \text{ \AA}$ . We also compared the adsorption energy of a diatomic MgO

molecule on the  $\text{Mg}_6\text{O}_6$  cluster calculated by the MD simulation with the DFT quantum chemical calculation value. The obtained MD value of 59.2 kcal/mol is also close to the DFT value of 69.4 kcal/mol.

For the epitaxial growth simulation, the reproduction of the MgO properties at high temperature, such as the expansion coefficient and melting point of bulk MgO, is essential in addition to room temperature properties, because the temperature effect of the substrate on the homoepitaxial growth process on the MgO(001) surface and the surface migration of MgO molecules should be quantitatively represented in MD simulations. The expansion coefficient of bulk MgO derived from MD simulation is  $0.15 \times 10^{-4}/\text{K}$ , which agreed with the experimental result of  $0.14 \times 10^{-4}/\text{K}$ .<sup>50</sup> The change in MSD of Mg and O atoms in bulk MgO during 10 000 time steps of MD simulation at several temperatures is shown in Table II. Below 2800 K MSD values increased gradually with increasing temperature, and at 3000 K large MSD values were suddenly observed. This indicates that the simu-

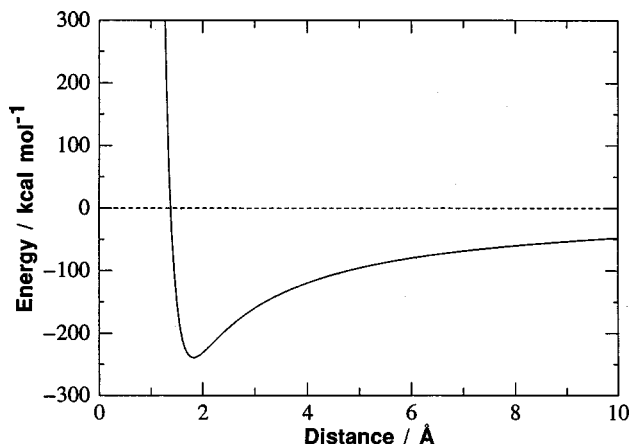


FIG. 3. Potential curve of the Mg - O interaction.

TABLE I. The potential parameters of Mg and O atoms.

| Atom | $Z_i$ | $a_i/\text{\AA}$ | $b_i/\text{\AA}$ |
|------|-------|------------------|------------------|
| Mg   | +1.2  | 1.060            | 0.080            |
| O    | -1.2  | 1.580            | 0.085            |

TABLE II. The change in the mean square displacement of atoms in bulk MgO during 10 000 time steps of MD calculation with increasing temperature.

| Temperature /K | MSD(Mg)/Å <sup>2</sup> | MSD(O)/Å <sup>2</sup> |
|----------------|------------------------|-----------------------|
| 294            | 0.011                  | 0.010                 |
| 1000           | 0.039                  | 0.034                 |
| 2500           | 0.167                  | 0.144                 |
| 2800           | 0.195                  | 0.179                 |
| 2900           | 1.293                  | 0.270                 |
| 3000           | 98.876                 | 90.246                |

lated bulk MgO was melted at around 3000 K. It indicates that the experimental melting point of 3098 K (Ref. 51) is quantitatively reproduced by the MD simulation. The determined potential parameters for MgO reproduced various properties of MgO and therefore can be used for the simulation of the deposition and epitaxial growth processes.

### B. Homoepitaxial growth process of MgO(001) at 300 K

We applied MD and CG techniques to the investigation of the homoepitaxial growth process of the MgO(001) surface. A 16.844 Å × 16.844 Å substrate surface was used as a unit cell of MD calculation. Totally 32 MgO molecules were deposited on the MgO(001) plane, this amount is equal to the number of the Mg and O atoms which constitute a single MgO layer of the MD unit cell.

Fig. 4 shows the homoepitaxial growth process of the MgO(001) surface at 300 K. The MgO substrate is shown by atomic bonds, while the deposited MgO molecules are shown by spheres. After any MgO molecule migrated on the MgO(001) plane, the 2-dimensional and epitaxial growth of the MgO thin layer was observed at 300 K. Moreover, the deposited MgO molecules kept the NaCl type structure and

the (001) oriented configuration during the MD simulation. This indicates that the epitaxial growth of the MgO(001) plane follows the Frank-van der Merwe growth mode.<sup>52</sup> Experimentally, Yadavalli *et al.*<sup>10</sup> employed a beam of evaporated MgO for the homoepitaxial growth of MgO(001) plane, and confirmed that the beam involves mainly MgO molecules because the binding energy of the ionic molecules exceeds 10 eV. They experimentally observed the epitaxial growth of MgO(001) plane with NaCl type structure in the wide temperature range of 140 K–1300 K. Hence the present MD simulation at 300 K was found to well reproduce their experiments on an atomic scale.

However, after all the 32 MgO molecules were deposited on the MgO(001) plane, some defects in the first constructed MgO layer were observed, and some MgO molecules already started to form a second MgO layer. Thus, the layer-by-layer homoepitaxial growth of MgO thin film without defects was not realized at low temperature of 300 K.

### C. Homoepitaxial growth process of MgO(001) at 1000 K

Experimentally, the substrate temperature is one of the important parameters for the construction of well-defined MgO thin layers. Therefore, the understanding of the effect of the substrate temperature on the homoepitaxial growth process is essential to optimize the fabrication conditions of atomically controlled MgO thin films. Hence we simulated the homoepitaxial growth process of the MgO(001) surface at high temperature of 1000 K and the result is shown in Fig. 5. Even at this temperature, the MgO grows epitaxially keeping the NaCl type structure and (001) oriented configuration. Moreover, the formation of a single two-dimensional uniform and flat layer of MgO without any defects was observed at 50 000 time step, which is significantly different from the results at 300 K. Thus, high temperature was found to be

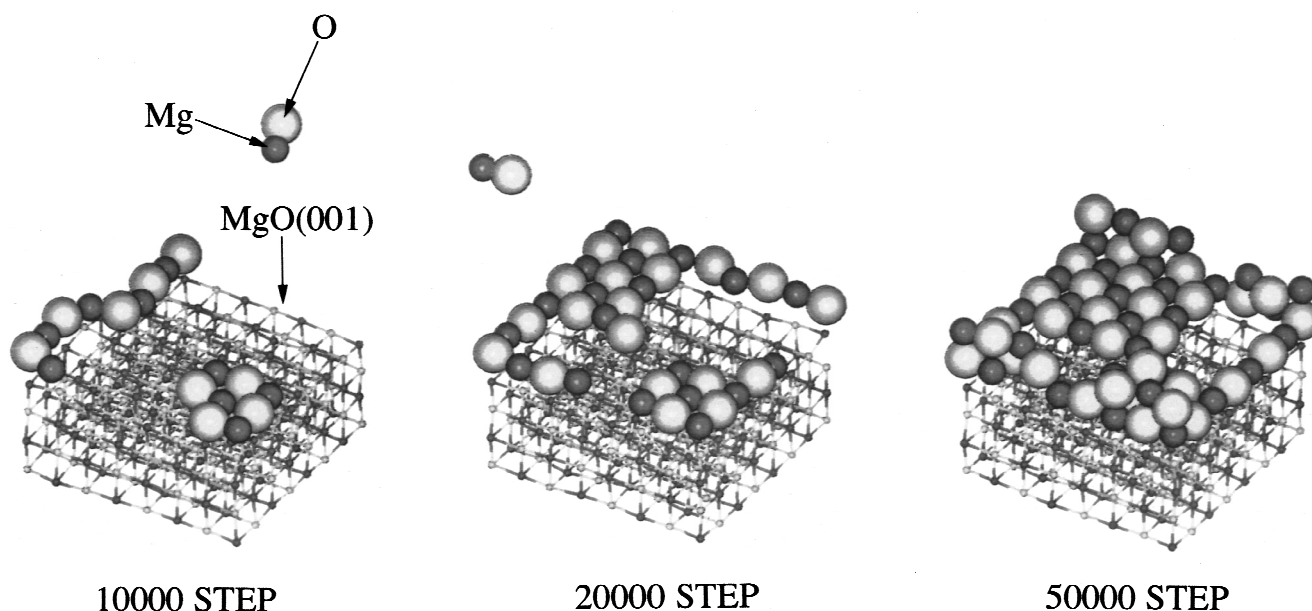


FIG. 4. Homoepitaxial growth process of the MgO(001) plane at 300 K.

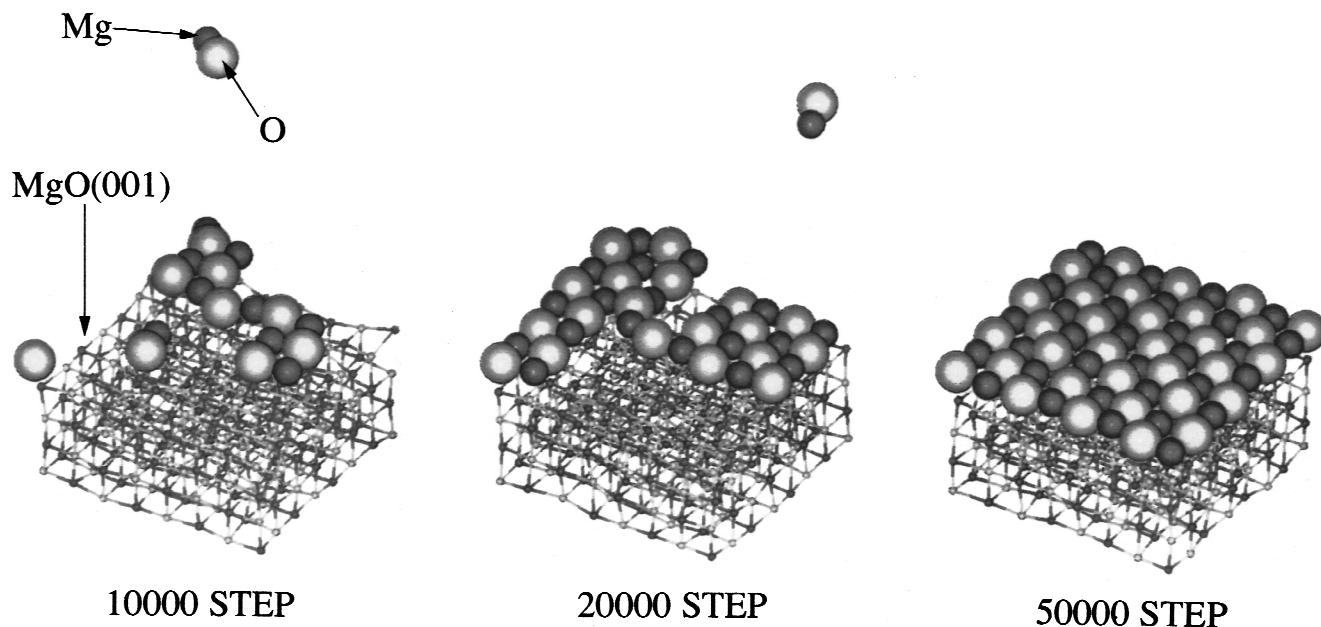


FIG. 5. Homoeptaxial growth process of the MgO(001) plane at 1000 K.

favorable for a complete layer-by-layer homoeptaxial growth. Experimentally, Chambers *et al.*<sup>11</sup> applied the MBE technique to the homoeptaxial growth of the MgO(001) surface and analyzed the surface morphology of the grown MgO film at various temperatures by using RHEED, LEED and AFM measurements. Moreover they used real time AES and XPS techniques to analyze the surface stoichiometry. The ratio of Mg and O atoms in the grown thin films was almost unified, which is similar to our MD simulations. Moreover, they revealed that the surfaces of MgO films grown at 923 K and 1023 K are smoother than those obtained at lower temperatures such as 298 K. This is in agreement with our simulations. Therefore, the effect of substrate temperature on the homoeptaxial growth was reproduced by MD simulations.

#### D. Self-diffusion coefficient and activation energy of a single MgO molecule on MgO(001)

In order to clarify the temperature-dependency of the homoeptaxial growth process of the MgO(001) surface, the surface migration of a single MgO molecule on the flat MgO(001) plane was investigated at various temperatures. The dissociative adsorption of MgO molecules was rarely observed in our MD simulations neither at 300 K nor at 1000 K, therefore the diffusion of a dissociated Mg and O ion is not considered in the preset study.

The 30 000 time step calculations were repeated 5 times for different initial positions of a single MgO molecule on the surface at a selected temperature. This will allow an accurate time and temperature dependency of MSD. As a typical example, a MSD(*t*) of a single MgO molecule on the MgO(001) plane as a function of time at 1000 K is shown in Fig. 6. The linearity of the MSD(*t*) curve suggests that the present simulation is adequate to estimate the self-diffusion

coefficient (*D*) which is calculated from the derivative to time of the MSD. The self-diffusion coefficients at various temperatures are given in Table III. During 30 000 time steps, the migration of the single MgO molecule was not observed at 300 K and 400 K. The small diffusivity of the MgO molecule at 300 K lead to the formation of defects in the constructed MgO film on the MgO(001) plane, which is shown in Fig. 4. The deposited MgO molecules did not reach defect sites at 300 K because of their low migration mobility, and the MgO molecules were stacked close to the position where they hit the surface.

The *D* value increased with temperature, as shown in Table III. Especially, a remarkably high *D*,  $2.58 \times 10^{-9}$  m<sup>2</sup>/s, was observed at 1000 K. It means that the MgO molecule migrated on the surface with high mobility at 1000 K and the defects can be effectively and readily filled with the

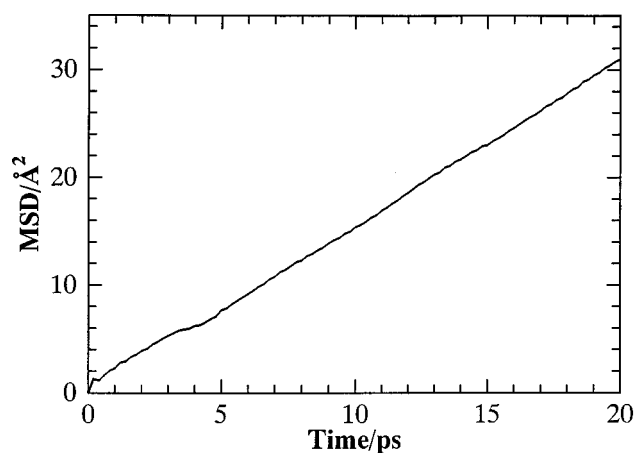


FIG. 6. Mean square displacement of a single MgO molecule with time on the MgO(001) plane at 1000 K.

TABLE III. Calculated self-diffusion coefficients ( $D$ ) of a single MgO molecule on the MgO(001).

| Temperature /K | $D \times 10^9 / \text{m}^2 \text{s}^{-1}$ |
|----------------|--|
| 1000           | 2.58                                       |
| 900            | 1.83                                       |
| 800            | 1.21                                       |
| 700            | 0.70                                       |
| 600            | 0.34                                       |
| 500            | 0.14                                       |
| 400            | not detected                               |
| 300            | not detected                               |

migrating MgO molecule. Therefore, we show that the increase of the diffusivity of deposited MgO molecules with temperature is responsible for a complete layer-by-layer homoepitaxial growth (Fig. 5), which agrees with experimental results.<sup>11</sup>

The knowledge of the activation energy of the surface migration also assists us to design the artificially defined metal oxide layers and to optimize the experimental conditions. Fig. 7 shows an Arrhenius plot derived from Table III. Since the almost linear relation was obtained, the activation energy of the surface migration of a single MgO molecule on the smooth MgO(001) plane was estimated to be 5.8 kcal/mol from the slope of the Arrhenius plot. The estimated activation energy seems to be almost accurate, because the present MD simulations reproduce the temperature-dependency of the homoepitaxial growth process which is experimentally well-known.<sup>11</sup>

#### IV. CONCLUDING REMARKS

We successfully simulated the dynamic features of the homoepitaxial growth process of the MgO(001) surface and the substrate temperature effect on the structure of the formed MgO layer. At a low temperature of 300 K, the surface diffusivity of deposited MgO molecules is low. Therefore molecules remain on the position where they hit the surface. This leads to clustering of deposited MgO molecules, and the grown film presents many defects. At a high temperature of 1000 K, the surface diffusivity becomes

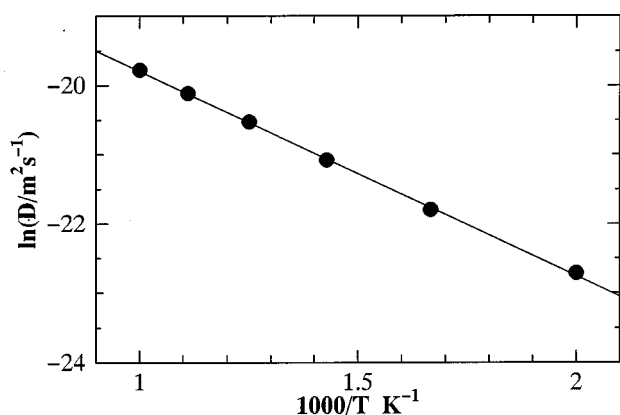


FIG. 7. An Arrhenius plot for the surface diffusion of a single MgO molecule on the MgO(001) plane.

higher and MgO molecules move on the surface to fill up all available sites. Therefore, a smooth and flat MgO thin film was constructed and layer-by-layer homoepitaxial growth was realized.

Further works are also quite interesting to clarify the effects of the Miller index of the MgO surface, the deposition rates of MgO molecules, the surface defects, the deposition interval of MgO molecules etc. on the formation process of MgO thin films as well as the energy transfer of depositing MgO molecules to substrates. Moreover, the MD simulation of the heteroepitaxial growth process of MgO thin films on various substrates, such as, silicon, sapphire, silica, GaAs, TiO<sub>2</sub> etc. is also an exciting topic in relation to the design and fabrication of novel electronic, magnetic, and optical devices.

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