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A Theoretical Study on Deposition Processes of MgO Thin Films: Ultra-Accelerated Quantum Chemical Molecular Dynamics Approach

Akira Endou[1], Kazumi Serizawa[1], Hiroaki Onuma[1], Hiromi Kikuchi[1], Ai Suzuki[2], Michihisa Koyama[3], Hideyuki Tsuboi[1], Nozomu Hatakeyama[1], Hiromitsu Takaba[3], Carlos A. Del Carpio[1], Ramesh C. Deka[4], Momoji Kubo[5], Hiroshi Kajiyama[6], and Akira Miyamoto[1,2,3]

[1]Tohoku Univ., Dept. of Appl. Chem., Grad. School of Eng.
6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
Phone: +81-22-795-7233 E-mail: miyamoto@aki.che.tohoku.ac.jp
[2]Tohoku Univ., NICHe
6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[3]Tohoku Univ., Dept. of Chem. Eng., Grad. School of Eng.
6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[4] Tezpur Univ., Dept. of Chem. Sci., School of Sci. & Tech.
Napaam 784028, Tezpur, Assam, India
[5]Tohoku Univ., FRI, Grad. School of Eng.
6-6-11-701 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[6]Hiroshima Univ., Dept. of Semiconductor Electronics and Integration Sci., Grad School of Adv. Sci. Matter
1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8350, Japan

1. Introduction

Much attention has been attracted for plasma display panel (PDP) as a high definition TV due to its flatness, slenderness, and large area. To realize higher efficiency of PDP, the improvement of secondary electron emission efficiency and durability to sputtering of MgO protecting layer material has been paid for much effort. One of critical issues in the improvement of the MgO protecting layer is a lack of the electronic/atomistic findings. It is caused by the difficulty in accessing electronic/atomistic information for the MgO protecting layer under the working condition of PDP, and hence theoretical investigation is strongly demanded. In this sense, the first-principles molecular dynamics (FPMD) method is powerful tool in order to understand a dynamics of matter from the electronic and atomistic points of view. However, FPMD method requires extremely huge computation cost. On the other hand, our group has developed tight-binding quantum chemical molecular dynamics (TB-QCMD) simulator, 'Colors' [1-3]. This has an advantage in computation time compared to the conventional FPMD simulator. Recently, we succeeded to develop a novel ultra-accelerated QCMD (UA-QCMD) simulator, which realizes 10,000,000 times faster calculation than the conventional FPMD method. In this study, we applied our novel method to the deposition processes of the MgO protecting layer material.

2. Method

UA-QCMD method consists of two parts: TB-QCMD simulator, 'Colors' [1-3] and classical MD simulator, 'New-RYUDO' [4]. 'Colors' is used for the determination of Morse-type 2-body interatomic potential functions between atoms, described as eq. (1),

$$E_{AB} = D_{AB} \cdot \left\{ \exp\left[-2\beta_{AB}\left(R_{AB} - R^*_{AB} \right) \right] - 2\exp\left[-\beta_{AB}\left(R_{AB} - R^*_{AB} \right) \right] \right\} \quad (1)$$

where E_{AB}, D_{AB}, β_{AB}, R_{AB}, and R^*_{AB} refers to the interatomic potential energy between atom A and B, binding energy between atom A and B, factor for potential curve, interatomic distance between atom A and B, and equilibrium distance between atom A and B, respectively.

An electronic structure calculation in this study performed is by solving the Schrödinger equation (**HC** = ε**SC;** **H**, **C**, ε, and **S** refers to the Hamiltonian matrix, eigenvectors, eigenvalues, and overlap integral matrix, respectively) with the diagonalization condition (**C**$^{\mathrm{T}}$**SC** = **I**; **I** refers to the unit matrix). To determine the off-diagonal elements of **H**, H_{rs}, the corrected distance-dependent Wolfsberg-Helmholz formula [5] was used. To solve the Schrödinger equation in this simulator, parameters for Hamiltonian matrix **H** are used, which are derived on the basis of first-principles calculation results. Electronic total energy is decomposed as following,

$$\sum_{k=1}^{occ} n_k \varepsilon_k = \sum_{k=1}^{occ} \sum_{r} n_k \left(C_{kr} \right)^2 H_{rr} + \sum_{k=1}^{occ} \sum_{r} \sum_{s} n_k C_{kr} C_{ks} H_{rs} \quad (2)$$

where the first and second term on the right-hand side refers to the monoatomic contribution to the binding energy and the diatomic contribution to the binding energy, respectively (n_k is the number of electrons occupied in k-th molecular orbital). The binding energy calculated from the second term of eq. (4) is used for the determination of D_{AB} parameter in eq. (1).

3. Results and Discussion

Parameterization for TB-QCMD simulator

First, we determined parameters for the TB-QCMD simulator. Based on the monoatomic parameters deter-

mined on the basis of the first-principles calculations, we adjusted interatomic parameters for the H_{rs} elements in the Schrödinger equations so as to reproduce the electronic structures (atomic charges (Z), atomic populations (AP), and atomic orbital populations (AOP)) obtained by the first-principles calculations. We also attempted to reproduce the optical band gap (E_g) obtained by experiments [6] because the first-principles calculations tend to underestimate E_g values of oxides. The obtained results for MgO bulk crystal are summarized in Table I. This table shows the validity of our TB-QCMD method on the description of the electronic structures of MgO. The error of the binding energy of MgO compared to that obtained by the first-principles calculation was 0.7 %. This also justifies the accuracy of our TB-QCMD method. The present parameters for TB-QCMD method were employed the following UA-QCMD simulations.

Table I Comparison of electronic structures obtained by our TB-QCMD method and the target values obtained by the first-principles calculations (only E_g value is referred from the experimental results).

	Z	AP	AOP *s*	AOP *p*	E_g (eV)
TB-QCMD method					
O	-0.37	6.37	1.74	4.63	7.41
Mg	0.37	1.63	0.69	0.94	
Target values					
O	-0.39	6.39	1.72	4.67	7.4 ~
Mg	0.39	1.59	1.36	0.23	7.78

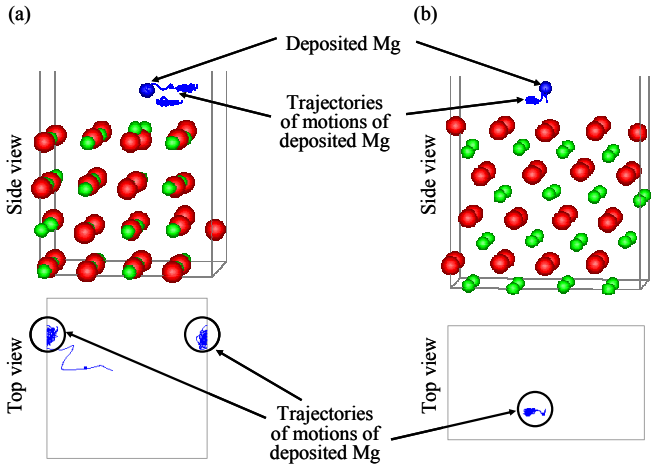

Fig. 1 Trajectories of motions of Mg deposited on (a) MgO (100) and (b) MgO (111) surfaces. The upper and lower part of this figure shows the slant-wise view and top view of the Mg/MgO model, respectively.

Dynamic behavior of deposited species on MgO surfaces

Next, we performed UA-QCMD simulations for the study of the dynamic behavior of species deposited on the MgO (100) and MgO (111) surfaces at room temperature. Initial velocity of deposited Mg was set to 0.45 km/s. Fig. 1 shows the trajectories of motions of Mg deposited on the MgO (100) and (111) surfaces. The time period was ca. 5 x 10-12 s. From this figure, it was seen that the degree of the motion of the deposited Mg on the MgO (100) was much larger than that on the MgO (111) surface. It indicated the possibility of the deposited Mg on the MgO (111) surface as the 'favorable' starting growth point of MgO thin film. A decomposition of the binding energies based on the eq. (2) suggested that one of reasons for the different 'mobility' of the deposited Mg on the MgO surface was caused by the different stability due to the molecular orbital energy. Uetani et al. reported that the MgO film prepared by the ion-plating deposition method showed mainly (111) oriented texture [7]. This result suggests the priority of the growth of (111) direction and is in agreement with the theoretical finding obtained by the present UA-QCMD method qualitatively. We stress the effectiveness of our novel UA-QCMD simulator in clarifying the deposition process of MgO thin film in terms of chemical reactions.

4. Conclusions

In the present study, we developed UA-QCMD simulator, which realizes 10,000,000 times faster calculation than the conventional FPMD method, and applied 'New-Colors' to the deposition processes of the MgO protecting layer material. The justification of our UA-QCMD simulator was shown by the excellent agreement of UA-QCMD result with the first-principles results and experimental results for the physicochemical properties of the MgO bulk crystal. The surface dynamics of the deposited Mg on the MgO (100) and (111) surfaces were simulated by using UA-QCMD method. It is suggested that the mobility of Mg deposited on the MgO (100) surface is much larger than that on the (111) surface. The details will be presented at the conference.

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