Quantum Chemical Molecular Dynamics and Kinetic Monte Carlo Approach to the Design of MgO Protecting Layer in Plasma Display Panel

Momoji Kubo[1,2], Hiromi Kikuchi[1], Hideyuki Tsuboi[1], Michihisa Koyama[1], Akira Endou[1], Carlos A. Del Carpio[1], Hiroshi Kajiyama[3], and Akira Miyamoto[1,4]

[1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-11-1302 Aoba Aramaki, Aoba-ku, Sendai 980-8579, Japan

[2]PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

[3]Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

[4]New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba Aramaki, Aoba-ku, Sendai 980-8579, Japan

Phone: +81-22-795-7236, E-mail: momoji@aki.che.tohoku.ac.jp

Abstract

We developed new quantum chemical molecular dynamics and kinetic Monte Carlo programs to simulate the destruction processes of MgO protecting layer in plasma display panel. Our simulation results proposed that MgO(111) surface with nano-dot structures covered by (001) facets has the highest stability, which is against the previous knowledge. The formation of nano-dot structures on the MgO(111) surface covered by (001) facets was found to be the reason for the high stability of the MgO(111) surface. Furthermore, the effect of grain boundary on the stability of MgO surfaces was also clarified.

1. Introduction

Plasma display panel (PDP) has gained much attention for a high definition TV, since it is a flat, thin, and large-size display. However, in spite of many experimental efforts, the display performances are still unsatisfactory and the lifetime of the PDP is one of the main problems. Experimentally it is pointed out that the electric charges accumulated in the MgO protecting layer and the sputtering of the MgO protecting layer by the energetic plasma particles degrade the PDP performances (Fig 1). However, the experimental observation of the above effects is very difficult and the theoretical analysis is strongly demanded.

Therefore, we developed a tight-binding quantum chemical molecular dynamics program, which can simulate the atomic and electronic states dynamics of the MgO protecting layer in the PDP under the electric field condition [1]. Moreover, in order to realize the huge scale calculations, we also developed a new kinetic Monte Carlo simulator for investigating the destruction processes of the MgO protecting layer under the electric field condition [2]. In the present paper, we review our recent successful applications of the above new simulators to the design of the MgO protecting layer in the PDP.

2. Method

Recently, we have succeeded in the development of a tight-binding quantum chemical molecular dynamics simulator Colors based on our original tight-binding theory. The total energy

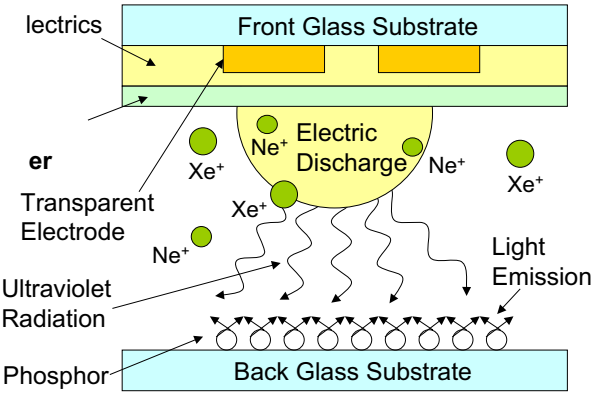

Fig. 1 Schematic picture of one pixel in the PDP

in the system is calculated by the following Eq. (1).

$$E = \sum_{i=1}^{n} \frac{1}{2} m_i v_i^2 + \sum_{k}^{occ} \varepsilon_k + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{Z_i Z_j e^2}{R_{ij}} + \sum_{i=1}^{n} \sum_{j=i+1}^{n} E_{ij}^{repul}(R_{ij}) \quad (1)$$

where m_i is the atomic weight, v_i is the atomic velocity, e is the elementary electric charge, and R_{ij} is the interatomic distance. Z_i is the atomic charge obtained by the electronic states calculation. The first term refers to the kinetic energy, the second term is the summation of the eigenvalues of all occupied orbitals calculated by the electronic states calculation, and the third term represents the Coulombic interaction. The last term corresponds to the short-range repulsion energy. We have already confirmed that the above simulator is more than 5000 times faster than the regular first-principles molecular dynamics program, and hence it can perform the large-scale simulation employing 100-1,000 atoms. In the present study, we implemented a new function into the above simulator to simulate the effect of the electric field.

We also succeeded in the development of a new kinetic Monte Carlo program [2], which can consider the electric field condition. Two-body interatomic potential as shown in Eq. (2) is employed in the present study. In Eq. (2), the first and second terms refer to Coulombic and exchange-repulsion interactions, respectively.

$$u_{ij}(r_{ij}) = Z_i Z_j e^2/r_{ij} + f_o(b_i+b_j) \times \exp\{(a_i+a_j-r_{ij})/(b_i+b_j)\} \quad (2)$$

where Z_i is the atomic charge, e the elementary electric charge, r_{ij} the interatomic distance, and f_o is constant for unit adaptations. The parameters a_i and b_i represent the size and stiffness of atom i, respectively in the exchange-repulsion term. Evaporation probability is calculated by Eq. (3).

$$p = -A \times \exp(-\Delta E/kT) \quad (3)$$

Here, ΔE is difference in the energies of the MgO surfaces after and before evaporation of the selected atom. A is frequency factor, k is Boltzmann's constant, and T is temperature. The electric field is applied normal to the MgO surface and the direction of the electric field is changed every 1000 steps. This program realizes the large-scale simulation employing more than 10,000-1,000,000 atoms, which enables us to investigate the effect of grain boundary on the destruction process of the MgO protecting layer under electric field condition.

We also developed a new modeling program to construct the grain boundary structures in the MgO surfaces. Here, we employed three different MgO surfaces, (001), (011), and (111), and various grain boundary structures were constructed on the above MgO surfaces by using the above new modeling program.

3. Quantum Chemical Molecular Dynamics Simulations on Destruction Process of MgO Surfaces under Electric Field Condition [1]

Our tight-binding quantum chemical molecular dynamics method was applied to the simulations on the destruction processes of the MgO(001), MgO(011), and MgO(111) surfaces under the electric field of 0.2 V/Å. Fig. 2 (a)-(c) show the final structures of the MgO(001), MgO(011) and MgO(111) surfaces, respectively. The evaporation of O atom was observed from the MgO(001) and MgO(011) surfaces. However, the structure of the MgO(111) surface was not destroyed in this condition. This result suggests that the MgO(111) surface has the highest stability among the MgO(001), MgO(011) and MgO(111) surfaces, although it is well known that the MgO(001) has the highest thermal stability.

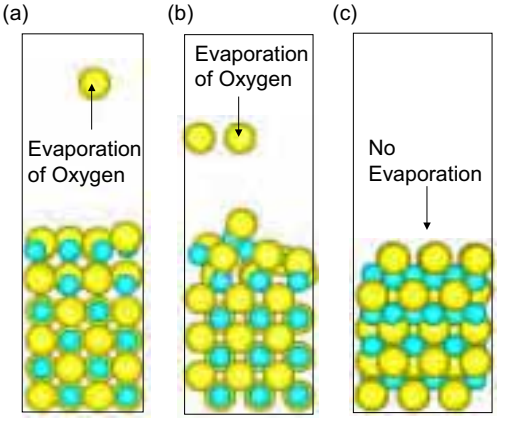

Fig. 2 Final structures of (a)MgO(001), (b)MgO(011), and (c)MgO(111) after the quantum chemical molecular dynamics simulations under the electric field of 0.2 V/Å

4. Monte Carlo Simulations on Destruction Process of MgO Surfaces under Electric Field Condition [2]

In order to confirm the highest stability of the MgO(111) surface, we employed huge simulation models and the destruction processes of MgO(001), MgO(011) and MgO(111) surfaces under the electric field of 0.1 V/Å were simulated by our new kinetic Monte Carlo simulator. The final structure of the MgO(001) surface is shown in Fig. 3(a). The MgO(001) surface was randomly destroyed and the selective evaporation of atoms or clusters was not observed. Here, in order to compare the stability of the different MgO surfaces, we introduced an evaporation index. This value is defined by the number of the evaporated atoms per unit surface area ($Å^2$) during 75,000 steps. The evaporation index of the MgO(001) surface was estimated to be 2.425 $Å^{-2}$.

Fig. 3(b) shows the final structure of the MgO(011) surface. The MgO(011) surface was selectively destroyed and the nano-dot structures were formed on the surface. Moreover, we found that the nano-dots on the MgO(011) surface were covered by (001) facets. This result is completely different from that of the MgO(001) surface. The obtained evaporation index of the MgO(011) surface is 2.405 $Å^{-2}$, which is smaller than that of the MgO(001) surface. It indicates that the MgO(011) surface has higher stability than the MgO(001) surface.

Fig. 3(c) shows the final structure of the MgO(111) surface. This figure indicates that the MgO(111) surface was also selectively destroyed and the nano-dot structures were formed. The nano-dots on the MgO(111) surface were also covered by (001) facets. The obtained evaporation index of 0.663 $Å^{-2}$ is significantly smaller than those of the MgO(001) and (011) surfaces. Therefore, we propose that the MgO(111) surface has the highest stability among the MgO(001), (011) and (111) surfaces. Experimentally,
it is well known that MgO(111) has the highest thermal stability and hence we confirmed that the stability of the MgO surfaces under the electric field condition is different from its thermal stability. This may be due to the fact that the thermal stability is not directional, although the stability under the electric field condition is directional. Moreover, we also proposed that the formation of nano-dot structures covered by (001) facets strongly stabilizes the MgO(111) surface.

5. Effect of Grain Boundary on Destruction Process of MgO Surfaces under Electric Field Condition

In addition to the effect of the surface index, the effect of grain boundary on the stability to the electric field is also important subject in order to propose the atomically-controlled MgO structure with high stability. Hence, we also applied our kinetic Monte Carlo program to the simulations on the destruction process of MgO surfaces with grain boundary. Fig. 4 shows the MgO(011) surface with Σ3 boundary structures. In addition

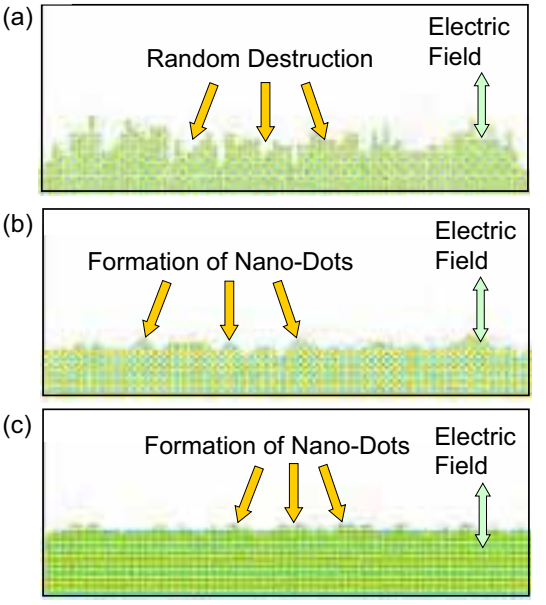

Fig. 3 Final structures of (a)MgO(001), (b)MgO(011) and (c)MgO(111) after the Monte Carlo simulations under the electric field of 0.10 V/Å

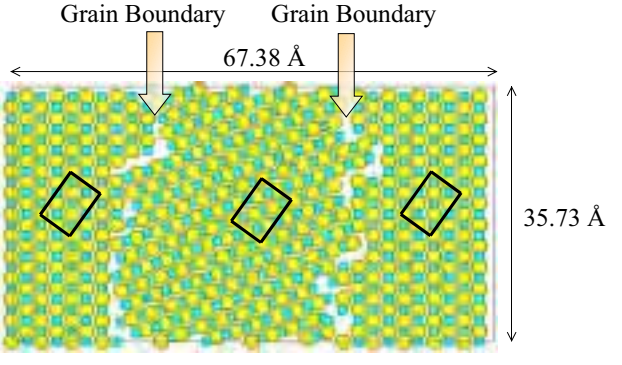

Fig. 4 Large-scale model of MgO(011) surface with Σ3 grain boundary

to the Σ3 boundary structures, we also constructed several boundary structures with different Σ values in order to investigate the effect of the boundary structures on their stabilities.

First, we applied our new kinetic Monte Carlo simulator to the simulation on the destruction process of the MgO(011) surface with Σ3 boundary structure under 1.0 V/Å electric field condition. Fig. 5 shows the initial and final structures of the MgO(011) surfaces with Σ3 boundary structures during the destruction process simulation at 300 K. This figure indicates that the MgO(011) surface was selectively destroyed under the electric field condition and the formation of nano-dot structure was observed at grain boundary position. Here, it is interesting to see that the destruction process of the MgO(011) surface with grain boundary is different from that without grain boundary. Our previous simulation result shows that the MgO(011) surface without grain boundary was randomly destroyed and the selective evaporation of atoms or clusters was not observed.

Furthermore, we evaluated the stability of the MgO(011) surfaces with and without grain boundary by the analysis of the simulation results. Here, the stability is estimated by the number of the evaporated atoms per unit surface area during 10,000 steps. The above values were 0.892 and 0.881 for MgO surfaces with and without grain boundary, respectively. These results indicate that the MgO(011) surface with Σ3 grain boundary was found to have the slightly higher stability than that without grain boundary. Hence, the above simulation result suggests that the Σ3 grain boundary increases the stability of the MgO protecting layer in the plasma display. We also clarified that the specific coordination structures of the Mg and O atoms at the grain boundary increase the stability of the MgO surfaces.

Moreover, we also performed the simulation on the destruction process of the MgO(111) surface with and without grain boundary. In this case, we found that the Σ 5 grain boundary increases the stability of the MgO(111) surface. These results suggest that some specific grain boundary structures increase the stability of the MgO surface. The effect of grain boundary cannot be simulated by small-scale simulation. Hence, the effectiveness of large-scale simulation by our new kinetic Monte Carlo simulator is confirmed.

6. Conclusion

We succeeded in the development of tight-binding quantum chemical molecular dynamics and kinetic Monte Carlo simulators to investigate the destruction processes of MgO protecting layer in PDP under the electric field condition. The simulation results propose that the MgO(111) surface has the highest stability under the electric field condition, although it is well known that the MgO(001) has the highest thermal stability. We investigated the reason for the above result and confirmed that the stability of the MgO surfaces under the electric field condition is different from its thermal stability. Moreover, the formation of nano-dot structures on the MgO(111) surface covered by (001) facets was found to be the responsible for the high stability of the MgO(111) surface. We also suggested that some specific grain boundary structures increase the stability of the MgO surface.

7. References

[1] M. Kubo, K. Sasata, T. Yokosuka, T. Kusagaya, S. Takami, H. Kajiyama, A. Kato, A. Imamura, and A. Miyamoto, Proc. 9th IDW, 753-756 (2002).

[2] M. Kubo, H. Kikuchi, H. Tsuboi, M. Koyama, A. Endou, H. Kajiyama, and A. Miyamoto, Proc. 12th IDW/Asia Display 2005, 427-430 (2005).

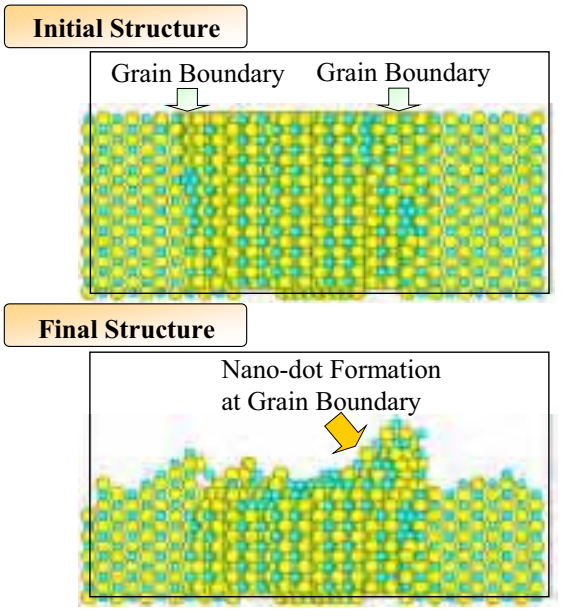

Fig. 5 Initial and final structures of MgO(011) with Σ3 grain boundary during the destruction process under 1.0 V/Å electric field.