Trans-disciplinary Approach to Molecular Modeling and Experiment in PDP Materials

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Abstract

We developed ultra-accelerated quantum chemical molecular dynamics and spectroscopic characterization simulators for development of PDP materials. By combination of these simulators, realistic structure of PDP materials is drawn on the computer. Furthermore, based on the structures, various properties such as cathode luminescence spectrum and secondary electron emission, is successfully evaluated. The strategy of "Experiment integrated Computational Chemistry" using developed simulators will presented that has the potential in being powerful tool for designing the PDP materials..

1. Introduction

Recently, one of the great successes of flat display panel is plasma display panel (PDP), which has the advantage in its flatness, slenderness, and large area. To establish the technology for the efficient PDP, durability to sputtering and improvement of the secondary electron emission (SEE) efficiency of the protective layer material are key factors. Hence, the better understanding of both atomistic and electronic structures of the PDP related materials is strongly required. Computational chemistry is expected to play an important role for solve these issues.

Recently, we have successfully developed "Experiment integrated Computational Chemistry" technology to tackle practical problems in industry (see Fig. 1). We have developed ultra-accelerated quantum chemical molecular dynamics (UA-QCMD) on the basis of our original tight-binding theory, which realizes 10 million times faster in the calculation speed compared to conventional first-principles molecular dynamics (FPMD) method. We have successfully applied our original simulation techniques to the electronic structure evaluation of MgO protective layer materials [1] and BAM:Eu^{2+} blue phosphor [2]. In addition to that, we recently developed original characterization simulators for X-ray diffraction (XRD), neutron diffraction (ND), vibrational spectroscopy, electron spectroscopy, and extended X-ray absorption fine structure (EXAFS), by combining with an UA-QCMD. In this paper, we report our novel characterization simulators based on an UA-QCMD and recent application to the PDP related materials will be presented.

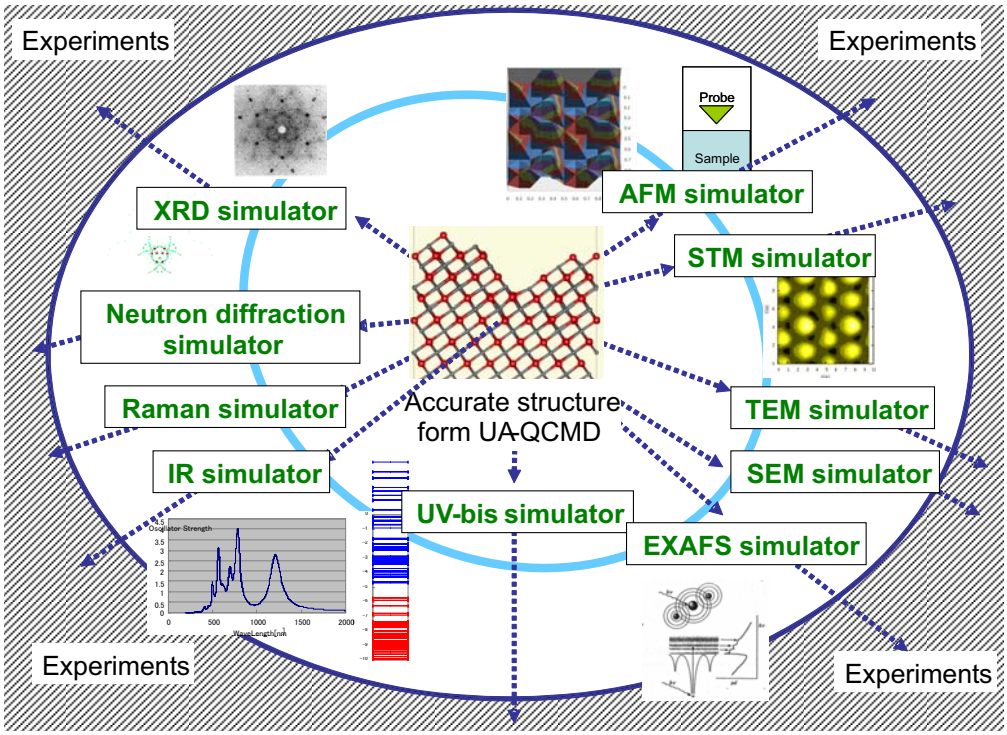

Fig. 1. Schematic of the experiments integrated computational chemistry.

2. Methods

2.1 Ultra-accelerated quantum chemical molecular dynamics

The UA-QCMD simulator consists of two parts. The first part is a tight-binding (TB) -QCMD simulator, Colors [3]. The former simulator is used for the determination of Morse-type 2-body interatomic potential functions (eq. (1)) between atoms, by performing electronic structure calculations:

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

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

In TB-QCMD simulator, the electronic structure calculation is performed by solving the Schrödinger equation ($\boldsymbol{HC} = \varepsilon\boldsymbol{SC}$; $\boldsymbol{H}$, $\boldsymbol{C}$, ε, and $\boldsymbol{S}$ refers to the Hamiltonian matrix, eigenvectors, eigenvalues, and overlap integral matrix, respectively) with the diagonalization condition ($\boldsymbol{C}^{T}\boldsymbol{SC} = \boldsymbol{I}$; $\boldsymbol{I}$ refers to the unit matrix). The level of theory corresponds to the extended Hückel method. To determine the off-diagonal elements of $\boldsymbol{H}$, H_{rs}, the corrected distance-dependent Wolfsberg-Helmholz formula (eq. (2)) was used.

$$H_{rs} = \frac{K}{2}S_{rs}\left(H_{rr}+H_{ss}\right) \quad (2)$$

To solve the Schrödinger equation in this simulator, In electronic structure calculations using Colors, a total energy of a system is obtained by using the following equation:

$$E = \sum_{k=1}^{occ} n_k\varepsilon_k + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{Z_i Z_j e^2}{r_{ij}} + \sum_{i=1}^{N}\sum_{j=i+1}^{N}E_{ij}^{\mathrm{repul}}\left(r_{ij}\right) \quad (3)$$

where the first, second, and third term on the right-hand side refers to the molecular orbital (MO) energy, Coulombic energy, and exchange-repulsion energy, respectively. All parameters in eq. (3) are derived on the basis of the first-principles calculation results. The first term on the right-hand side of eq. (3) is rewritten as follows:

$$\sum_{k=1}^{occ} n_k\varepsilon_k = \sum_{k=1}^{occ}\sum_{r} n_k\left(C_{kr}\right)^2 H_{rr} + \sum_{k=1}^{occ}\sum_{r}\sum_{s} n_k C_{kr}C_{ks}H_{rs} \quad (4)$$

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).

The second part of the UA-QCMD simulator is combined with our MD simulator, New-RYUDO [3]. Our MD simulator, New-RYUDO can perform MD simulations by solving equation of motion for atoms. Temperature scaling method equivalent to the Woodcock algorithm is implemented.

2.2 Structural Simulators

Our novel quantum-theory-based characterization simulator was developed by a combination of an UA-QCMD simulator, "New-Colors". By combining UA-QCMD and our quantum-theory-based structural simulators, the model used in the simulations is precisely examined by comparison with the experimental results. Vibrational spectroscopy simulator was developed based on GF matrix method. We implemented a function for calculating the oscillator strength to the New-Colors program to calculate the electron spectroscopy [4]. Necessary parameters such as backscattering amplitude and phase shifts due to center and scattering atoms for calculating EXAFS single scattering functions were chosen from the literature by Teo and Lee [5].

3. Results and discussion

3.1 Dynamics of crystal growth

Understanding of crystal growth mechanism is of fundamental for developing high quality protective layer. UA-QCMD simulation was carried out for MgO crystal growth. Fig. 2 shows the simulation model of deposition by plasma gun. Here, we explain the result of the deposition process at the beginning. Initial atomic speed of 0.45 km/s was given to the Mg to simulate the deposition to the (111) and (001) MgO surfaces and dynamics of the ions were analyzed. UA-QCMD successfully illustrated the migration of deposited Mg atoms. Fig. 3 presents the means square displacement (MSD) of deposited Mg atoms. It is clearly shown that the Mg atom on (001) surface shows large motion meaning Mg atom is stable on (111) surface more than that on (001) surface. Calculated charges of atoms were indicated in TABLE

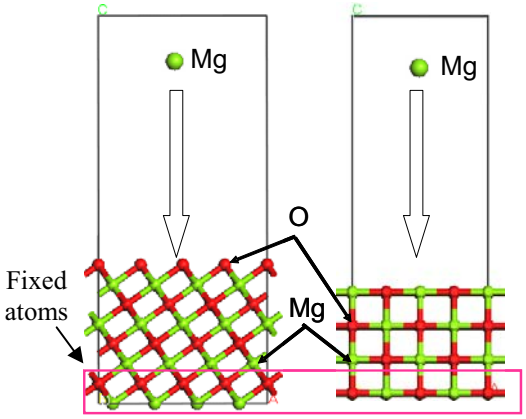

Fig. 2. Simulation model for crystal growth of MgO protective layer.

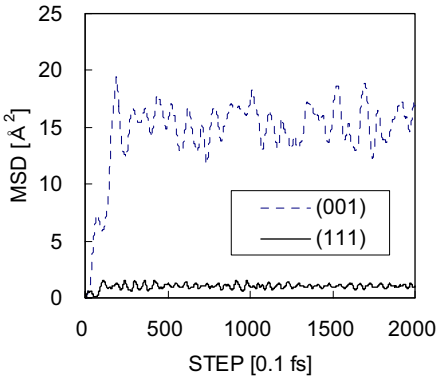

Fig. 3. MSD of deposited Mg atoms on MgO surfaces.

1. The charges of Mg atoms on both surfaces have positive charge but are smaller than those of Mg in the crystal layers. Electron from Mg atoms flows to the surface of which amount is larger for that on (111) surface. This electronic structure difference of Mg atom determined the diffusion dynamics of deposited atoms on the surface and results in the (111) preference crystal growth.

TABLE 1. Calculated charges of the Mg atom and the atoms in the top layers of MgO crystal.

	Charge [e]
(111) model	
O of surface	-0.40 ~ -0.43
Mg of surface	0.35 ~ 0.38
Adsorbed Mg	0.26
(001) model	
O of surface	-0.37 ~ -0.41
Mg of surface	0.35 ~ 0.37
Adsorbed Mg	0.14

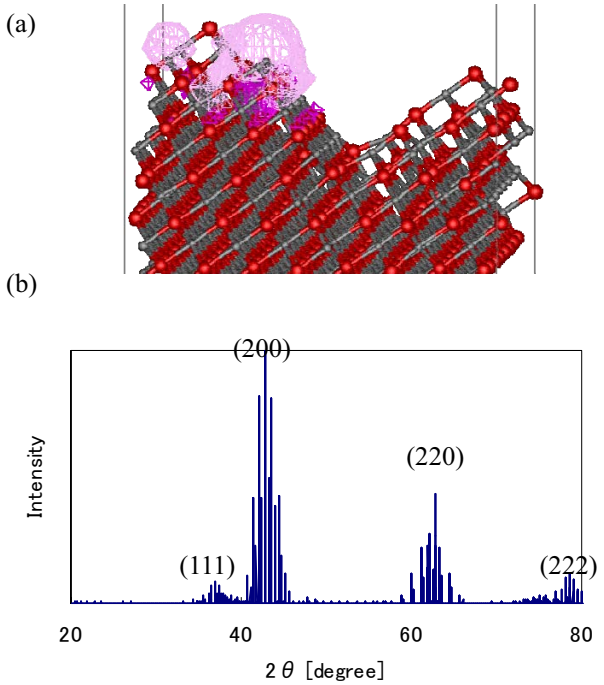

Fig. 4. (a) MgO(111) surface model with its LUMO. (b) Simulated XRD patter for this structure.

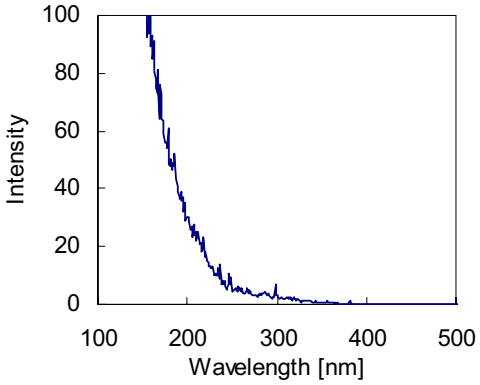

Fig. 5. Simulated CL spectrum for the MgO model shown in Fig. 4 (a).

3.2 Structural and electronic properties

Structural simulators were carried out for the models of MgO protective layer. The (111) surface models were constructed, which is shown in Fig. 4 (a), by using annealing molecular dynamics based on the UA-QCMD study. Calculated XRD pattern for the model is shown in Fig. 4 (b). The XRD pattern quantitatively agreed with the experimental result [6]. This result validated the accuracy of the constructed model. The combination of other structural simulators such as EXAFS and cathode luminescence (CL) spectrum enable the detail discussion about the doping and oxygen defects in the layers. The electronic structure calculation for this model tells us that LUMO is localized on the projection of the top of layer. The calculated CL spectrum is shown in Fig. 5. Experimentally, CL spectrum is observed for MgO protective layer in the wavelength range below 350 nm given by a band transition [7], which agrees with our calculated one. By using these simulators, we can evaluate the physical properties of PDP materials on the basis of genuine material structures.

4. Summary

UA-QCMD was successfully applied to the investigation of the growth of MgO thin film. By using our novel characterization simulator, the validity of constructed models based on UA-QCMD is effectively examined by direct comparison with the experiments. Furthermore, electronic properties, such as CL spectrum and SEE, are readily evaluated in the basis of a quantum theory. This strategy of experiments integrated computational chemistry is expected to drastically promote the speed of the development of PDP related materials.

5. References

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