First-principles molecular dynamics study of Al/Alq$_3$ interfaces

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Abstract

We have carried out first-principles molecular dynamics simulations of Al deposition on tris (8-hydroxyquinoline) aluminum (Alq$_3$) layers to investigate atomic geometries and electronic properties of Al/Alq$_3$ interfaces. Al atoms were ejected to Alq$_3$ one by one with the kinetic energy of 37.4 kJ/mol, which approximately corresponds to the average kinetic energy of Al at the boiling temperature of metal Al. The first Al atom interacts with two of the three O atoms of meridional Alq$_3$. Following Al atoms interact with Alq$_3$ rather weakly and they tend to aggregate each other to form Al clusters. During the deposition process, Alq$_3$ was not broken and its molecular structure remained essentially intact. At the interface, weak bonds between deposited Al atoms and N and C atoms were formed. The projected density of states (PDOS) onto the Alq$_3$ molecular orbitals shows gap states in between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs), which were experimentally observed by ultraviolet photoelectron spectroscopy (UPS) and metastable atom electron spectroscopy (MAES). Our results show that even though the Alq$_3$ molecular structure is retained, weak N–Al and C–Al bonds induce gap states.

Keywords: Metal/organic interface; Alq$_3$; Interfacial dipole; Energy level alignment; Density functional theory; Molecular dynamics; Gap state; Electronic structure

1. Introduction

The electronic properties at metal/organic interfaces are quite important in organic based devices such as organic light emitting diodes (OLEDs), organic field effect transistors, and organic solar cells, and they often play important roles in determining the performance of organic devices. Tris (8-hydroxyquinoline) aluminum (Alq$_3$) is the most famous electron transport and emission materials of OLEDs [1–3] and the Alq$_3$/metal interfaces have been intensively studied experimentally [4–17] and theoretically [18–24]. By using ultraviolet photoemission spectroscopy (UPS) and metastable atom electron spectroscopy (MAES), interfacial gap states were observed at Al/Alq$_3$ interfaces [10,15]. Furthermore, large interfacial dipole layer of $-1.4$ eV was observed [15]. These interface phenomena were ascribed to strong chemical interaction between Alq$_3$ and Al. It is very desirable to clarify the microscopic origins for the above observations.

In previous density functional theoretical (DFT) studies, Alq$_3$ adsorbed on Al surfaces have been investigated to clarify the geometries and the electronic properties at the interfaces [20,23,24]. Two of the present authors have investigated Alq$_3$ adsorbed onto the Al(1 1 1), Al(3 3 2), and Al adatom adsorbed Al(1 1 1) surfaces [23,24]. It turned out that Alq$_3$ molecules are bound to Al substrates through their O atoms and the stability of adsorbed Alq$_3$ depends on the number of Al–O bonds formed at the interface. These geometrical conditions result in the alignment of permanent dipoles of Alq$_3$ and therefore, the dipole at Alq$_3$/Al interfaces mainly comes from the alignment of molecular permanent dipoles of Alq$_3$. We also pointed out the coexistence of small amount of minority
configurations, which contribute to the interface gap state observed by UPS and MAES experiments.

Although Alq₃ on metal surfaces have been intensively investigated theoretically, in actual device processes, Al is deposited on Alq₃ layers. Those interfaces should be much more complex than Alq₃ adsorbed Al surfaces because Al atoms are more reactive than Al surfaces and Al atoms interact strongly with Alq₃ layers and furthermore, they may diffuse into Alq₃ layers. Several first-principles studies investigated the interaction between Alq₃ and a single metal atom [19–22]. But it is necessary to investigate the interaction of more than one Al atoms with Alq₃ to investigate the interface structure formed by Al deposition on Alq₃ layers. In the present study, we have carried out first-principles molecular dynamics simulations of Al atoms deposited on Alq₃ molecular layers.

2. Computational methods

Calculations were carried out by using the first-principles molecular dynamics program “STATE” (Simulation Tool for Atom TECnology) which has been applied to organic/metal interfaces [23–26]. We employed the local density approximation (LDA) [27,28] and the generalized gradient approximation (GGA) [29] for the exchange-correlation energy functional. The electron–ion interaction was described by \textit{ab initio} pseudopotentials [30,31] and the wavefunctions and the charge density were expanded by plane-wave basis sets with the cutoff energies of 25 and 225 Ry, respectively.

The meridional Alq₃ thin film was modeled by periodic slabs, in which one slab consists of one Alq₃ molecular layer and vacuum region of about 1 nm. Alq₃ molecules are periodically arranged with rectangular unit cell of 0.85 nm × 1.0 nm and Al atoms are ejected one by one from the vacuum region onto the Alq₃ molecular film as shown in Fig. 1. Ejected Al atoms are also arranged with the same periodicity as Alq₃ molecules and lateral positions of Al atoms in the unit cell were randomly generated. In our molecular dynamics simulations, all H atoms were deuterized to allow longer time step of 2.4 fs. Before the deposition of Al, a Alq₃ molecular film was equilibrated at 300 K for about 0.3 ps by a velocity scaling method. After the equilibration, Al atoms were ejected towards the Alq₃ layer. The initial kinetic energy of Al atoms was set to be 37.4 kJ/mol, which is slightly larger than the average kinetic energy of Al atom at the boiling temperature of metallic Al \((T_{\text{vap}} = 2759 \text{ K})\). Al atoms were ejected one by one up to seven Al atoms per one Alq₃ molecule. For each deposition process, molecular dynamics simulation was carried out for about 2.4 ps with no temperature control. Several meta-stable structures appeared in the molecular dynamics simulations and those meta-stable structures were used to estimate the binding energies of Al with Alq₃. Although the total simulation time is not long enough to compare with the actual deposition processes and obtained interface structures maybe meta-stable structures, we think they still show characteristics of interfaces formed by Al deposition on Alq₃ layers.

3. Results and discussions

Fig. 2 shows top views of Al deposited Alq₃ films with (a) one, (b) two, and (c) seven Al atoms per one Alq₃ molecule. Although the first Al atom attached to C atom of quinoline ligand, the interaction between Al and C is rather weak and Al was immediately attracted by the center O atom. Finally, Al was bound to two oxygen atoms of Alq₃ in the out-of-plane configuration. In the out-of-plane configuration, the added Al is bound to two oxygen atoms of Alq₃, i.e., O atoms of the center and the left quinoline ligands as shown in Fig. 2(a). In this configuration, the Al atom is not on the same plane as the two quinoline ligands to which the Al atom is bound. This
configuration was reported previously by Curioni [19]. Zhang and co-workers, however, reported that the co-planar configuration is slightly more stable than the out-of-plane configuration by 25 kJ/mol. In the co-planar configuration, the Al atom is bound to O atoms of the center and the right quinoline ligands and the Al atom is on the same plane as one quinoline ligand to which the Al atom is bound. Although the out-of-plane configuration seems to be a meta-stable state, the energy difference between the two configurations is small compared with the binding energy of Al (see Fig. 3).

The second Al atom also attacked C atoms of Alq₃ but it bounded and it was attracted by the first Al atom and the resulting structure is shown in Fig. 2(b). Further deposited Al atoms were also attracted by previously deposited Al atoms and they aggregated to form Al clusters. The optimized structure after depositing seven Al atoms is shown in Fig. 2(c).

The coverage dependence of the adsorption energy of Al atoms on a Alq₃ molecular film \( E_{ad}(N) \) is defined by

\[
E_{ad}(N) = E((N-1)\text{Al}/\text{Alq}_3) + E(\text{Al atom}) - E(N\text{Al}/\text{Alq}_3),
\]

where \( E(\text{Al atom}) \), \( E((N-1)\text{Al}/\text{Alq}_3) \), and \( E(N\text{Al}/\text{Alq}_3) \) correspond to total energies of isolated Al atom, \( N-1 \) Al atoms adsorbed Alq₃ layer, and \( N \) Al atoms adsorbed Alq₃, respectively. The results are shown in Fig. 3. The adsorption energy of the first Al atom is calculated to be 170 kJ/mol, which is in reasonable agreement with previous results of 151–155 kJ/mol [19,21]. The initial adsorption energy of Al onto Alq₃ molecular film is much smaller than the cohesive energy of bulk Al (experimental value is 327 kJ/mol, theoretical value is 349 kJ/mol). But it increases up to the bulk cohesive energy of Al as the number of Al atoms per Alq₃ molecule increases.

Fig. 2. Top views of Al deposited Alq₃ molecular layer. Numbers of Al atoms per one Alq₃ molecule are (a) one, (b) two, and (c) seven, respectively.

Fig. 3. Adsorption energy \( E_{ad} \) of Al atoms onto a Alq₃ molecular film as a function of number of Al atoms per Alq₃ molecule.
As discussed above, interfacial gap states were observed at Al/Alq₃ interfaces by UPS and MAES experiments and they were ascribed to strong chemical interaction between Alq₃ and Al [10,15]. During our molecular dynamics simulations, adsorbed Al atoms interact with O atoms of Alq₃ but they did not induce breaking of Alq₃ and its molecular structure essentially remained intact. In our previous study, we investigated adsorption structures and electronic properties of Alq₃ on Al surfaces by using the same computational techniques as the present ones [23,24]. Fig. 4 shows projected density of states (PDOS) onto molecular orbitals of Alq₃ for (a) meridional Alq₃ adsorbed on Al(111), (b) one Al atom adsorbed on Alq₃, and (c) seven Al atoms adsorbed on Alq₃. The PDOS for Alq₃ adsorbed on Al(111) (Fig. 4(a)) and those for one Al adsorbed on Alq₃ (Fig. 4(b)) are similar to each other. In both cases, Alq₃ is bound to Al substrate or Al atom through two O atoms of Alq₃. Peaks located around −2 eV correspond to the highest occupied molecular orbitals (HOMOs) of Alq₃ and peaks located around the Fermi energy correspond to the lowest unoccupied molecular orbitals (LUMOs) and in between these two peaks, there is no gap states observed. However, in the case of seven Al atoms adsorbed on Alq₃, several peaks are observed in between the HOMO and LUMO peaks. In this configuration, adsorbed Al atoms are bound not only to O atoms but also to N and C atoms of quinoline ligands. Although these bonds are weak, they were frozen due to further deposited Al atoms. Our results show that even though the Alq₃ molecular structure is retained, weak Al–N and Al–C bonds induce gap states. It is known that the LUMO state of Alq₃ is distributed around N atoms of quinoline ligands [32]. Our PDOS analysis indicates that the gap state is originated from the LUMO state, suggesting that the LUMO state is stabilized by the adsorbed Al atoms through weak Al–N bonds.

4. Conclusions

We have carried out first-principles molecular dynamics simulations for the deposition processes of Al onto Alq₃ molecular layers. The first Al atom is bound to two O atoms of Alq₃, in good agreement with previous simulations. Further deposited atoms mainly interact with Al atoms and they aggregate each other to form Al clusters. During the molecular dynamics simulations, Alq₃ molecules were not broken and their molecular structures remained essentially intact. Weak Al–N and Al–C bonds were formed during the deposition processes and although they were not the most stable configuration, they were frozen due to further deposited Al atoms. These weak bonds induce interfacial gap states in between the HOMO and the LUMO levels of Alq₃.

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