Theoretical investigation of the electronic structure of the Alq$_3$/Mg interface

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Abstract

We have studied the atomic geometries and the electronic properties of the
tris-(8-hydroxyquinoline) aluminum (Alq$_3$)/Mg interface by using density functional theoretical
calculations. We have found that the chemical bond is formed between the O atoms of Alq$_3$ and
the substrate Mg atoms, and the stability of the interface structures depends on the number of
O–Mg bonds. In the up configurations, where two or three O–Mg chemical bonds are formed
and the Alq$_3$ molecular dipoles are oriented up to the vacuum side, the work function is
decreased by as much as 1.1 eV or more. The interface dipole is dominated by the orientation of
the molecular dipoles of Alq$_3$. The interface gap state reported from experiments is ascribed to
the highest occupied molecular orbital (HOMO) levels of the down configurations, which may
coexist with the dominant up configurations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the demonstration of tris(8-hydroxyquinoline) aluminum (Alq$_3$) as an electroluminescent material for organic light-emitting devices (OLEDs) [1, 2], the interface electronic properties of Alq$_3$ with a metal have been intensively studied. The interfacial dipole layer, which alters the vacuum level at the organic layer relative to that at the metal layer [3], dominates the energy level alignment between the molecular and the metal Fermi levels, thus determining the barrier for carrier injection. For a basic understanding of the electron injection barrier, the interfaces comprised of Alq$_3$ and a low work function metal such as Al [3–10] and Mg [5, 11–15] have been studied both experimentally and theoretically.

Recently, we have shown by first-principles calculations that the interface dipole at the Alq$_3$-on-Al interfaces is dominated by the alignment of molecular dipoles right at the interface [8, 10]. The highest occupied molecular orbital (HOMO) levels of the Alq$_3$ molecules significantly depend on the orientation of the molecular dipoles, i.e. the upward (downward) orientation of the molecular dipoles of the adsorbates results in the downward (upward) shift of the adsorbate molecular levels relative to the metal Fermi level. The interface gap state observed by experiments [5, 6] can be ascribed to the co-existence of the upward and downward orientations of the molecular dipoles.

Interfaces comprised of Alq$_3$ and Mg have attracted much attention. The electron injection barrier is lower than that of the interface comprised of Alq$_3$ and Al [5]. The Mg-on-Alq$_3$ (Mg/Alq$_3$) interfaces were investigated in several experimental and theoretical studies [5, 11–15], while a few experimental studies of the Alq$_3$-on-Mg (Alq$_3$/Mg) interface have been reported [5, 11]. The common observation among these studies is that a gap state located between the HOMO and the lowest unoccupied molecular orbital (LUMO) levels was observed [5, 11–15]. The gap state at the Mg/Alq$_3$ was ascribed to the emission from the filled LUMO of Alq$_3$ due to electronic charge donation from Mg to the N atom in a quinoline ligand, at which the LUMO is localized. The origin of the interface dipole of Mg/Alq$_3$, however, remains unclear, with some experimental values of work function shift reported as 0.0 and -0.3 eV [11, 12].

The Alq$_3$/Mg interface, on the other hand, has been investigated in a few photoemission experiments, with the

interface dipole observed as −0.5 [5] and −0.2 eV [11], and the gap state similar to that of the Mg/Alq₃ interface was observed [5]. Interestingly, the Alq₃/Mg interface was found to show similar efficiency in current–voltage (CV) measurements as that of the Mg/Alq₃ interface, even though the XPS measurement showed larger chemical shifts for the Mg/Alq₃ [5], thus implying larger chemical interactions. This situation motivated us to theoretically investigate the interface dipoles of the Alq₃/Mg. The mechanism of the energy level alignment and the interface dipole may also help us elucidate the mechanism of the Mg/Alq₃ interface.

　　In the present study, we have carried out density functional theoretical calculations of the adsorption states of Alq₃ on Mg(001), in order to clarify the nature of the interface interaction and the origin of the interface dipole.

2. Theoretical methods

Calculations were carried out by using the first-principles molecular dynamics program 'STATE' (Simulation Tool for Atom Technology) which has been applied to various organic/metal interfaces [8, 10, 16–18]. We employed the generalized gradient approximation (GGA) [19] for the exchange–correlation energy functional. The electron–ion interaction was described by *ab initio* pseudopotentials [20, 21]. The wavefunctions and the charge density were expanded by plane-wave basis sets with cutoff energies of 25 and 225 Ryd, respectively.

　　The Mg surface was modeled by periodic slabs, in which one slab consists of six Mg(001) atomic layers, and vacuum regions equivalent to ten atomic layers were inserted between slabs. In constructing the slab, we employed an equilibrium lattice constant of 0.321 nm, which is obtained by the GGA calculation of the Mg hcp bulk and which is in good agreement with the experimental value (0.321 nm) [16].

　　We considered both the stable Alq₃ isomers, i.e. facial (*fac*) and meridional (*mer*) (for the molecular structures, see [10]). Alq₃ molecules were arranged in a 4 × 4 superstructure on the Mg(001) (area of 1.423 nm² per one adsorbate). The molecules were adsorbed on one side of the slab, as illustrated in figure 1. In order to compensate the work function difference between two surfaces of a slab, we employed a dipole correction [22]. A 2 × 2 uniform mesh of **k**-points was sampled in the surface Brillouin zone for the geometry optimization, and 4 × 4 mesh points were used in the projected density of states (DOS) calculations and in the dipole-corrected calculations.

　　In order to find the global minimum of potential energy surfaces, we considered as many initial geometric structures as possible and they were annealed by finite-temperature molecular dynamics method at 300 K before geometry optimizations. In the geometry optimization of the slab, only the Mg atoms in the upper three layers were allowed to relax.

　　Work functions were calculated from the energy difference between the Fermi energy of the system and the mean potential energy at the center of the vacuum region.
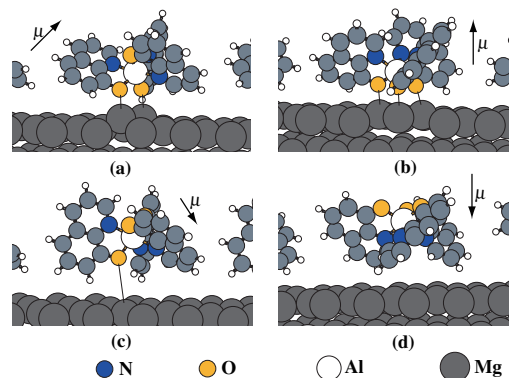

Figure 1. Atomic structures of the (a) *mer*/up, (b) *fac*/up, (c) *mer*/down, and (d) *fac*/down configurations on the Mg(001), obtained by the GGA. O–Mg bonds are indicated by solid black lines. The distances in nm units are (a) 0.221 (left), 0.228 (right); (b) 0.222 (left), 0.220 (middle), 0.225 (right); (c) 0.420. The periodical situation in the calculation is displayed. The orientation of the permanent dipole of the Alq₃ is indicated by arrows.

3. Results and discussions

3.1. Geometry of Alq₃/Mg(001) interfaces

We have found two stable adsorbed configurations of the Alq₃/Mg(001) interface, which we will denote as up and down configurations, in which the molecular dipoles are oriented to the vacuum and substrate side, respectively. These adsorbed configurations are similar to the ones that we found in the study of the Alq₃/Al [8, 10].

　　Figure 1 shows adsorption geometries of Alq₃ on Mg(001). As seen in figure 1, surface Mg atoms are shifted up due to O atoms in the up configurations, with O–Mg bond lengths of 0.22–0.23 nm. On the other hand, N interacts with substrate Mg weakly. Although this result is in line with that of the Alq₃/Al(111) interface, the Mg–O bond lengths are longer than the substrate Al–O distances in the Alq₃/Al of 0.19–0.21 nm in the up configurations [8, 10], corresponding to the difference in atomic radii.

　　In the down configuration of each isomer, the adsorbate is located further from the substrate than in the up configuration. The closest interatomic distance between the molecule and the substrate occurred between the H atom of the benzene ring and the substrate Mg atom, with distances of 0.26–0.27 nm.

　　Table 1 displays the distances between the central Al atom and N and O atoms of Alq₃ (adsorbed or isolated molecule). It is found that the Al–O and Al–N distances are in general longer in the up configurations than those of the isolated molecule, while those in the down configurations are almost identical to those of the isolated molecule. Given that the weakened Al–O and Al–N bonds in the up configurations originate from the chemical interaction with the Mg substrate, it is confirmed that the adsorbate–substrate interaction in the down configurations is dominated by weak physical interactions such as van der Waals (vdW) interactions.

3.2. Binding energy of Alq₃/Mg interfaces

Table 2 displays the calculated binding energies of the Alq₃/Mg interface for the facial (*fac*) and meridional (*mer*) isomers. The

Table 1. Bond lengths between the central Al atom and O and N atoms of Alq$_3$ adsorbed on the Mg(001) and those of the isolated molecule in nm units.

Al–O	Up	Down	Isolated[a]	Al–N	Up	Down	Isolated[a]
mer	0.197	0.188	0.188	*mer*	0.205	0.211	0.211
	0.197	0.191	0.191		0.205	0.206	0.204
	0.190	0.192	0.191		0.208	0.209	0.206
fac	0.194–0.195	0.188	0.187	*fac*	0.205–0.208	0.211	0.211

[a] Reference [10].

Table 2. Binding energies of the Alq$_3$/Mg(001) interface in kJ mol^{-1} units.

	mer/up	*mer*/down	*fac*/up	*fac*/down
GGA[a]	6.0 (16.9)[b]	− 12.6 (35.6)	38.0 (0.0)	− 31.5 (69.5)

[a] For the definition of binding energy, see equation (1).
[b] Total energies relative to that of the *fac*/up are in parentheses. Note that the *mer* isomer of isolated Alq$_3$ is more stable than the *fac* isomer by 15.1 kJ mol^{-1} [10].

binding energy E_B is defined by

$$E_B = E(\text{Alq}_3) + E(\text{Mg}) - E(\text{Alq}_3/\text{Mg}), \qquad (1)$$

where $E(\text{Alq}_3/\text{Mg})$, $E(\text{Alq}_3)$, and $E(\text{Mg})$ are the total energies of the adsorbed system, the isolated Alq$_3$, and the Mg substrate, respectively. Negative values mean energetically unfavourable states relative to the isolated state.

Table 2 indicates that the adsorbed structures in the down configurations are less stable than the isolated state, with binding energies of −32 to −13 kJ mol^{-1}. As discussed above, the adsorbed states in the down configurations involve weak physical interaction such as the vdW interaction. The present semi-local GGA functional cannot describe the long-range vdW attraction properly, resulting in repulsive interaction between the Alq$_3$ and Mg substrate in the down configurations. We showed that by incorporating the long-ranged non-local correlation based on the recently proposed vdW density functional (vdW-DF) [23], the interaction between Alq$_3$ and the metal substrate becomes attractive even in the down configurations [10].

In the up configurations of the Alq$_3$/Mg, on the other hand, GGA predicts bound adsorption. However, the quinoline ligands are located rather close to the substrate, with the shortest interatomic distance of 0.27 nm between the H atom of quinoline and the substrate Mg atom, and therefore it is quite likely that the GGA fails to incorporate the long-ranged vdW attraction between the ligands and the substrate, which may artificially lower the binding energies, similarly to the down configurations. Nevertheless, as we found in the previous Alq$_3$/Al study, the adsorbed structure is determined by the chemical bonds between the Alq$_3$ O atoms and substrate metal atoms, and the corresponding adsorbed structure is correctly reproduced by the GGA [8, 10].

For both isomers, it is found that the up configurations are more stable than the down configurations. This result supports our conclusion that the binding at the Alq$_3$/Mg interface is dominated by the O–Mg chemical bond; in the up configurations of both isomers, more O atoms can form chemical bonds with the Mg substrate than in the down configurations (see figure 1). As shown by the total energy differences in table 2, the total energy of the *fac*/up configuration is lower than that of the *mer*/up. However, this result does not necessarily lead to the existence of the *fac* isomer at the interface because of the barrier for isomerization [24], along with the observation of the predominance of the *mer* isomer based on the infrared reflection-absorption spectroscopy of Alq$_3$ on Ag using synchrotron radiation [25].

3.3. Molecular levels at the Alq$_3$/Mg interface

In order to clarify the nature of the chemical bond at the interfaces, we have calculated the projected DOS (PDOS). The PDOS of the Alq$_3$/Mg(001) are displayed in figure 2. For PDOS calculation, total wavefunctions were projected onto adsorbate molecular orbitals [26]. The calculated HOMO–LUMO gap is about 2.0–2.5 eV, which is rather small compared with the experimentally reported HOMO–LUMO gap of Alq$_3$ on Cu(111) ($\approx$5.5 eV) [27]. As is well known about the local density approximation (LDA) and GGA, the HOMO energy levels are systematically higher and the LUMO energy levels are systematically lower than the experimentally observed positions [28, 29]. The LUMO levels that are predicted to be in close proximity to the metal Fermi level in the up configurations (figure 2) may have resulted from such an error. Similar results were obtained in the Alq$_3$/Al study [8, 10]. We will discuss properties of energy levels which should not be affected by the present band gap problem.

In the *mer*/up configuration, the HOMO levels split at 2.0 and 2.7 eV below the Fermi level. In the *mer*/down configuration, the HOMO levels are located at similar levels. In the adsorbed configurations of the *fac* isomer, the HOMO levels are positioned with a difference of 1.5 eV between the up and down configurations. The HOMO level differences between the up and down configurations are similar to those that we found in the Alq$_3$/Al study, and can be ascribed to the difference in the interface dipole made by molecular dipoles; i.e. in the up (down) configurations, the molecular dipoles are directed towards the vacuum (substrate) and the electronic levels in the adsorbates are shifted down (up) compared to those of the substrate.

As was indicated in section 1, a small peak located about 1.6 eV above the HOMO peak at Alq$_3$/Mg was observed [5]. At Mg/Alq$_3$ interfaces, the gap state was ascribed to the partially filled LUMO state [5, 11–14]. On the other hand, as seen in figure 2, no state between the HOMO and LUMO levels appears in PDOS. We will discuss the assignment of the gap state later.
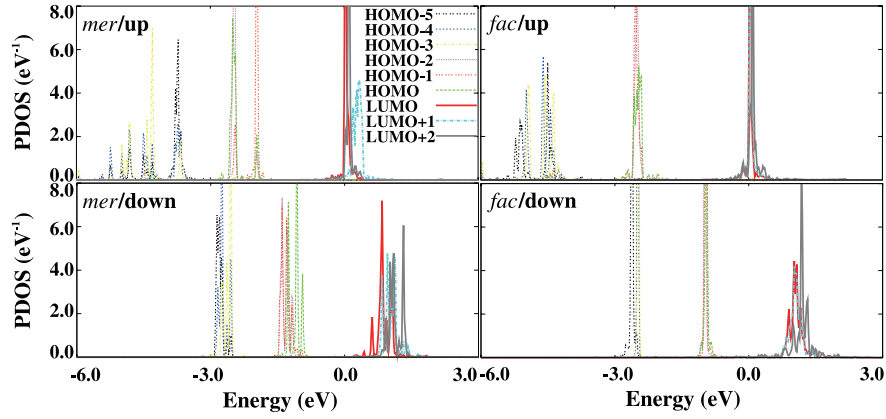
Figure 2. PDOS of the up and down configurations of the *mer* and *fac* isomers on the Mg(001). The axis of abscissa denotes the energy relative to the Fermi level.

Table 3. Work function change ($\Delta\phi$) in eV and the corresponding dipole moment ($\mu(Alq_3/Mg)$) at the Alq_3/Mg interface, dipole moments of the Alq_3 molecule ($\mu(Alq_3)$) and the Mg substrate ($\mu(Mg)$) in the supercell, and the difference $\Delta\mu = \mu(Alq_3/Mg) - \mu(Alq_3) - \mu(Mg)$ in debye.

	$\Delta\phi^a$	$\mu(Alq_3/Mg)$	$\mu(Alq_3)$	$\mu(Mg)$	$\Delta\mu$
mer/up	−1.08	4.02	3.93	0.28	−0.19
mer/down	0.02	−0.13	−0.79	0.02	0.64
fac/up	−1.30	4.99	6.90	0.06	−1.97
fac/down	0.95	−3.55	−4.93	−0.02	1.40

[a] The calculated work function of clean Mg(001) is 3.76 eV.

3.4. Interface dipole and subsequent work function change

The work function shift $\Delta\phi$ is defined by

$$\Delta\phi = \phi(Alq_3/Mg) - \phi(Mg), \qquad (2)$$

where $\phi(Alq_3/Mg)$ and $\phi(Mg)$ is the work function of the combined system and that of the isolated relaxed Mg(001) substrate, respectively.

As shown in table 3, the calculated work function shifts of the up configurations are −1.3 to −1.1 eV, while those of the down configurations are 0.0 to +1.0 eV. These results seemingly disagree with the experimentally determined vacuum level shift of −0.2 to −0.5 eV (Alq_3/Mg) [5, 11] and from 0.0 to −0.3 eV (Mg/Alq_3) [11, 12]. However, the extrinsic effects in the experiments should be taken into account, especially the oxidization of the Mg surface during the deposition of the substrate, which may lead to a weak interaction between the oxidized layer and the adsorbate. In contrast to that, the present calculation includes no such extrinsic effect, and therefore intrinsic interface dipoles can be extracted. Given that the up configurations are more energetically favorable than the down configurations, we suggest that the downward shift of work function at the Alq_3/Mg interface should be more than 1.0 eV, where the up configurations exist as major species.

The work function shift due to molecular adsorption is proportional to the surface normal component of the dipole moment induced by molecular adsorption. In order to examine

the origin of the work function shift, we divided the surface dipole moment of the adsorbed systems $\mu(Alq_3/Mg)$ into three contributions,

$$\mu(Alq_3/Mg) = \mu(Alq_3) + \mu(Mg) + \Delta\mu \qquad (3)$$

where $\mu(Alq_3/Mg)$, $\mu(Alq_3)$, and $\mu(Mg)$ are surface normal components of the dipole moments of the Alq_3 adsorbed Mg slab, Alq_3 layer, and Mg slab, respectively, while $\Delta\mu$ is the dipole moment induced by the electronic interaction between Alq_3 and the Mg substrate. $\mu(Alq_3)$ and $\mu(Mg)$ are calculated for the separated Alq_3 layer and Mg slab with their geometries fixed to the adsorbed system. Table 3 summarizes these contributions. The sign of the interface dipole $\mu(Alq_3/Mg)$ clearly corresponds to that of the isolated Alq_3 molecular dipole $\mu(Alq_3)$. This result indicates, as was found for the Alq_3/Al interfaces [8, 10], that the dipole layer induced by Alq_3 adsorption is dominated by the permanent dipole of the Alq_3.

Table 3 indicates that $\Delta\mu > 0$ in the down configurations of both the isomers, thus implying that the dipole oriented to the vacuum side is added to the dipoles of the isolated adsorbate and the substrate. The mirror force effect or the push back effect enhances the dipole directed to the vacuum side [3, 30], and most of the induced dipole can be ascribed to such effects.

In contrast, in the *fac*/up configurations, where $\Delta\mu$ is largely negative, the dipole oriented to the substrate side is induced upon adsorption. This is ascribed to the charge transfer from the substrate to the adsorbate side. We have found by Mülliken population analysis that the unoccupied levels of the Alq_3 (*fac*) in the up configurations are fractionally occupied, with the occupation numbers estimated to be 0.7. Nevertheless, the resulting $\Delta\mu$ of −2.0 D is not so significant as to alter the interface dipole dominated by the molecular permanent dipole $\mu(Alq_3)$ of +6.9 D.

3.5. Elucidation of the gap state

As mentioned in section 3.4, we found no states that can be assigned to the experimentally reported interface gap state [5]. Although the gap state at Mg/Alq_3 interfaces was ascribed to
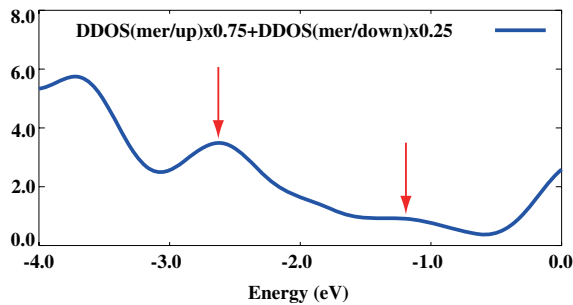
Figure 3. Superposed DDOS between the adsorbed system and the bare substrate in the up and down configurations of the *mer* isomer on the Mg(001). The axis of abscissa denotes the energy relative to the Fermi level. The HOMO levels are indicated by arrows. A peak at around the Fermi level is ascribed to the LUMO level, which is artificially lowered due to the gap problem in DFT calculations.

the partially occupied LUMO level [5, 11–14], we have found that the partially filled LUMO is located in close proximity to the metal Fermi level, in contrast to the higher binding energy region of ≈ 2.2 eV below the Fermi level, where the gap state was observed [5]. This result leads us to another conclusion for the assignment of the gap state, as we found in the study of the Alq_3/Al, i.e. the co-existence of the up and down configurations. As is found in figure 2, the HOMO levels of the up and down configurations of the *mer* isomer relative to the Fermi levels differ by 1.0–1.7 eV. The difference DOS (DDOS) of the up and down configurations of the *mer* isomer were obtained by subtracting the DOS of the substrate from that of the adsorbed system, and the two DDOSs were superposed in the ratio 3:1, as shown in figure 3. A small peak, which is ascribed to the HOMO level of the down configurations, appears ≈ 1.5 eV above a large peak (the HOMO levels of the up configurations). The two peaks agree well with the experimental spectra of [5]. We therefore suggest that the HOMO level of the down configurations, which may coexist with the most stable up configurations, is ascribed to the gap state observed for the Alq_3/Mg interface.

3.6. Energy level alignment at the Alq_3/Mg interface

Lastly, let us discuss the alignment between the metal Fermi level and the HOMO and LUMO levels of Alq_3. The LUMO in the up configurations that is predicted to be in close proximity to the metal Fermi level may be ascribed to the artificial lowering of the unoccupied levels by the DFT. The gaps of isolated Alq_3 obtained in the present study are 1.9 eV (*mer*) and 2.1 eV (*fac*), in contrast to the experimental gaps determined by the ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) of 5.4 eV for Alq_3 of 50–100 Å thickness on Au [31] and 5.5 eV for Alq_3 of 10–20 molecular layer thickness on Ag(111) [32]. Note that these gaps may correspond to that of the Alq_3 in the top surface layer of thick Alq_3 film.

On the other hand, the reduction of the gap at the metal/organic interface is found by the scanning tunneling microscope (STM) measurement of Alq_3 on metal, with which the electron and hole polaron energies (the injection barriers)

at the interface were determined [33, 34]. Using the technique, the barrier for electron injection of 0.4 ± 0.1 eV and the hole injection barrier of 1.7 eV for Alq_3 on Al were observed [34].

The authors proposed the origin of the decreased gap at the interface compared to those observed by UPS/IPES experiment to be the difference in the polarization of surrounding media; i.e. the polarization effects are weakest at the film surface, because about half of the surrounding space is a vacuum, and they are strongest at the electrode interface, because the molecules are facing highly polarizable metal [34].

Based on the STM result, the gap of Alq_3 on Al at the interface can be estimated to be about 2.1 eV. This value is in fair agreement with the gaps of Alq_3 on Al obtained in our previous study [10] and those obtained in the present study of Alq_3 on Mg. Although the agreement between our calculated gap and that by the STM observation is due to fortuitous cancelation of two errors in GGA calculations, i.e. the underestimation of the HOMO–LUMO gap and the lack of gap narrowing by the image effect at the metal/organic interface, this result may confirm a reasonable estimation of the energy level alignment at the Alq_3/Mg in the present study, along with the accurate work function shift at the Alq_3/Al interface given by the calculation method similar to the present study [10]. The contribution of the image potential to the energy gap may be examined by the many-body methods, as was done for benzene on graphite [35].

4. Conclusions

In summary, we investigated the atomic structures and the electronic properties of the Alq_3/Mg interface by the density functional theoretical method. We modeled the Mg electrode surface by the Mg(001). Alq_3 molecules are bound to Mg substrates through their O atoms. The binding at the Alq_3/Mg interface is dominated by the chemical bond between O and surface Mg atoms, which can be correctly described by the GGA. Up configurations, in which molecular permanent dipole moments are directed to the vacuum side, reduce the work function by 1.1 (*mer*) and 1.3 (*fac*) eV. Down configurations, in which molecular dipoles are directed to the substrate, increase the work function. We also pointed out the co-existence of a small number of down configurations, which contribute to the interface gap state observed by the UPS experiment.

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