

## The Surface Electronic Structure of Mg-doped Tris(8-hydroxyquinolato) Aluminum

### Beamline

08A Low Energy SGM beamline  
24A Wide Range SGM beamline

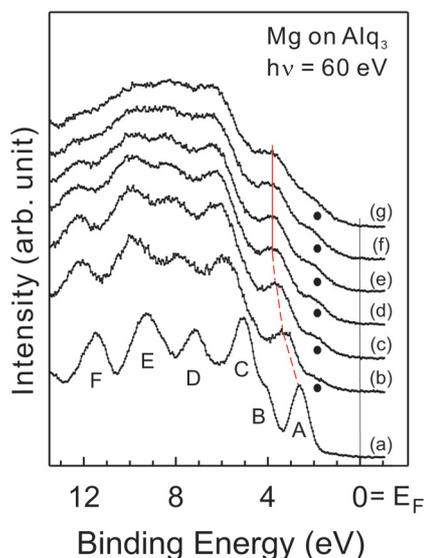
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*Synchrotron radiation photoemission was used to investigate the electronic structure of magnesium deposited on tris(8-hydroxyquinolato) aluminium ( $Alq_3$ ). Upon Mg deposition, the highest occupied molecular orbital of  $Alq_3$  shifts monotonically towards high binding energy, and the lowest unoccupied molecular orbital remains fixed in energy. The N 1s core appears a charge-transfer component with a binding energy lower than that of the original component. This new component grows gradually in intensity with increasing Mg concentration, and separates from the original component by -1.51 eV at small exposure, but up to -1.85 eV at large exposure. Moreover, the O 1s core was also affected, the induced component of which lies at +1.09 eV. The Mg 2p core-level spectra exhibit a shift towards lower binding energy with increasing Mg vapour. All these experimental evidences suggest that Mg residing in the surface  $Alq_3$  molecules forms actually clusters. It attaches to a pyridyl ring, affecting not only the nitrogen atom at that ring, but the oxygen atom in the adjacent phenoxide ring. The depleted charge in the affected oxygen flows then about its adherent ligand and resides on the pyridyl ring at that ligand, resulting in a high  $Alq_3$  anion state.*

Magnesium on tris(8-hydroxyquinolato) aluminium ( $Alq_3$ ) remains a prototypical system to understand the physics of the actively studied organic light emitting devices (OLEDs). Among the experimental techniques, photoemission is an indispensable tool to probe the electronic structure of the organomagnesium complexes for its high sensitivity to the change of charge environments of the constituent elements. To be brief on the review of the published photoemission works, all has unanimously observed new Mg-induced peaks appearing in the valence band measurements as well as in the core level spectra of the constituents. The charge redistribution arising from the foreign Mg vapour fills the lowest unoccupied molecular orbital (LUMO) of  $Alq_3$  and adds an extra charge to the nitrogen atom at one of the quinolinol ligands. With these results, a model is then come to pass which proposes that each  $Alq_3$  molecule is coordinated with one magnesium atom.

Figure 1 exhibits the valence band spectra taken at a 60 eV photon energy. The representative molecular states A to F of the pristine  $Alq_3$  clearly appear at their proper energies. Upon Mg adsorption, the HOMO peak initially appeared at 2.60 eV shifts monotonically towards higher binding energy, and stops at 3.90 eV associated with 1 Å of thickness (Fig. 1(d)). This manner of movement is in contrast with the previous reports which claimed a rigid-band shift. Moreover, the intensities of features A to F have dropped immediately in half at the outset of Mg adsorption, say, 0.2 Å. Exposing the  $Alq_3$  solid to more Mg vapour does not weaken significantly further these molecular states. It is not until 19



**Fig. 1:** The valence-band spectra of Mg deposited on thick  $\text{Alq}_3$  film. The thickness is in unit of angstrom, t: (a)  $t = 0$ ; (b)  $t = 0.2$ ; (c)  $t = 0.5$ ; (d)  $t = 1.0$ ; (e)  $t = 3.0$ ; (f)  $t = 13$ ; (g)  $t = 19$ .

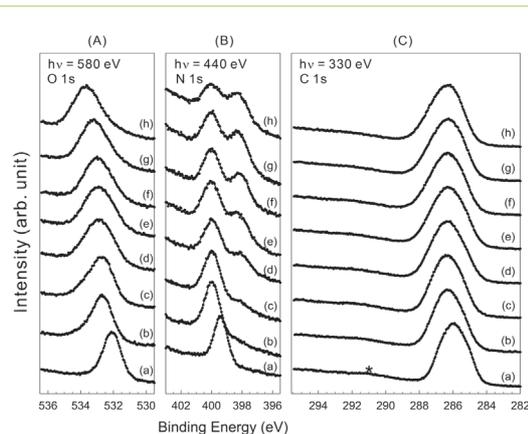
$\text{\AA}$  of evaporation where the Mg dopant starts to wear away the sharpness of the molecular states. This result leads us to reach a conclusion that as far as the valence-band structure is concerned, no great differences exist between the surface and the bulk of Mg-saturated  $\text{Alq}_3$  film.

Upon exposing the pristine  $\text{Alq}_3$  to the Mg vapour, there appears immediately a state at 1.8 eV below the Fermi level ( $E_F$ ), which is due to the filled LUMO of  $\text{Alq}_3$ . There are two peculiar behaviours of the filled LUMO state; namely, the constant peak height and peak position irrespective of the Mg thicknesses. With regard to the strength of the peak, on the one hand, it is detected not only nearly at a constant height, but has a constant relative height to the HOMO peak from the onset to 19  $\text{\AA}$ . As a matter of fact, the line profile emerged from the HOMO and LUMO states remains virtually the same throughout the whole course of evaporation. This tells us that once there exists organomagnesium species in the  $\text{Alq}_3$  film, even in a minimal amount, it quickly predominates the valence band structure. Since the Mg concentration is rather dilute at 0.2  $\text{\AA}$  of thickness, the band between the organomagnesium complexes is unlikely to form.

On the other hand, the fixed energy position of the LUMO elucidates that its separation from the HOMO depends on the concentration of Mg. To be

specific, the separation is 1.5 eV in a small exposure but gradually widens up to 2.1 eV in larger ones. This behaviour differs noticeably from the published reports, which claimed a constant energy separation between the HOMO and the LUMO independent of the Mg concentration. It is worth mentioning that fixed HOMO-LUMO gaps have been observed in both the  $\text{K}_3\text{C}_{60}$  and  $\text{K}_6\text{C}_{60}$  crystalline phases.

Figure 2 displays the evolution of the O 1s, N 1s, and C 1s core-level spectra with various thicknesses of Mg taken at photon energies of 580, 440 and 330 eV, respectively. As can be seen in Fig. 2, the little change of the line shape of the C 1s core suggests that the incorporated Mg have small influence on carbon. For the O 1s core, one can easily see that the Mg dopant has altered the line shape to become asymmetric with a tail structure skewing towards higher binding energy. Greater Mg deposition has further strengthened the tail structure while concurrently weakening the original component. In order to extract these two components out of the broad envelope, we have processed each O 1s curve with a fit. In a fit, each component containing a core hole lifetime and phonon broadening is represented by a Voigt function and the goodness of a fit is determined via a least-squares algorithm. As a result, the pristine O 1s spectrum appears as a sole peak in accompany with the shake-up satellite. Upon Mg deposition the model function with one component is no longer representable for the measured curves. In fact, an second component must be included



**Fig. 2:** The O 1s, N 1s, and C 1s core-level spectra of Mg deposited on thick  $\text{Alq}_3$  film. The thickness is in unit of angstrom, t: (a)  $t = 0$ ; (b)  $t = 0.03$ ; (c)  $t = 0.06$ ; (d)  $t = 0.2$ ; (e)  $t = 0.5$ ; (f)  $t = 1.8$ ; (g)  $t = 5.3$ ; (h)  $t = 16$ . The mark \* in (C) stands for the  $\pi \rightarrow \pi$  transitions.

whose line position emerges at +1.09 eV higher binding energy than the original component. This new component grows strongly with increasing Mg concentration and becomes dominant at 5.3 Å.

With regard to the N 1s core-level spectra, the Mg-induced component protrudes at a 400.40-eV binding energy lying on the low binding-energy side of the original component at 399.40 eV. The new component picks up rather quickly the intensity, and by about 0.5 Å of thickness it has already achieved half of the intensity of the original component. After that, the peak area of the new component continues to gain additional strength, though in a slower rate. We found that the new component has the same peak area as the original component at about 2 Å of thickness, and runs over it afterward. In contrast, the literature have reported that the new component stays always at an 1:2 area ratio to the original component, regardless of the amount of the Mg vapour. The 1:2 constancy has been reasoned as only one of three tris(8-hydroxyquinolato) ligands that has accepted charge from Mg, leaving the other two intact. Obviously, the model of one-atom in one-molecule fails to comprehend the result of Fig. 2. Moreover, this model also suggests a constant energy separation of 1.8 eV between these two components. Nevertheless, the separation is actually 1.51 eV at 0.03 Å, but gradually widens up to 1.85 eV at 2 Å. All these evidences indicate that the Mg/Alq<sub>3</sub> surface behaves quite differently from the bulk.

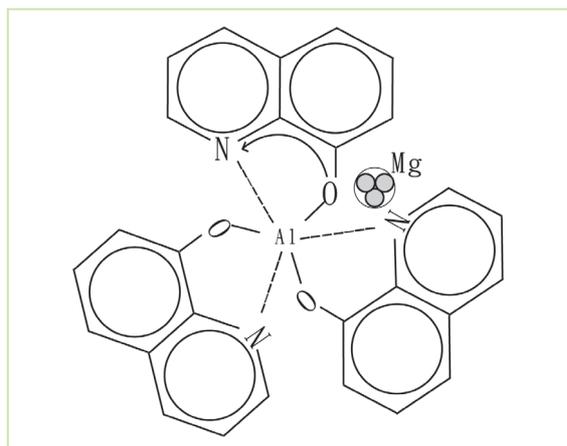
To cope with the finding that the peak area ratio of the new and original components goes beyond 1:2, one might naturally propose that a second Mg atom should be incorporated into another 8-hydroxyquinolato ligand, as in the case of alkalis-doped Alq<sub>3</sub>. In this case, one would expect to have the ratio changed discretely from 1:2 to 2:1, or even to 3:0 if a third Mg atom is allowed to be in Alq<sub>3</sub>. Although this proposal might take care of the issue of the rising intensity of the Mg-induced peak, it however basically ignores the fact that the ratio increases gradually, not discretely, from the lowest value of 0.1.

Seeing the deficiency of Mg being incorporated in Alq<sub>3</sub> as atoms, we then propose that as far as the surface Alq<sub>3</sub> molecules are concerned Mg appears as clusters grown in sizes with doping. Our clusters proposal is rather encouraging since the core-level behaviours of magnesium follow rather closely with that of the supported clusters on a non-conducting

substrate. Although the present Mg clusters are not supported but doped in Alq<sub>3</sub>, the electrical nature of the organic solid resembles more or less the non-conducting background. In the previous cluster study, the binding energy of a cluster was found to be size-dependent; that is, the smaller the size, the greater the binding energy. Indeed, the Mg 2p cores move gradually from a low binding energy in small concentrations to high binding energy in large exposures (not shown). At small Mg concentration, the small clusters have limited charge to donate onto a nitrogen atom, giving rise to a small energy separation from the original peak. As the size of cluster becomes greater, more charge is available for the donation, thereby widening up the energy separation.

The schematic drawing of a Mg cluster residing between two quinolinol ligands. The cluster donates charge to the nitrogen atom in a quinolinol ligand, and also causes the oxygen atom in the adjacent quinolinol ligand to transfer its charge to the nitrogen atom at that ligand. At here, we need to dissolve two concerns that relate to the behaviours of the Mg 2p cores as doping. On the one hand, one might attribute the negative shift as due to the change of Mg ionization state. This concern is readily excluded since the shift continues without disruption as the metallic Mg 2p cores commence to appear at great concentrations. On the other hand, the binding energy for initial Mg deposition which is close to that of Mg<sup>2+</sup> seems to suggest that the dopant is doubly ionized, similar to the Ca dopant. In the latter, it is claimed that two Alq<sub>3</sub> molecules share concurrently the released s electrons from calcium, thereby giving rise to the 1:2 area ratio of the new and original components. The absence of such a constant area ratio in the present Mg study suggests that the Ca model might be inapplicable to the Mg case. Moreover, if each Alq<sub>3</sub> molecule accepts truly a full s charge from Mg, the filled LUMO should come forth a peak as sharp as that in K-doped Alq<sub>3</sub>.

In Fig. 3 a diagram of a Mg cluster on Alq<sub>3</sub> is sketched in which we summarize all the results given in core-level spectra. The cluster is affiliated at the pyridyl ring of a quinolinol ligand and served as a charge donor so that the LUMO state is filled and the N atom has obtained additional charge. Moreover, the cluster also causes the oxygen atom in the adjacent phenoxide ring to lose charge (see Fig. 2). The



**Fig. 3:** The schematic drawing of a Mg cluster residing between two quinolinol ligands. The cluster donates charge to the nitrogen atom in a quinolinol ligand, and also causes the oxygen atom in the adjacent quinolinol ligand to transfer its charge to the nitrogen atom at that ligand.

depleted charge in the chelated oxygen flows about its adherent ligand and settles down upon the nitrogen atom at that ligand. Consequently, the intensity of the new negatively-shifted N 1s component increases gradually as Mg doping with the expanse of the new positively-shifted O 1s component. It is worth mentioning that although the Mg vapour bombarding the Alq<sub>3</sub> solid forms clusters in the surface, Mg diffusing further down to the bulk as atoms is highly permissible, thus delivering the experimental results in the published reports.

### Experimental Station

High-resolution photoemission chamber

### Publications

- T.-W. Pi, C.-H. Liu, and J. Hwang, *J. Appl. Phys.* (2006), in press.
- T.-W. Pi, T. C. Yu, C.-P. Ouyang, J.-F. Wen, and H. L. Hsu, *Phys. Rev. B* **71**, 205310 (2005).
- T.-W. Pi, C.-P. Ouyang, T. C. Yu, H. L. Hsu, and J.-F. Wen, *Phys. Rev. B* **70**, 235346 (2004).
- T.-W. Pi, C.-P. Ouyang, T. C. Yu, H. L. Hsu, J.-F. Wen, and J. Hwang, *Appl. Phys. Lett.* **85**, 908 (2004).

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