University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Peter Dowben Publications | Research Papers in Physics and Astronomy

9-26-2005

Metal hybridization and electronic structure of Tris(8-hydroxyquinolato)aluminum (Alq_3)

Anthony N. Caruso
North Dakota State University, anthony.caruso@ndsu.edu

D. L. Schulz
North Dakota State University

Peter Dowben
University of Nebraska - Lincoln, pdowben1@unl.edu

Follow this and additional works at: http://digitalcommons.unl.edu/physicsdowben

Part of the Physics Commons

Caruso, Anthony N.; Schulz, D. L.; and Dowben, Peter, "Metal hybridization and electronic structure of Tris(8-hydroxyquinolato)aluminum (Alq_3)" (2005). *Peter Dowben Publications.* Paper 215.
http://digitalcommons.unl.edu/physicsdowben/215

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Published in *Chemical Physics Letters* **413**:4-6 (September 26, 2005), pp. 321–325; doi 10.1016/j.cplett.2005.07.098
Copyright © 2005 Elsevier B.V. Used by permission. http://www.sciencedirect.com/science/journal/00092614

Submitted April 18, 2005; revised July 22, 2005; published online August 19, 2005.

Metal hybridization and electronic structure of Tris(8-hydroxyquinolato)aluminum (Alq_3)

A. N. Caruso,* D. L. Schulz,* and P. A. Dowben †

* Center for Nanoscale Science and Engineering, North Dakota State University, 1805 Research Park Drive, Fargo, ND 58102, USA

† Department of Physics and Astronomy and the Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln, NE 68588-0111, USA

Corresponding author — A. N. Caruso, anthony.caruso@ndsu.edu

Abstract

The metal-organic complex Tris(8-hydroxyquinolato)aluminum (Alq_3) has been studied by energy and light polarization dependent photoemission. Resonant photoemission was used to identify the molecular orbitals involved in metal chelation. When adsorbed on cobalt and gold surfaces, marked differences in the Alq_3 metal-to-ligand bonds were observed. The results indicate intramolecular aluminum-to-ligand bonding through the oxygen heteroatom when Alq_3 is adsorbed on gold, but through the nitrogen heteroatom when on cobalt. These results indicate that substrate interfacial complex formation plays an important role in the Alq_3 molecular configuration and intramolecular bonding.

1. Introduction

The metal-organic complex (OMC) Tris(8-hydroxyq uinolato)aluminum (Alq_3) is a widely utilized component in organic electroluminescent devices [1] and has recently shown promise as a thin non-magnetic layer in a giant magnetoresistive device [2]. Recent studies have suggested that charge transfer [3, 4] effects at the Alq_3/metal interface, as well as interface states [5, 6] and possibly metal induced gap states [5, 6] play an important role in charge injection and device performance. The alignment of the molecular orbitals with respect to the Fermi level and the electronic structure of a metal-organic/metal interface are expected to have a profound effect on charge injection in molecular electronics. These aspects of electronic structure are, in turn, influenced by the molecular interactions with the metal substrate. In the case of Alq_3, there have been a number of studies which indicate that the band offset and charge polarity are key to device performance [3, 4], but the molecular configuration [3, 6] and perturbations to the Al–hydroxyquinolate bonds may have a more profound effect.

In this study, resonant photoemission is used to identify the molecular orbitals (MOs) associated with the complexed aluminum metal center and show that these molecular orbitals are strongly perturbed by the choice of metal substrate. The substrates were chosen to understand the metal-organic/metal interface formed in the magnetoresistive device (cobalt) compared to the more standard metal electrode (gold). The effect of molecular orbital perturbation is important to device performance, as already the quantum efficiency and color of luminescence in light emitting diodes composed from Alq_3 has been shown to be dependent on the stereoisomer and phase of composition [7]. The two isomers of Alq_3 are the *facial* and *meridinal* with C_3 and C_1 point group symmetries, respectively, shown in the inset of Figure 1. Other molecular configurations may exist as well, as "distortions" to the *facial* and *meridinal* structures of Alq_3 in the "relaxed" geometries, as might occur in isolation.

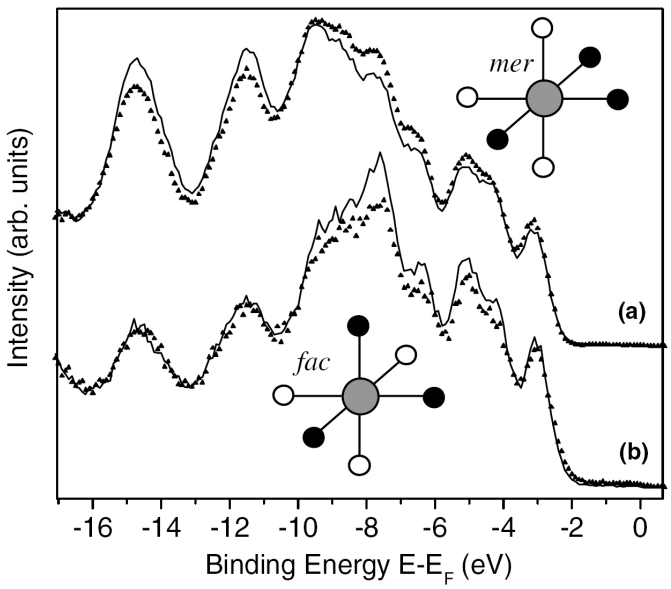

Figure 1. Polarization dependent photoemission at (a) 32 eV and (b) 72.8 eV photon energy of Alq_3 adsorbed on Au(1 1 1). p polarization is represented by a solid line whereas s + p polarization is the scatter plot (▲). Inset are the octahedral metal coordination spheres for the *meridinal* and *facial* isomers of Alq_3 with nitrogen and oxygen atoms as black and white circles, centered about an aluminum in gray.

2. Experiment

Alq_3 was studied by angle resolved and polarization dependent ultraviolet photoemission spectroscopy under ultra high vacuum (3×10^{-10} Torr). The commercially purchased Alq_3 powder (Aldrich) was purified before loading into an evacuated reservoir. The Alq_3, adsorbed by vapor from sublimed powder, was admitted to the UHV chamber through a leak valve for adsorption on the UHV prepared metal thin film substrates.

The photoemission measurements, as described in detail elsewhere [8], were carried out at the Center for Advanced Microstructures and Devices synchrotron radiation facility in Baton Rouge, Louisiana with synchrotron light, monochromated by a 3m torodial grating monochromator. Alq_3 adsorptions were completed on cooled (~100 K) epitaxial Au/Si(1 1 1) and polycrystalline Co/Au/Si(1 1 1) substrates. The thicknesses of the Alq_3 molecular layers, reported herein, are 14 Å. The gold coatings exhibited a (1 1 1) orientation by X-ray diffraction and both gold and cobalt coatings exceeded 100 nm. All binding energies reported herein are referenced to the Fermi level as calibrated by tantalum foil in intimate contact with the sample surface with all photoelectrons collected normal to the substrate surface ($k_\parallel = 0$ or $\bar{\Gamma}$). Polarization dependent photoemission was accomplished by varying the incident angle of the linearly polarized synchrotron light with the following provisions: s + p polarization is given by 45° incidence with respect to surface normal; and, p polarization is given by 70° incidence, to yield the vector potential **A** more normal than parallel to the surface. The polarization dependence can be coupled to the photoemission selection rules under the local point group of adsorbed Alq_3 to yield symmetry specific molecular orbital representations as a function of binding energy; the details of selection rule formalism are laid out elsewhere [9]. Energy dependent photoemission was employed to determine the bandwidth of molecular orbitals normal to the interface (for a crystalline overlayer thickness which did not exceed the mean free path of the substrate and its overlayer). The reciprocal space position normal to the interface $k_\perp$ is given as a function of incident photon energy by Eq. (1), where $h\nu$ denotes the incident photon energy, E_b the binding energy, θ is the emission angle (0° in this work), the work function is given by φ and U represents the inner potential.

$$k_\perp = \sqrt{\frac{2m}{\hbar^2}\{(h\nu - E_b - \varphi)\cos^2\theta + U\}}. \quad (1)$$

Resonant photoemission measurements were undertaken by comparing photoemission spectra collected with $h\nu = 32$ and 72.8 eV to be clearly off and on the Al $2p_{1/2} \rightarrow 3s$ (core to bound) absorption thresholds. The resonant photoemission, at 72.8 eV, is a core-to-bound excitation in which the incident photon excites an electron from the Al 2p core to an unoccupied state just above E_F that largely includes Al, O and N weight. The bound electron decays, providing a resonant effect with the direct photoelectron emission process, and is localized to molecular orbitals with weight in the vicinity of the Al 2p core hole due to the strong Coulombic interaction.

2.1. Aluminum to quinolinate ligand bonding for Alq_3 at the substrate metal interface

Alq_3 does preserve some quinolinate to Al metal center bond symmetry. Figure 1 shows the light polarization dependent photoemission at incident photon energies of 32 and 72.8 eV for Alq_3 adsorbed on Au(1 1 1) from vapor. The light polarization dependence, of the photoemission spectra, reveals that the Alq_3 molecule, adsorbed on gold, does preserve some symmetry [9], particularly in the vicinity of the Al metal center. Although the light polarization dependence is different at different photon energies, the polarization dependence is significant for the photoemission feature at −7.8 eV binding energy. As this feature is enhanced at the Al 2p threshold (Figure 1), we can assign this feature to molecular orbitals that contain Al weight.

With the Alq_3 adopting a C_3 point group symmetry, the irreducible representations that can be observed in photoemission are *a* and *e*, where *a* represents the symmetry axis of rotation (120° through trisection of the octahedral oxygen and nitrogen) whereas *e* signifies those molecular orbitals which have symmetries directions (x, y, xz, yz, $x^2 - y^2$) orthogonal to *a* (z, $x^2 + y^2$, z^2). The orthogonal symmetries of the *facial* Alq_3 can be reconciled with the light polarization dependent photoemission, in contrast to the C_1 point group *meridional* Alq_3 isomer (with little or no symmetry). This identification of the *facial* Alq_3 isomer, at least in the vicinity of the Al metal center, is also favored by others [10], but not all [11, 12].

As noted above for Figure 1, the light polarization dependent photoemission intensity is reversed as the photoemission cross section changes with incident photon energy. At 72.8 eV photon energy, where there is resonant enhancement of molecular orbitals with aluminum weight, there is also enhancement of the same molecular orbitals (at −7.8 eV binding energy) with p polarized light. The polarization and energy enhancement indicates that the molecular orbitals with aluminum weight form as a result of atomic contributions with s and p_z components rather than the p_x or p_y. The assignment of the *a* irreducible representation may also apply to intramolecular bonding within the quinolate ligand, but is not necessary to satisfy the observed behavior. Such a picture of aluminum bonding to the octahedral nitrogen and oxygen orbitals, from the point of view of symmetry, is consistent with that proposed by Curioni et al. [11].

The light polarization dependence of the photoemission (Figure 1) is indicative of a strong preferential bonding orientation of Alq_3 to the gold substrate. While the molecular film need not be crystalline, the results are consistent with strong texture to the molecular thin film growth in the thin film limit, unlike that suggested elsewhere for thicker molecular films [12].

For depositions of Alq_3, from the vapor, on cobalt (Figure 2a), the photoemission reveals very different molecular orbital photoemission intensities and small increases in the Alq_3 molecular orbital binding energies when compared to the molecular orbital induced photoemission features for Alq_3 adsorption on gold (Figure 2b). As shown in Figure 2a, there is an obvious enhancement in photoemission intensity for the four major molecular orbitals photoemission features at −4.6, −7.8, −9.7 and −11.9 eV binding energy at the Al 2p resonance (taken at 72.8 versus 32 eV photon energy). By way of comparison, as shown in Figure 2b, the photoemission spectra taken at the Al 2p resonance (again 72.8 versus 32 eV photon energy) for Alq_3 on Au show strongly enhanced features at −7.8 and −5.2 eV binding energies. The resonant enhancements in the Alq_3 photoemission spectra demonstrate that the molecular orbitals with

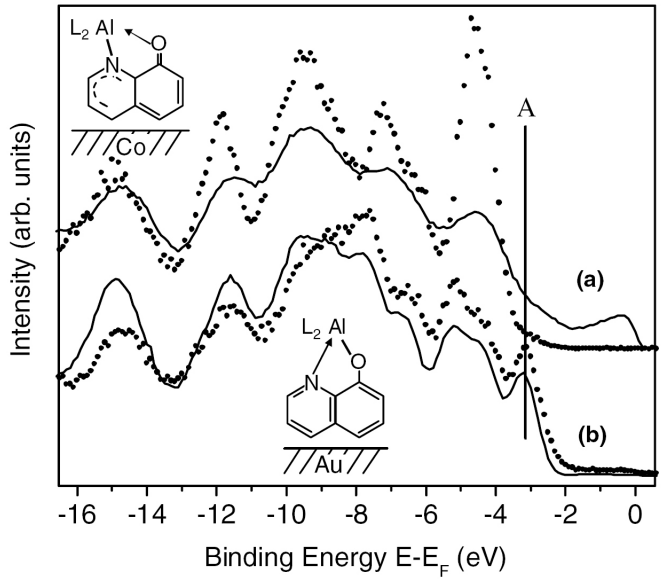

Figure 2. Photoemission of adsorbed Alq_3 on (a) cobalt and on (b) gold at 32 eV (solid line) and at 72.8 eV (●) incident photon energy. All spectra were taken by s + p polarization.

strong aluminum weight differ for Alq_3 on cobalt than on gold.

If we compare the binding energies of the molecular orbitals, enhanced at the Al 2p threshold in resonant photoemission, with the projected density of state calculations, provided by Curioni et al. [13] for each Alq_3 component, we find that those molecular orbitals enhanced in Figure 2a are molecular orbitals with the nitrogen weight, whereas those photoemission features that are enhanced at the Al 2p edge, in Figure 2b, are representative of molecular orbitals containing a strong oxygen projected density of states. These results indicate that for Alq_3 adsorbed on cobalt, the Al metal center tends to bond the quinolinate ligands through the nitrogen whereas on gold, the Alq_3 ligands bond to the Al more through the oxygen. This large difference in ligand-to-metal bonding suggests different molecular configurations are adopted by Alq_3 at the different substrate surfaces.

Organometallic complex formation has been suggested for Alq_3 adsorbed on magnesium and aluminum surfaces [6]. In the present study, interfacial Alq_3 to metal substrate interaction induces intramolecular iminate ligand-to-metal bonds (i.e. Al–N) for Alq_3 on cobalt and enolate (i.e., Al–O) bonds for Alq_3 on gold. Furthermore, the fact that Alq_3 adopts a very different molecular configuration at some interfaces does lend considerable weight to the interface model proposed by Rajagopal et al. [3, 5] and others [6] and supports the premise that molecular configuration has a profound electronic effect at Alq_3 interfaces. Nonetheless, Al to quinolate ligand molecular orbitals are identified for Alq_3 adsorption on both gold and cobalt, in spite of the

profound differences of the Alq_3 electronic structure on the different substrates. Adsorption on both metals must be largely associative.

2.2. The Alq_3 density of states close to the fermi level

An explanation of the effect of the substrate on the molecular orbital binding energies for condensed Alq_3 are not easily addressed by a single factor such as work function. Prior studies have advocated two competing pictures for the Alq_3 molecular orbitals relative position on metal surfaces. There are advocates of a model where the molecular orbitals are pinned to the Fermi level [5, 14] and others who have argued that charge transfer and substrate work function dominate E_F placement within the molecular HOMO–LUMO gap [4]. By compiling available photoemission spectra, a comparison of the position in binding energy of the highest occupied molecular orbital (HOMO) as shown in Figure 3, does not show a strong dependence upon substrate work function. Therefore, it seems more likely that the density of states near the Fermi level are dominated by impurities, decomposition or the different molecular phases now known to exist in the interfacial region, as demonstrated here and elsewhere [3, 5, 6].

In comparing the spectral density between Alq_3 adsorbed on gold versus cobalt, there is a much larger photoemission intensity at −4.6 eV binding energy and a very weak molecular orbital contribution to the photoemission spectra at −3.1 eV binding energy (labeled as "A" in Figure 2). This absence of photoemission intensity for Alq_3 on Co may be indirectly linked with a previous study [2] where Alq_3 film thicknesses under 100 nm deposited on cobalt, exhibited high resistances values in the range of 10^4–10^5 Ω. That is, an absence of photoemission intensity for the HOMO indicates the absence of a density of states for the valence orbital and hence a greater insulating material.

The diminished Alq_3 photoemission intensity at −3.1 eV binding energy for Alq_3 when adsorbed on cobalt (vertical line "A" in Figure 2a), does not appear to fit with a model of charge injection into Alq_3 that relies upon the substrate work function [4]. This point is illustrated in Figure 3, where the highest occupied electronic state binding energies (derived from photoemission) for Alq_3 on Co are compared with our results on Au and measurements of others for Alq_3 on a variety of substrates. Again, there seems to be no obvious correlation between the highest occupied electronic state binding energy and substrate work function.

The presence of the photoemission peak "A" that was attributed to the highest occupied electronic state for Alq_3 on gold, cannot be attributed to an interface state. Our reasoning is due to the small but finite dispersion of "A" in Figure 4, compiled from energy dependent photoemission. The presence of dispersion indicates that this peak is not localized to the interface, that is to say, the state does not preserve two dimensionality of state. Furthermore, peak "A" still exists for Alq_3 films on many substrates (Figure 3), where the film thickness is much greater than the photoelectron mean free path. Hence the peak "A" is due to the true HOMO and not an interface state as suggested in other studies [6, 15].

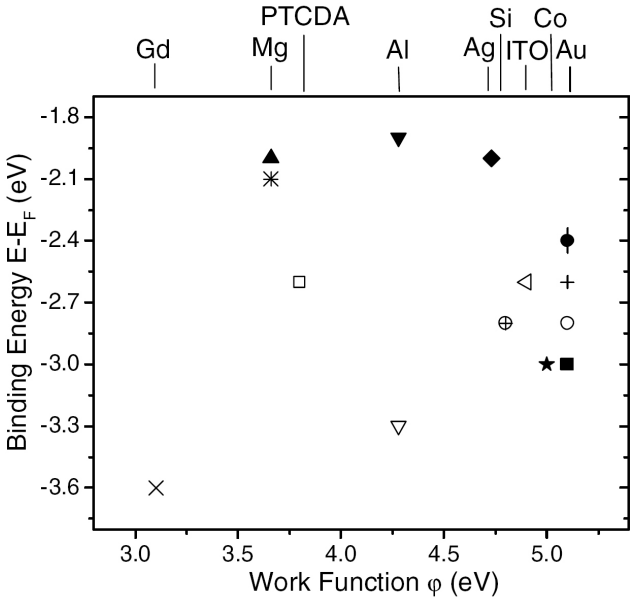

Figure 3. Comparison of the Alq_3 highest occupied electronic state (state "A" in Figure 2) binding energy for various photoemission studies as a function of work function for the substrates used in the respective studies. The references to each symbol: ★, ■– this work; □ [3]; × [4]; ▲ [5]; ∗,▼ [6]; ◁, ● [14]; ⊕ [16]; | [17]; ○ [18]; +, ▽ [19]; ♦ [20].

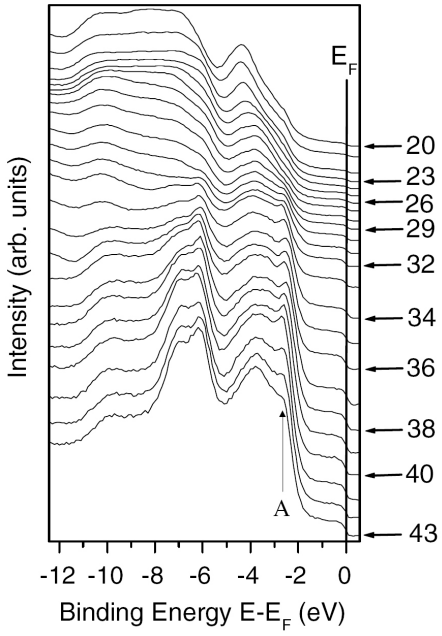

Figure 4. Energy dependent photoemission of Alq_3 adsorbed on gold. The right side denotes the incident photon energies. Notice the photoemission cross section changes and dispersion directions as the photon energy is swept. All spectra were taken by p polarization.

With the deposition of Alq_3 on gold, the thin adlayers of Alq_3 are periodic in the direction normal to the surface. As observed in Figure 4, the photoemission features due to the Alq_3 highest occupied electronic state at −2.7 eV and at least two other Alq_3 photoemission features at −6.1 and −7.0 eV binding energy ($h\nu$ = 43 eV) exhibit little dispersion, while the photoemission features due to the Alq_3 molecular orbitals at −3.7 and −9.8 eV binding energy ($h\nu$ = 43 eV) exhibit significant photon energy dependence. These changing binding energies with photon energy occur over small values of $k_\perp$ consistent with the fact that Alq_3 is a larger molecule compared to most molecular adsorbates with molecular orbital wave vector dependence.

3. Conclusion

We have investigated the occupied electronic structure of Alq_3 adsorbed on epitaxial Au/Si(1 1 1) and polycrystalline cobalt. The light polarization dependent photoemission indicates the presence of the *facial* isomer of Alq_3. The suppression of highly lying occupied Alq_3states adsorbed on Co is consistent with the large resistance values [2] for Alq_3 on Co. The relative binding energy positions of the highest occupied electronic state, as compared in Figure 3, cannot be easily explained by charge transfer or the work function of the metals; rather it is the interface conditions which ultimately dictate the binding energy positions. Issues pertaining to charge injection into the molecular film will undoubtedly be affected by both the deposition method, which dictates the physical structure of the molecular film, as well as the complications that arise from the substrate dependent hybridization.

Overall, the molecular orbital structure of Alq_3 [16] is far from complete unless the influence of the substrate is considered. In this regard Kahn and coworkers [3, 6] are correct that the details of the interface matter. The results presented here indicate that interface states are partly the result of the changes in the configuration and geometry of the Alq_3 molecules caused by substrate interaction that, in turn, induce intramolecular iminate or enolate bonding rather than by the substrate to molecule interaction alone [6]. Arguments involving band bending are difficult to invoke in a system where the molecular configuration and intramolecular bonding configuration changes so dramatically at an interface. The intermolecular interactions, by comparison, are likely quite weak so that a rigid band model seems more likely to be applicable (except at the interface). States that have been interpreted as interface states are shown by photon energy dependent photoemission to be attributable to Alq_3 alone and disperse normal to the surface for a crystalline Alq_3 thin film grown on Au. In spite of the agreement of the results here with Curioni et al. [13], the role of Al in the molecular orbitals is quite significant and the Al–ligand bond can contribute significantly to the highest occupied molecular orbitals; a result not directly suggest by Curioni and coworkers [11, 13]. We may summarize by noting that the aluminum seems to play a very small role in intermolecular bonding but a large, although indirect role in intramolecular bonding induced by the metal substrate.

Acknowledgments

This work was supported by the National Science Foundation through Grant CHE-0415421 and the NSF "QSPINS" MRSEC (DMR-0213808), the Defense Microelectronics Activity (DMEA) under agreement CMEA90-02-2-0218 and the NSF through ND EPSCoR Grant EPS-0447679. The authors also wish to thank the Center for Advanced Microstructures and Devices, which is funded by the State of Louisiana. The authors also wish to thank Yaroslav Losovyj and Rob Sailer for the help with experimental setup.

References

1. C.W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.* **51** (1987), p. 913.
2. Z.H. Xiong, Di Wu, Z. Valy Vardeny and Jing Shi, *Nature* **427** (2004), p. 821.
3. A. Rajagopal, C.I. Wu and A. Kahn, *J. Appl. Phys.* **83** (1998), p. 2649.
4. S.C. Kim, S.N. Kwon, M.-W. Choi, C.N. Whang, K. Jeong, S.H. Lee, J.-G. Lee and S. Kim, *Appl. Phys. Lett.* **79** (2001), p. 3726.
5. A. Rajagopal and A. Kahn, *J. Appl. Phys.* **84** (1998), p. 355.
6. C. Shen, A. Kahn and J. Schwartz, *J. Appl. Phys.* **89** (2001), p. 449.
7. M. Braun, J. Gmeiner, M. Tzolov, M. Cölle, O. Wendland, F.D. Meyer, W. Milius, H. Hillebrecht, J.U. Schütz and W. Brütting, *J. Chem. Phys.* **114** (2001), p. 9625.
8. P.A. Dowben, D. LaGraffe and M. Onellion, *J. Phys.: Condens. Matter.* **1** (1989), p. 6571.
9. E.W. Plummer and W. Eberhardt, *Adv. Chem. Phys.* **49** (1982), p. 533.
10. M. Cölle, R.E. Dinnebier and W. Brütting, *Chem. Commun.* (2002), p. 2908.
11. A. Curioni, M. Boero and W. Andreoni, *Chem. Phys. Lett.* **294** (1998), p. 263.
12. M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi and A. Sironi, *J. Am. Chem. Soc.* **122** (2000), p. 5147.
13. A. Curioni, W. Andreoni, R. Treusch, F.J. Himpsel, E. Haskal, P. Seidler, C. Heske, S. Kakar and L.J. Terminello, *Appl. Phys. Lett.* **72** (1998), p. 1575.
14. S.T. Lee, X.Y. Hou, M.G. Mason and C.W. Tang, *Appl. Phys. Lett.* **72** (1998), p. 1593.
15. C. Shen and A. Kahn, *Org. Electron.* **2** (2001), pp. 89–95.
16. L.S. Liao, X.H. Sun, L.F. Cheng, N.B. Wong, C.S. Lee and S.T. Lee, *Chem. Phys. Lett.* **333** (2001), p. 212.
17. K. Sugiyama, D. Yoshimura, T. Miyamae, T. Miyazaki, H. Ishii, Y. Ouchi and K. Seki, *J. Appl. Phys.* **83** (1998), p. 4928.
18. I.G. Hill, A. Kahn, J. Cornil, D.A. dos Santos and J.L. Brédas, *Chem. Phys. Lett.* **317** (2000), p. 444.
19. S.N. Kwon, S.C. Kim, Y. Kim, J.-G. Lee, S. Kim and K. Jeong, *Appl. Phys. Lett.* **79** (2001), p. 4595.
20. A. Schmidt, M.L. Anderson and N.R. Armstrong, *J. Appl. Phys.* **78** (1995), p. 5619.