Electronic Properties of Structures Containing Films of Alq₃ and LiBr Deposited on Si(111) Crystal

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The electronic structures of Alq₃/Si(111) and Alq₃/LiBr/Si(111) interfaces are presented in this report. The studies were carried out *in situ* in ultrahigh vacuum by ultraviolet photoelectron spectroscopy. Alq₃ and LiBr layers were vapour deposited onto a single crystal of *n*-type Si(111). The energy level diagrams were prepared for the structures. The formation of the LiBr interfacial layer results in a decrease of the energy barrier at the interface.

1. Introduction

There has been much interest in organic semiconductors for use in electronic devices in recent years. It started in 1987 with the first report of electroluminescence from tris (8-hydroxyquinoline) aluminium (Alq₃) [1]. Extensive work on the organic thin films yielded a rapid expansion of light-emitting diodes (OLEDs), field-effect transistors (OFETs) and photovoltaics (OPVs). These organic semiconductor (OS) devices are efficient and require a relatively smaller amount of power compared to traditional devices, furthermore OLEDs have great properties such as fast response speed and very good colour performance. Much research has been carried out in the exploration of new materials which are used for OS devices to improve their performance [2, 3]. Nevertheless, the semiconducting monomer Alq₃ (Al(C₉H₆NO)₃) with the band gap (i.e. the difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels) in the gas phase equal to 2.7 eV [4], has been widely and continuously used as a light-emitting and/or electron-transporting material in such technology. Properties of all OS devices depend on charge injection at the electrode/organic junction and in this context lowering the energy barrier at the interface is important in facilitating efficient charge injection through the interface. The influence of insertion of an interfacial layer of alkali metals halides such as LiF, NaF, MgF₂ have been studied to improve the electron injection but in general the layers were deposited on metal electrodes [5–7]. Semiconductors, like e.g. silicon crystals, can also be used as an electrode material for OS devices as was reported in paper [8]. Despite the fact that the Alq₃/inorganic semiconductor interfaces are of great importance for potential application in OS devices, there has been a deficit of research on such interfaces published thus far.

Herein we present the results of electronic structure studies of the system of organic semiconductor Alq₃ on silicon crystals Si(111) with and without the interfacial layer of LiBr.

2. Experimental details

Silicon samples, $15 \times 10 \times 0.3$ cm³ in size, cut from single crystal wafers of *n*-type Si(111), were used for the experiments. The substrate was chemically cleaned using standard procedures and mounted by Mo strips on the holder, and placed into the ultrahigh vacuum (UHV) chamber with the base pressure $\leq 1 \times 10^{-10}$ Torr. Cleaning inside the UHV was done using heating by a direct current. Chemical cleanliness of the substrates was checked by a LEED-Auger camera of RFA type. After the preparation, the Si(111)-(7 × 7) structure was obtained and used as an output surface in further photoelectron experiments. The investigated structures — Alq₃/Si(111) and Alq₃/LiBr/Si(111) — were obtained *in situ* by the evaporation of the Alq₃ and LiBr from a heated quartz crucible. The Alq₃ layers were grown gradually; the thickness of one deposited layer was 10 Å. The coverage and the evaporation rate were controlled by means of quartz-crystal resonator. The shapes of the valence bands at the interfaces were determined from UV photoelectron spectroscopy (UPS). The photoemission experiments were performed using the He(I) line (21.2 eV) as a radiation source from a DC discharged lamp with two-stage differential pumping which allows the chamber to remain under UHV condition whilst the lamp is operating. Photoelectrons were collected with an electrostatic Hughes–Rojansky type electron energy analyser with energy resolution equal to about 50 meV. The detector acceptance angle was about 25° relative to the optical axis of the analyser entrance which was normal to the substrate surface. The measurements were carried out with –5 V applied to the samples to clear the detector work function. The position of the Fermi level ($E_{\rm F}$) was determined using a clean referential polycrystalline silver sample. Measurements for each coverage of Alq₃ were performed on a freshly evaporated

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layer to reduce the exposure time to the residual gas. All investigations were done at room temperature.

3. Results and discussion

The photoelectron spectrum of the valence band for the clean Si(111) surface and its evolution with Alq$_3$ overlayer thickness is shown in Fig. 1. The position of the valence band maximum (VBM) for clean silicon crystal is found to be 0.7 eV below E_F. Deposition of Alq$_3$ layers caused modifications in the electron energy distribution recorded by UPS. Significant changes in the valence band occur in the low binding energy parts, for Alq$_3$ layers 30 Å thick. We can see the formation of an additional peak which is assigned to the highest occupied molecular orbital of Alq$_3$. The HOMO level is 2.2 eV below E_F and was found from linear extrapolation of the leading edge of the peak to the background. Its position stays unchanged for thicker layers. The differences in the spectrum also occur in the cut-off energy which results in changes in the work function (WF) as shown in the inset in Fig. 1. The major changes are for Alq$_3$ layers up to 50 Å thick, where the WF decreases from 4.8 eV to 3.8 eV and remains roughly the same for thicker layers. Combining all spectral changes the energy level diagram for the Alq$_3$/Si(111) interface was elaborated and is shown in Fig. 2.
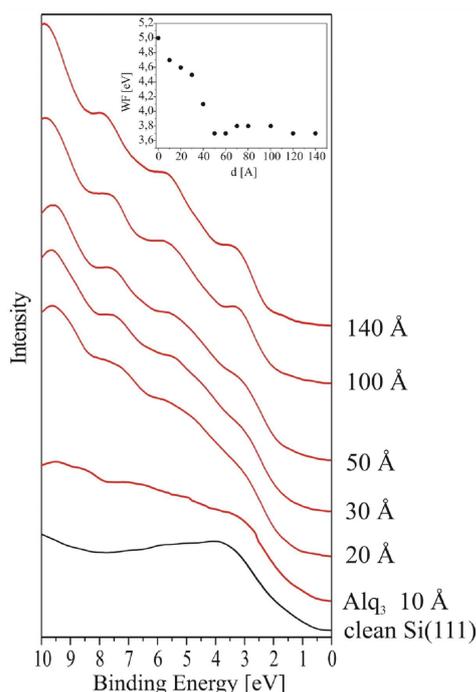
Fig. 2. The energy level diagram of the Alq$_3$/Si(111) interface.

Fig. 1. UPS spectra of the valence band for the clean Si(111) surface and covered with Alq$_3$ overlayer of different thickness. The inset shows changes in the WF as a function of the overlayer thickness.

We can see that the electron affinity for the substrate is 4.4 eV, the HOMO level is 1.5 eV below the VBM for Si(111). Then taking into account the value of the
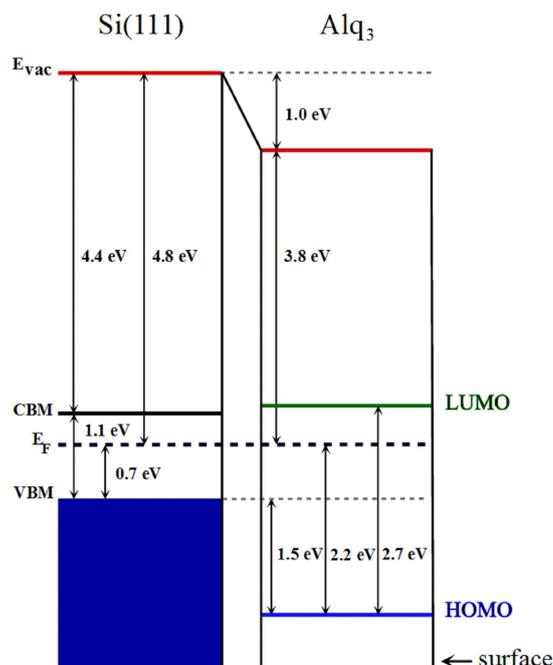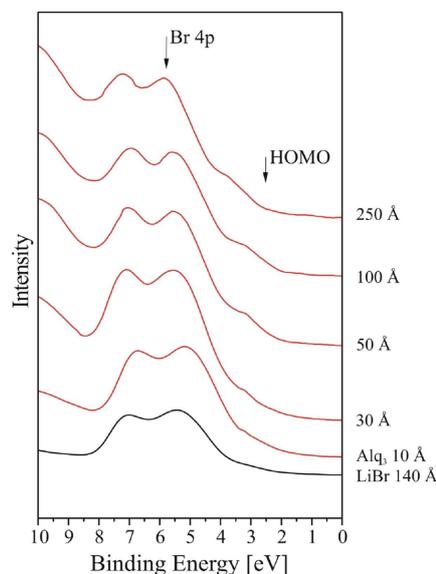
Fig. 3. UPS spectra of the valence band for the LiBr/Si(111) interface and covered with Alq$_3$ overlayer of different thickness. The LiBr interfacial layer is 140 Å thick.

band gap of Alq$_3$ for the molecule in the gas phase we can consider that the position of the LUMO is 1.2 eV above the VBM and 0.5 eV above E_F. Note that vacuum level (E_{vac}) for the Alq$_3$/Si(111) interface decreases about 1.0 eV relative to the value of the E_{vac} for clean Si(111) surface.

To check the influence of insertion of an interfacial layer of LiBr on the position of the Alq$_3$ LUMO level relative to VBM of the substrate first the LiBr/Si(111) structure was formed, where the thickness of the LiBr layer was

140 Å. This was the minimum layer thickness for which the UPS spectrum remains unchanged with further growth of LiBr. The spectrum of the valence band for the LiBr/Si(111) structure and its evolution with Alq$_3$ overlayer thickness is shown in Fig. 3. The obtained spectra vary mainly in the low binding energy parts, whereas their cut-off energy remains unchanged.
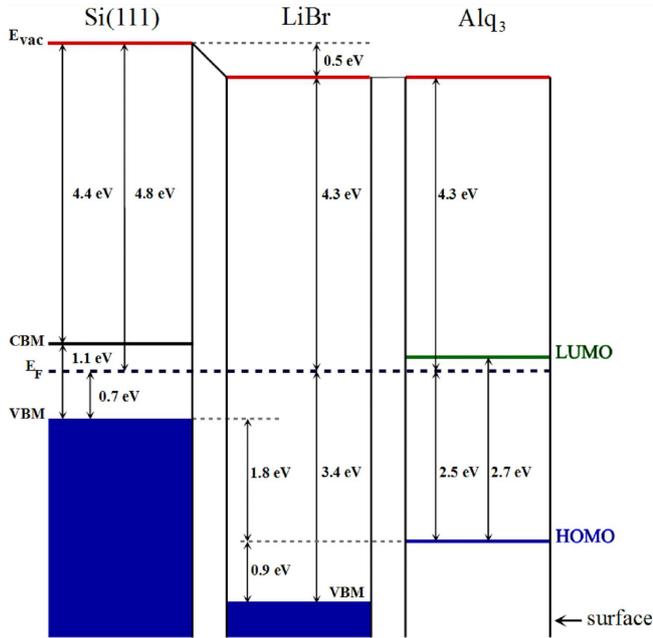

Fig. 4. The energy level diagram of the Alq$_3$/LiBr/Si(111) structure.

On the spectrum the prominent peak emerges at about 5.0 eV which comes from the doublet Br $4p$ line. This line is presented even for high coverage of Alq$_3$ (up to 250 Å thick), which indicates that Alq$_3$ grows in a 3D mode forming grains. The HOMO level appears in the UPS curves for Alq$_3$ layers of thickness above 40 Å at 2.2 eV below E_F and during further deposition shifts to the position of 2.5 eV. Upon analyzing the USP results the energy level diagram for the Alq$_3$/LiBr/Si(111) structure was prepared as shown in Fig. 4. The VBM of LiBr is located 2.7 eV below the upper edge of the valence band for clean Si(111). The offset between the VBM of Si(111) and the HOMO level is 1.8 eV. The HOMO level shifted toward to the high binding energy resulting a position of the LUMO of 0.9 eV above the VBM of Si(111) and only 0.2 eV above E_F, which is a very good result. The vacuum level after deposition of LiBr 140 Å thick decreases by about 0.5 eV comparing to the E_{vac} of Si(111) and stays the same after deposition of Alq$_3$.

Comparing the data of the electronic structure diagrams for Alq$_3$/Si(111) (Fig. 2) and Alq$_3$/LiBr/Si(111) (Fig. 4), the application of the interfacial layer of LiBr between the substrate and the molecular layers reduced the height of the energy barrier between the VBM of Si and the LUMO level from 1.2 eV to 0.9 eV.

4. Conclusions

UPS was used to investigate electrical properties of the Alq$_3$/Si(111) and Alq$_3$/LiBr/Si(111) interfaces. The electron affinity of the clean Si(111) surface was found to be 4.4 eV and the position of the VBM was 0.7 eV below E_F. The offsets between the VBM of Si(111) and the HOMO level are 1.8 eV and 1.5 eV for the interface with and without the interfacial layer of LiBr, respectively. The WFs for both structures decrease about 1.0 eV and 0.5 eV for Alq$_3$/Si(111) and Alq$_3$/LiBr/Si(111), respectively.

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