Dissociation of sexithiophene on Al(111) surface

J. Ivanco a,b,*, F.P. Netzer a, M.G. Ramsey a

a Institute of Physics, Surface and Interface Physics, Karl-Franzens University Graz, Universitätsplatz 5, A-8010 Graz, Austria
b Institute of Physics, Slovak Academy of Sciences, Vrbovská cesta 102, SK-921 01 Piešťany, Slovakia

Received 23 September 2006; received in revised form 28 March 2007; accepted 29 March 2007

Abstract

The growth of sexithiophene ultra-thin films on an atomically clean Al(111) surface has been investigated by angle-resolved ultraviolet photoemission spectroscopy. Although sexithiophene on Al(111) represents a weakly interacting system, sexithiophene molecules were found to dissociate even below room temperature, presumably via reactive sites. The mechanism is distinctly different to that claimed on the reverse system, i.e. aluminum evaporated on thiophene oligomers films, where isolated aluminum atoms were reported to covalently bond to thiophene rings and thus dramatically affect the molecule geometry and the conjugation. The effect of the insertion of an ultra-thin separator film of sexiphenyl, on the dissociation of sexithiophene was also examined.

© 2007 Elsevier B.V. All rights reserved.
PACS: 81.05.Hd; 79.60.–i; 68.43.–h; 73.30.+y

Keywords: Organic semiconductors; Oligothiophenes; Metal–organic interfaces; Heterojunctions; Ultraviolet photoelectron spectroscopy; Work function

1. Introduction

The performance of molecular devices relies on both bulk properties of conjugated organic films and their interfaces with a contacting material. In particular, understanding and controlling the interfaces represents an ongoing challenge to realizing the full potential of organic electronics. The sequence of the contact formation is relevant: organics-on-contact material and contact material-on-organics usually represent different problems. The former approach is mostly adopted in structural and morphological studies of molecular films employing the substrate in the role of a growth template, while the latter one focuses on a stable planar metal contact formation on the top of an organic film. Junction characteristics of a particular organic film and metal are not yet predictable from the nature of the metal. The interaction at the interface, which is specific for every system, dramatically affects the interfacial electronic structure and therefore understanding this interaction is crucial for the control of transport properties/charge injection of contacts.

Both pioneering [1] and recent [2] attempts to employ sexithiophene and polythiophene thin films,
respectively, as active layers in organic field-effect transistors justify the ongoing studies on these relevant systems. Since aluminum is among the most common contact metallizations, several theoretical [3–6] and experimental studies [7–9] on the formation of aluminum layers on thiophene oligomers films have been reported. Theoretical investigations on the reaction of aluminum with terthiophene indicate that aluminum atoms covalently bond to the α-carbons of thiophene monomers and thus form complexes. The reaction, which presumes the supply of isolated aluminum atoms, heavily distorts the molecular geometrical structure and thus disrupts its π conjugation. In contrast, vibrational [10], valence band photoemission and desorption [11,12] studies on (bi)thiophene films condensed at liquid nitrogen temperature on Al(111) surface suggested a weakly interacting system where the covalent bonding between thiophene and aluminum can be excluded. These results lead to the question of whether the isolated Al atoms are per se more reactive to the thiophenes than those at the surface of the bulk metal.

In this work, we present examinations on sexithiophene films grown at different temperatures on the Al(111) surface. It is shown that the conjugation of a sexithiophene molecule deposited at liquid nitrogen temperature distorts upon warming-up to room temperature in spite of the absence of isolated aluminum atoms. The effect of the insertion of a molecular spacer layer between the 6T and Al(111), an ultra-thin film of sexiphenyl (6P), will be illustrated and discussed.

2. Experimental

The film growth and photoemission characterization were carried out in situ in a UHV VG-ADES 400 angle resolving ultraviolet photoemission spectrometer (ARUPS) with a base pressure less than 10\(^{-10}\) mbar. The samples could be cooled down to liquid nitrogen temperature (LNT, about 90 K) and resistively heated. The movable hemispherical analyser enables the variation of the electron take-off angle with respect to surface normal and to the photon incident angle of an unpolarized HeI (21.2 eV) radiation. A resolution of 80 meV as measured via the Fermi edge width (in the intensity range from 10% to 90%) of the clean Al(111) at LNT has been employed. Work functions were measured using the secondary electron cut-off of spectra in normal emission with the sample biased by −9 V.

The system was also equipped with facilities for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES).

The Al(111) single crystals was cleaned by cycles of sputtering with 1 keV Ar\(^+\) ions at room temperature (RT) followed by annealing for 5 min at about 700 K. Both the surface order and cleanliness were checked before applying the molecules by LEED and UPS, respectively; both a sharp LEED pattern and a featureless valence band, the latter being otherwise extremely sensitive to the surface contamination, classified the Al(111) surface for interface studies.

Sexithiophene (Syncom, B.V.) and sexiphenyl (Tokyo Chemical Industry Co., Ltd.) are unsubstituted π-conjugated oligomers of benzene and thiophene, respectively, build up by six aromatic rings joined together in para positions (Fig. 1). Both were deposited from a thoroughly outgassed specially designed evaporator such that the pressure in the system remained in the low 10\(^{-10}\) mbar range during the film growth. The exposures were monitored by a water-cooled quartz microbalance and are given in terms of nominal thickness using the 6T and 6P density of 1.55 g/cm\(^3\) [13] and 1.29 g/cm\(^3\) [14]. The typical growth rates used were 1.5 ± 0.5 Å/min. It is worth noting that a thickness of ~3–4 Å and ~25 Å would correspond to complete monolayers (ML) formed by molecules either lying parallel (flat-on) or perpendicular (“end-on”) to the substrate, respectively.

3. Results

3.1. The 6T/Al(111) interface

Fig. 2 shows the evolution of photoemission spectra of the clean Al(111) surface upon increasing coverage of 6T grown at LNT. The valence band of the 6T qualitatively corresponds to spectra reported previously [15–17]. Particularly for small coverages,
the spectra are strongly angular dependent, which is apparent on the well-resolved π band. Both the photoemission intensity evolution with the coverage and the angular dependence suggest that the 6T molecules are lying down [18]. While the Fermi edge is still visible for the 24 Å-thick film, it is not observed anymore for the 66 Å-thick film. This indicates islands on monolayers (Stranski–Krastanov) molecular film growth at LNT.

The π stabilization, i.e. the differential shift of molecular π orbitals induced by the interaction between molecules and the substrate surface, is a measure of the molecule-substrate bond strength. Apart from being somewhat better resolved, the spectra of the lying monolayer at LNT are identical to those of the thick multilayer films both in terms of orbital energy position and angular effects in the orbital emissions. This indicates that the screening from the substrate and intermolecular screening are similar, which in turn indicates a weak bonding to the substrate. In other words, there is no evidence for any strong covalent bond or charge transfer from the substrate.

Fig. 3 illustrates the work function evolution with the 6T coverage of films grown at LNT (full circles). The work function drops abruptly with the 6T thickness up to about 6 Å and remains near constant upon further deposition. Such dependence is typical for the layer-by-layer (Frank-Van der Merwe) and Stranski–Krastanov molecular film growth, where the work function of the substrate drops near linearly up to the coverage corresponding
to 1–2 ML due to an interfacial dipole formation, and it does not change with further coverage. The work function decrease of about 0.4 eV corresponds to the interfacial dipole similar to that observed for thiophene and bithiophene on Al(111) [11]. Parenthetically we note that aluminum is not a low work function metal, as it is sometimes regarded [5,7,8,19]. Its work function of about 4.2 eV for Al(111) falls rather in the “middle” range of metal work functions. However, the work function of aluminum is very sensitive to the amount of the chemisorbed oxygen with a total drop for the oxygen-saturated surface by more than 1 eV. A low work function of aluminum would indicate surface contamination (its partial oxidation), which will considerably modify its reactivity [20,21].

The 6T has been found to be stable on other studied surfaces like SiOx [17], TiO2(110) [18], Cu(110), and Cu(110)–(2 x 1)O [22], whether grown at RT or elevated temperatures up to 400 K. In contrast, the RT-grown sexithiophene films on Al(111) displayed a progressive degradation within several tens of minutes. The same effect – particularly manifested in the smearing-out of the upper π band and an increase in the background – occurs upon overnight warming-up of the LNT-grown sexithiophene films. This is illustrated in Fig. 4, where the valence band of the clean Al(111) surface taken at a take-off angle of 50° (curve a), the LNT-growth of 13 Å-thick sexithiophene film recorded at normal emission (curve b), and with a take-off angle of 50° (curve c), and after warming-up to RT (curve d) are shown. Note that the spectra are referenced to the vacuum level by adjusting to the work functions of the respective films, and thus the HOMO position of about 5.8 eV gives the ionization potential of the sexithiophene thin film. The 6T film warmed-up to RT does not display any dependence on the take-off angle. Notably, the spectra of the 6T films kept at RT in UHV on Al(111) progressively degraded over several days till the π-band signature was eliminated. This was particularly manifested in the disappearance of the HOMO, -1, and -2 orbitals, which have their principle weight on the π-carbons of the molecule [16]. The thicker films (66 Å) showed virtually the same degradation of the valence band upon warming-up to RT; moreover the Fermi edge, entirely eliminated at LNT, reappeared suggesting the formation of islands.

The work function returns almost to the original substrate work function upon overnight warming-up to RT as indicated by empty circles in Fig. 3.

Fig. 4. Photoemission spectra of clean Al(111) measured at a take-off angle of 50° (curve a), and after the growth of 13 Å of 6T at LNT taken at normal emission (curve b) and take-off angle of 50° (curve c), and after warming-up to RT at take-off angle of 50° (curve d). The spectra are referenced to the vacuum level. Positions of Fermi edges for particular spectra are indicated. The highest individual π orbitals HOMO, HOMO-1, and HOMO-2 are labeled 0, 1, and 2, respectively. The nonbonding π orbitals are labeled A.

Apparently, the increase of the work function is not due to dewetting of the Al(111) surface since the integral intensity of the valence band of the 6T does not change much, i.e. it corresponds to 1–2 monolayer coverage. It rather reflects the change of the interfacial dipole due to the dissociation of the 6T molecule at the interface. The change of the interfacial dipole is evidenced by the fact that work function change on warming to RT (0.3–0.4 eV) is also reflected in the same shift of the whole 6T spectrum with respect to the Fermi level (Fig. 4).

The 6T degradation is not due to a radiation damage induced by the photoemission measurement itself, since no degradation was observed in films exposed to the HeI irradiation over the course of many hours at LNT. In contrast, a degradation of 6T films grown at Al(111) at RT was apparent after tens of minutes whether irradiated by HeI or not (the UPS characterization lasted only several minutes). The gradual changes in the work function upon warming-up were observed to commence...
already above \( \sim 160 \text{K} \) with concomitant degradation of the photoemission spectra. The 6T degradation is neither due to a contamination; the 6T films prepared on other surfaces (SiO\(_2\)[17], TiO\(_2\)(110) [18], and Cu(110)) under the same conditions and in the identical UHV system were stable.

3.2. The 6T/6P/Al(111) interface

A possible way to avoid the dissociation of 6T molecules could be the insertion of a stable ultra-thin organic spacer layer between the 6T and Al(111) to prevent their intimate contact. We have employed sexiphenyl (6P) as a separator since the 6P/Al(111) interface is stable up to at least 430 \text{K} [23–25], 6P forms a stable dense ordered monolayer on Al(111) [23,25], and the interfacial dipole on Al(111), i.e. the Al(111) work function change (Fig. 3, squares) [24], is comparable to that of the 6T on Al(111).

Fig. 5 shows the valence band evolution during the Al(111) + 6P + 6T heterostructure formation. The spectra were collected at a take-off angle of 50\(^\circ\), where the particular HOMOs are well pronounced. Nominal coverages of both 6P and 6T correspond to about two and three monolayers of lying molecules, respectively, and given the evolution of the photoemission intensity, the growth proceeds by layerwise fashion. Note that the Al(111) surface is fully covered by 6P (~2 ML) and the work function is saturated, i.e. no work function change is expected upon further deposition of molecules. This is actually what is observed upon addition of 9.5 Å of 6T (see the inset in Fig. 5). That 6T on 6P does not lead to any additional work function change indicates the absence of a dipole at the organic/organic (6P/6T) interface. Addition of 6T onto 6P has replaced the 6P valence band spectrum by the 6T one indicating the laminar growth. Although of similar shape and bandwidth, the \( \pi \) bands do not coincide because the ionization potential of the 6T is lower by about 0.6 \text{eV} compared to that of the 6P [26,27]. As a result, the addition of 6T onto 6P shifts the HOMO of the system by about 0.7 \text{eV}. Besides the \( \pi \) band, the fingerprints of the 6T are clearly distinguishable also in the bands labeled \( B, C, \) and \( D. \)

Upon warming-up to RT (the top spectrum in Fig. 5), features related to 6T strongly diminish and the spectrum resembles more that of the 6P layer (this is best distinguished via comparison of the bands \( C, D, \) and to some extent of the \( \pi \) band) combined with the spectrum of remnants of the 6T (compare to curve \( d \) in Fig. 4). We note that the 6T features vanish completely for the same heterostructure formed by single 6P and 6T monolayers. The disappearance of 6T-related features of the Al + 6P + 6T heterostructure could be the result of islanding of the 6T on the 6P – this is suggested by the reappearance of the Fermi edge. However, if the 6T islanding was uniquely responsible, the work function would remain rather constant since it should correspond to the work function of the 6P spacer layer, which is itself stable on the Al(111) [23–25]. Yet, as it is shown in the inset of Fig. 5, the work function increases similarly to that of the single 6T film on Al(111) (Fig. 3). This suggests that the interfacial dipole is modified in the same way as if the 6T were in intimate contact with Al(111). Here, the work function change also corresponds to the shift of the spectrum (Fig. 5). We therefore, believe that the separator made of 6P apparently does not prevent the dissociation of the 6T molecules; the heterostructure becomes unstable.
at RT in that the layer-by-layer morphology breaks down exposing the Al interface to the upper 6T layer while 6P presumably forms islands on the 6T film. The latter is deduced from the facts that 6P intensity becomes smaller in comparison with intensity of the pristine 6P film grown directly on the Al(111) surface and the 6T-related features were not eliminated completely.

4. Discussion

The studies on the reaction between aluminum and thiophene-based films performed on the reverse system (Al evaporated onto the organic film) in reality deal with the reaction between isolated Al atoms and individual molecules [3–9]. During the thermal deposition of aluminum, the temperature of the impinging aluminum atoms might be argued to enhance their reaction with the organic film, thus inducing the formation of Al/thiol complexes. Here, such kinetics-promoted effects are eliminated by measuring upon warming-up of the LNT-grown 6T on the Al(111).

It should be noted that the argon ion sputtering of the Al(111) surface at RT produces adatoms and vacancy clusters and induces the growth of adatom islands [28]. However, the adatom coverage becomes negligible after the annealing at 700 K [29], the temperature applied for the surface preparation here. Thus, the Al(111) surface employed in this study can be considered being free of isolated Al adatoms.

6T molecules have been observed to fragment spontaneously at RT on Si(100)–2×1 surfaces [30] and we suggest a similar process occurs on the Al(111) surface. Here, fragmentation is supported by two facts: firstly, the antibonding orbitals HOMO, -1, and -2 (labeled 0, 1, and 2, respectively, in Fig. 4), which are the result of the interaction between six monomer units, gradually vanish, while, secondly, the nonbonding orbitals (labeled A in Fig. 4), which are independent of the number of thiophene units [15], remain without significant variation of either energy or intensity. This suggests that the conjugation has been destroyed. If the 6T molecules were dissociated into thiophene and bithiophene oligomers, these would be absent at RT as both molecules are reported to adsorb molecularly and desorb intact from Al(111) at 156 and 255 K, respectively [11]. In contrast, in this study the break-up products appear to remain on the Al(111) surface: this is indicated by the carbon and sulfur that were observed by AES even after the annealing up to 700 K (both the amount and element ratio corresponding to about one 6T monolayer coverage).

The observed variations of the electronic properties of sexithiophene molecules on the atomically clean Al(111) surface suggest that a realistic 6T/Al(111) interface is thermodynamically unstable. It is important to remember that the 6T molecular film at RT dissociates gradually over a period of tens of minutes although the film thickness is only 1–2 monolayers, with most of molecules in intimate contact with the Al(111) surface. A flash of such a thin LNT-grown film to RT (the entire cycle, i.e. the warming-up to RT and cooling down to LNT, lasted about 10 min) has not affected the work function within the experimental accuracy of 0.1 eV and resulted only in a marginal deterioration of the 6T valence band. Thus, the activation energy of the dissociation plays a minor role and a further rate-limited reaction parameter, strongly dependent on the temperature, must be involved. The following mechanism can be proposed: The Al(111) surface is unreactive to 6T except for a fractional area acting as reactive sites, e.g. step edges, kinks or other defect sites, which facilitate the dissociation of molecules. For a particular catalytic system, the dissociation rate is determined by the concentration of active sites and the arrival rate, i.e. the diffusion constant of a molecule. If the former is very low, the latter becomes the limiting factor for the molecule dissociation. The mechanism is similar to that proposed for a weakly interacting system such as the 6T on H-passivated Si(100)–(2×1) surface, where STM examinations indicate highly mobile 6T molecules diffusing at RT over surface till they are captured by reactive defect sites [30]. In our case, the 6T molecules, which are deposited at LNT directly on the reactive sites may dissociate on a very short time scale, these however only represent a small fraction of the population, and are thus not observable by the area-averaging photoemission technique.

In terms of the interaction, the model is consistent with the weakly interacting (bithiophene/Al(111)) systems, where no break-up products were reported [11] in spite of the relatively high desorption temperature of bithiophene of 255 K. This can be explained by the high warming-up rate employed in desorption studies. In other words, the bithiophene molecules desorb before they reach a reactive surface site for dissociation.

Please cite this article in press as: J. Ivanco et al., Dissociation of sexithiophene on Al(111) surface, Org. Electr. (2007), doi:10.1016/j.orgel.2007.03.011
5. Conclusions

Sexithiophene films grown on the Al(111) at LNT and RT have been characterized by ultraviolet photoemission spectroscopy. While the 6T films grown at LNT were stable and no strong chemical bonds at the interface were detected, the 6T films grown at RT gradually deteriorated up to a point where their conjugation was eventually lost. Given the very slow degradation of the ultra-thin films and an absence of isolated aluminum atoms, it has been concluded that the dissociation of the 6T occurs on reactive surface sites attainable via the diffusion of the molecules. The origin of the reactive sites has not been investigated here, yet the reaction mechanism, which leads to the dissociation of sexithiophene molecules on the atomically clean Al(111) surface, is distinct from the mechanism claimed for reverse systems (i.e., aluminum-on-thiophene oligomers film). Further, the insertion of an ultra-thin sexiphenyl layer between the sexithiophene layer and Al(111) does not prevent the dissociation of the 6T molecules, because the heterostructure is morphologically unstable at room temperature.

Acknowledgements

This work was supported by the Austrian Science Foundation (FWF). Gratitude is also expressed to A. Fleming for his careful readings of the manuscript.

References