Energetic disorder impacts energy-level alignment of alpha-sexithiophene on hydrogen-terminated silicon and silicon oxide

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Abstract
The energy-level alignment at hybrid organic-inorganic interfaces is decisive for the performance of (opto-)electronic devices. We use ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) to measure the energy-level alignment of vacuum-sublimed α-sexithiophene (6 T) thin films with HF-etched n-type Si(100) and with Si with a native oxide layer (SiO$_2$). The 6 T thin films induce a small (≤0.1 eV) downwards band bending into both substrates as shown by XPS. The well-ordered growth of 6 T on Si leads to a relatively narrow density of states (DOS) distribution of the highest occupied molecular orbital (HOMO) as shown by UPS. Furthermore, the Fermi-level comes to lie at rather mid-gap position and, consequently, no energy-level bending occurs in the 6 T layer. Structural disorder in the 6 T thin film on SiO$_2$ leads to a broad HOMO DOS distribution and to tailing states into the energy gap. Consequently, downwards energy-level bending (by around 0.20 eV) takes place in the 6 T layer.

Introduction
The energy-level alignment (ELA) at the ubiquitous interfaces of (opto-)electronic applications is decisive for device performance [1–3]. Actually, hybrid organic-inorganic interfaces can add functionality to devices, e.g., they can serve as charge-carrier selective contacts for photovoltaic cells [4, 5] and thin layers of organic semiconductors (OSCs) can tune ELA at such interfaces [6]. The ELA between inorganic semiconductors like Si and OSCs can be rather complex, e.g., for rodlike organic semiconductors like pentacene or tetracene the orientation of the long molecular axis with respect to the surface (‘standing’ or ‘lying’ molecules) is decisive for ELA [7, 8]. In the absence of chemical interaction, ELA is mainly determined by the substrate work function (WF) and the ionization energy (IE) and electron affinity (EA) of the OSC thin film [3, 5]. In addition to these quantities also the width of the density of states (DOS) of the frontier molecular orbitals (highest occupied molecular orbital, HOMO and lowest unoccupied molecular orbital, LUMO) of the OSC thin film plays an important role for ELA, in particular, if Fermi-level pinning is involved [9, 10]. IEs of organic thin films and ELA at organic-inorganic interfaces can be experimentally accessed by ultraviolet photoelectron spectroscopy (UPS) [7, 11, 12]. Furthermore, UPS can be used to access structural properties of organic thin films [13]: Disorder leads to a broadening of HOMO-derived photoemission intensity [14, 15] and the IE differs by around 0.5 eV for thin films of most rodlike molecules in a lying and a standing orientation [16, 17]. Band bending in the inorganic semiconductor can be tracked by core-level shifts, which can be measured by x-ray photoelectron spectroscopy (XPS) [18, 19].

The organic semiconductor α-sexithiophene (6 T) has been frequently used for organic-field effect transistors (OFETs) [20, 21] and, more recently, it is used for spinterfaces [22], as model system for molecular electrical doping [23] and in organic photovoltaic (OPV) devices [24]. Strikingly, taking advantage of the orientation-dependent IE of 6 T thin films [16] even OPVs without a donor-acceptor interface could be
facilitated [25]. Furthermore, evaporated 6 T thin films are well-known for pronounced polymorphism [20] and for their aggregation-dependent optical properties [26]. The transport gap of 6 T multilayer thin films (as determined by the combination of UPS and inverse photoemission) is 2.8 eV [27] and the IEs range from 4.7 eV for standing 6 T to 5.4 eV for lying 6 T as determined by UPS [16, 27, 28] and by photoelectron yield spectroscopy [25]. On inert substrates like SiOx, which is frequently used as gate dielectric in OFETs, 6 T is usually standing [29, 30] but can show a transient monolayer structure of lying molecules [31]. On non-passivated Si(100)–(2 × 1) surfaces 6 T is decomposed upon contact formation, but passivation of this surfaces by H allows for intact adsorption of 6 T [32] and, in general, 6 T adopts a standing orientation for multilayer coverage on passivated silicon [33]. Furthermore, hydrogen-terminated Si surfaces are frequently used as substrates for hybrid organic–inorganic interfaces [6–8, 34]. There are a couple of photoelectron spectroscopy studies of 6 T thin films on (modified) Si surfaces [35–38]. However, no UPS data of 6 T on the HF-treated surface of Si(100) is available and it remains an open question whether the passivation is sufficient for electronic decoupling of Si and the 6 T thin film. Furthermore, although 6 T adopts a standing orientation on hydrogen-terminated Si as well as on SiOx [29, 30, 33] the structural defect densities can be expected to be higher on SiOx, which would affect ELA. Therefore, we use hydrogen-terminated Si(100) and SiOx for stepwise deposition of vacuum-sublimed 6 T to determine the ELA by UPS and XPS measurements. On both substrates the interfacial coupling is weak and 6 T induces a slight (<0.1 eV) downwards band bending in the inorganic substrates, which is consistent with the donor character of 6 T. On the 6 T side of the interfaces the well-ordered growth of 6 T on Si results in a narrow DOS distribution of the HOMO and no energy-level bending occurs. On SiOx, however, the 6 T thin film is more disordered, which results in a broader DOS distribution of the HOMO and, consequently, to energy-level bending by Fermi-level pinning.

**Methods**

Coupons cut from n-type (100)-oriented, single-side polished single crystal Si wafers (0.05–0.1 Ω cm) with a native oxide layer were used for all samples. The coupons were ultrasonically cleaned in acetone, ethanol, and deionized (DI) water, followed by UV-ozone treatment for 15 min. For Si substrates they were additionally immersed in HF solution for 5 min to remove the native oxide layer and then washed with DI water. Photoemission measurements were performed in an ultrahigh vacuum setup [39] including an analysis chamber (base pressure: 4 × 10⁻¹⁰ mbar), an evaporation chamber (base pressure: 2 × 10⁻¹⁰ mbar) and a sample loadlock. 6 T was sublimated from resistively heated cells with deposition rates of about 2 Å min⁻¹ and the nominal mass thickness of the films was monitored with a quartz crystal microbalance (QCM) positioned near the sample. A monochromatized Al Ka source (1486.7 eV) and a monochromatized HeI (21.22 eV) were used as excitation sources for XPS and UPS, respectively, and the photoelectrons were collected by a Specs PHOIBOS 150 analyzer. The binding energy (BE) was calibrated by using the Fermi-edge of a freshly sputtered Au(111) sample. Charge compensation was not performed as sample charging is usually not an issue for XPS and UPS measurements for organic semiconductor thin films with thicknesses up to several hundred Å [13] and was, indeed, not observed for 6 T thin films [27, 35]. All preparation steps and measurements were performed at room temperature (295 K). The kinetic energy in the plots of the secondary electron region (measured in normal emission with a bias potential of ~3 V) are corrected for the analyzer work function and the bias potential. Thus, the position of the secondary electron cut-off (SECO) corresponds to the position of the vacuum level (VL) w.r.t. the Fermi-level (EF). For the fitting of Si 2p the energy difference between the Si 2p₁/₂ and Si 2p₃/₂ components was fixed at 0.60 and the peak area ratio for was fixed at 1:2. The error bar of BE positions is estimated to be ±0.05 eV.

**Results and discussion**

Figure 1 shows thickness-dependent UPS spectra of 6 T deposited on Si and SiOx substrates. In the valence electron spectra of 6 T on Si (figure 1(a)) the peak centered at 1.68 eV BE can be assigned to the HOMO-level, the peak centered at ca. 2.5 e V BE to the HOMO-1 and the peak centered at ca. 3.5 eV to the localized π-band region [40]. The intensity of all peaks increases with increasing 6 T coverage and they do not show thickness-dependent BE-shifts. For clean Si (bottom spectra in figure 1(a)) the valence band maximum (VBM) is at ca. 1 eV BE; however, the VBM is hardly visible as the spectrum is dominated by emission from deeper lying states with the onset at ca. 4 eV BE. The position of VL can be derived from the SECO (figure 1(b)) and for the Si substrate VL locates at 4.03 eV above EF. Deposition of 6 T decreases VL slightly and for 6 T with multilayer coverage (QCM thickness: 128 Å) VL locates at 3.94 eV above EF. Figure 1(c) shows the valence electron spectra on a logarithmic
intensity scale and the VBM of clean Si can be precisely determined to 0.97 eV BE; the onset of the 6T HOMO for multilayer coverage can be found at 1.13 eV BE.

For the 128 Å thick 6T film on SiOₓ the HOMO is centered at 1.56 eV BE (figure 1(d)) and the peak shifts to lower BE with decreasing the 6T coverage. Furthermore, compared to the spectra on Si (figure 1(a)) the spectra are broadened and the intensity of the HOMO-1 peak (at ca. 2.5 eV BE) is decreased. Similar changes in the signature of 6T thin film spectra have been observed before and were ascribed to changes in the degree of thin

Figure 1. Thickness-dependent UPS spectra of 6T thin films on Si and on SiOₓ. (a) (d) show the valence electron region, (b) (e) the secondary electron region and (c) (f) the valence electron region on a log 10 intensity scale.
film order and/or the conformation of the 6 T molecules [41]. The energetic spacing between the peak of the localized $\pi$-states (at ca. 3.5 eV) and the HOMO peak, which is a fingerprint of conformation [42], is almost the same for the multilayer spectra on both substrates, which points to disorder as the main reason for the changes in spectral signatures. For the SiO$_x$ substrate VL locates at 4.33 eV above $E_F$ (figure 1(c)) and VL decreases by 0.24 eV upon 6 T deposition, i.e., for multilayer coverage VL locates at 4.09 eV above $E_F$. In the SiO$_x$ spectrum on a logarithmic intensity scale (figure 1(f)) no clear VBM is apparent. The insulator SiO$_x$ does not have a DOS in this BE range and the mean free path of photoelectrons with a kinetic energy of ca. 20 eV is smaller than the thickness of the native oxide layer and, consequently, the VBM of Si is not accessible by UPS for this sample. On logarithmic intensity scale the differences in the shape of the HOMO-derived peaks of the 6 T multilayer spectra on Si (figure 1(c)) and on SiO$_x$ (figure 1(f)) become obvious: On Si the 6 T HOMO-onset is clearly defined, while the HOMO-onset can be just estimated to 0.72 eV BE on SiO$_x$. Furthermore, on SiO$_x$ the DOS shows a tailing into the energy gap and with decreasing 6 T coverage the HOMO-onset shifts to lower BE and is located at 0.51 eV BE for the 4 Å film. The reasons for the DOS-broadening and how it leads to the energy shift will be discussed further below.

Figure 2 shows the core-level spectra as measured by XPS. For the Si substrate (figure 2(a)) the Si 2p$_{3/2}$ peak is centered at 99.84 eV BE, which is in the usual BE range for Si-Si bonds [43, 44]. By increasing the 6 T thickness the peak shifts slightly to higher BE and for the 128 Å thick 6 T film the Si 2p$_{3/2}$ peak is centered at 99.90 eV. For the SiO$_x$ substrate, the Si 2p$_{3/2}$ peak is also centered at 99.84 eV and an additional peak at ca. 103.5 eV BE (figure 2(b)) stems from Si-O bonds in the oxide layer [45]. In contrast to the UPS results, the Si features become accessible by XPS as the mean free path of photoelectrons increases with increasing kinetic energy [46]; in passing, it is noted that the oxide layer does not affect the BE of Si 2p. The 6T-induced Si 2p shift to higher BE on SiO$_x$ (0.09 eV) has almost the magnitude as that on Si (0.06 eV). For a 6 T thickness of 4 Å on Si no S 2p signal can be observed (figure 2(c)) and for thicknesses of 32 Å and 128 Å the BE positions are almost the same, which is in accordance with the likewise non-shifting HOMO-level (figure 1(a)). The S 2p peak on SiO$_x$ (figure 2(d)) shifts by 0.20 eV to higher BE upon increasing the 6 T thickness from 32 Å to 128 Å, which is almost parallel to the shift of the HOMO-level.

Based on the UPS and XPS results, we can draw energy-level diagrams of 6 T on Si and SiO$_x$ as shown in figure 3. The positions of VL, the VBM of Si and the HOMO-onsets are extracted from UPS (figure 1) and following Ref. [19] the band bending magnitudes in Si and SiO$_x$ are taken from the shift of the Si 2p core levels as measured by XPS (figure 2). The Si VBM in the sample with the native oxide layer is estimated by the S 2p level [43, 44]. On Si the shift of VL (0.09 eV) by 6 T deposition is almost parallel to that of Si 2p (0.06 eV). Downwards band bending of similar magnitude upon contact formation of 6 T was observed on other Si surfaces [37] and the associated electron doping into the conduction band of Si is in accordance with the donor character of 6 T. Within the 6 T layer no energy-level bending can be observed, which can be expected based on general considerations film [3, 9, 10]: The transport gap of 6 T thin films is 2.8 eV [27] and the HOMO-onset in the multilayer film on Si can be found at 1.13 eV below $E_F$, which is a rather mid-gap position. Furthermore, no tailing states at the low BE side of the HOMO can be observed (figure 1(c)) and, consequently, the position of $E_F$...
is mainly determined by VL of the substrate, i.e., effective VL-alignment takes place. The IE for 6 T multilayer film on Si, as determined by the energy difference between the VL position and HOMO-onset, is 5.07 eV (figure 3(a)), which is close to the range (4.7 eV to 5.0 eV) for 6 T thin films with an almost standing orientation [16, 25, 27, 28].

On SiOx the 6T-induced shift of Si 2p (0.09 eV) is smaller than ΔVL (0.24 eV) and, indeed, also S 2p (0.20 eV) and the HOMO-level (0.19 eV) show downward shifts with increasing 6 T thickness. The almost rigid shift of VL, valence and core levels is a tell-tale sign for energy-level bending, which in organic thin films is often due to tailing states of the frontier molecular orbital DOS [9, 10]. Indeed, for thin 6 T coverages the HOMO-onset almost reaches EF (figure 1(c)) and Fermi-level pinning can be expected [48]. As mentioned above, the general broadening of the DOS in the 6 T thin film on SiOx is, most likely, due to disorder, which can be due to the coexistence of domains with different polymorphs on the surface or due to local defects, e.g., molecules with a different inclination angle with respect to surrounding molecules. The relatively low intensity of the broad tailing states (figure 1(c)) points to local defect as source of energetic disorder [49]. Notably, such localized states do affect ELA, but do not contribute to charge transport in the thin film [14, 50]. For inhomogeneous thin films an exact IE determination is demanding as the SECO probes the area-averaged mean of the surface potential but the valence electron spectra are a superposition of local features [51]. This explains why the IE of the 6 T thin film on SiOx (4.81 eV) is apparently smaller than that on Si (5.07 eV).

Conclusions

Our photoelectron spectroscopy data show that the interfacial coupling between 6 T and HF-treated n-type Si(100) and Si with a native oxide layer is weak. Consequently, the ELA is governed by the DOS of the frontier molecular orbitals of the 6 T thin films. Hydrogen-terminated Si allows for well-ordered growth of 6 T thin films and the distribution of the HOMO DOS is relatively narrow with no tailing states into the energy gap. This leads to the absence of energy-level bending in the 6 T layer and the Si VBm and the 6 T HOMO-level are well-matched at the interface. Structural disorder in the 6 T thin film on SiOx leads to a broader HOMO DOS and to tailing states, which results in energy-level bending in the 6 T layer.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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