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Phys. Rev. Lett. **110**, 267602 — Published 25 June 2013

DOI: [10.1103/PhysRevLett.110.267602](https://doi.org/10.1103/PhysRevLett.110.267602)

## Gap States in Pentacene Thin Film Induced by Inert Gas Exposure

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## Abstract

We studied gas-exposure effects on pentacene (Pn) films on SiO<sub>2</sub> and Au(111) substrates by ultrahigh sensitivity photoelectron spectroscopy, which can detect the density of states of  $\sim 10^{16}$  states eV<sup>-1</sup>cm<sup>-3</sup> comparable to electrical measurements. The results show the striking effects for Pn/SiO<sub>2</sub>: exposure to inert gas (N<sub>2</sub> and Ar) produces a sharp rise in gap states from  $\sim 10^{16}$  to  $\sim 10^{18}$  states eV<sup>-1</sup> cm<sup>-3</sup> and pushes the Fermi level closer to the valence band (0.15 ~ 0.17 eV), as does exposure to O<sub>2</sub> (0.20 eV), while no such gas-exposure effect is observed for Pn/Au(111). The results demonstrate that these gap states originate from small imperfections in the Pn packing structure, which are induced by gas penetration into the film through the crystal grain boundaries.

PACS: 79.60.Fr, 79.60.Dp, 71.20.Rv, 81.05.Fb

The energy level alignment (ELA) at organic-substrate and organic-organic interfaces is a crucial issue for any organic-based device, given that the interface electronic structure controls the charge injection process in the organic semiconductor (OSC) [1, 2]. Despite considerable effort [1-5], however, there still remains a mystery why some organic semiconductors, such as pentacene, always show p-type charge transport property while some others, such as C<sub>60</sub>, show n-type property without heavy intentional doping, that is the transport property seems to be determined by molecule itself. Therefore, a consensus on ELA mechanism has yet to be reached.

Recently, the ELA mechanism was suggested to originate with the density of gap states (DOGS) caused by structural disorder in the intermolecular packing [1, 4, 6-8]. Such gap states also introduce electronic traps in the bulk of OSCs, which limit the electron or hole transport in the material [9,10]. Moreover, exposure of OSC films to various gaseous atmospheres was reported to affect the ELA and the charge transport properties [11-13, 14]. In general, such effects were discussed in terms of chemical reactions between gas molecules and organic molecules [11-13, 14]. However, in addition to *chemical* effects, the simple penetration of gas molecules in organic solids may alter the intermolecular packing structure [15, 16]. This more *physical* alteration can also modify the electronic properties of the organic films because (i) the gas penetration could induce changes in the intermolecular packing structure, thus resulting in gap states [17, 18] and (ii) the valence band structure of organic solid is strongly dependent on the intermolecular packing geometry due to planar molecular structure [19].

In this work, we report a direct study of the energy distribution of DOGS of the order of  $10^{16}$  states eV<sup>-1</sup> cm<sup>-3</sup>, which is comparable to DOGS detected by electrical measurements [9], in an organic layer by means of ultralow background, high sensitivity Ultraviolet Photoemission

Spectroscopy (UPS) technique. We investigate pentacene (Pn), an OSC that is widely used in organic field effect transistors [20], deposited on SiO<sub>2</sub>/Si(100) and Au(111) substrates at RT. The impact of exposure to 1-atm of inert N<sub>2</sub> atmosphere on the Pn electronic properties is evaluated. Despite the absence of chemical interaction between N<sub>2</sub> and Pn molecules, the DOGS and ELA at the Pn/SiO<sub>2</sub> interface are strongly modified by the exposure to N<sub>2</sub> gas. This effect is ascribed to the structural disorder caused by N<sub>2</sub> molecules penetrating into the Pn film. A similar effect is observed upon exposure to Ar, while in case of O<sub>2</sub> exposure, the DOGS formation is accelerated, presumably because of the difference in the chemical properties of the gas molecules.

The present results demonstrate that structural disorder has a significant impact on the electronic properties and interfacial ELA in organic thin films. This is related to the nature of organic semiconductor crystals, which consists of low-symmetry molecules held together by weak intermolecular forces. The results also have great practical significance, as they show that organic layer processing in inert atmosphere (N<sub>2</sub>), which is ubiquitous in organic electronics, does affect the electronic structure of the OSC, a point which had not been understood so far.

Si(100) wafers (*n*-type) with a thermally grown SiO<sub>2</sub> layer (thickness=3 nm) were cleaned in an acetone and isopropanol ultrasonic bath. The SiO<sub>2</sub> substrates were then annealed in a UHV preparation chamber ( $\sim 4 \times 10^{-8}$  Pa) at 673 K for 12 h. Pn molecules (C<sub>22</sub>H<sub>14</sub>, Sigma Aldrich), purified by three cycles of vacuum sublimation, were vacuum-deposited onto the SiO<sub>2</sub> substrate at room temperature (293 K, RT). The deposition rate (0.5 nm/min) was monitored by using a quartz microbalance. During the Pn deposition, the pressure was stably maintained below  $6 \times 10^{-8}$  Pa. As-deposited Pn thin films were reported to have an upright-standing molecular orientation and herringbone-like intermolecular packing, as judged from the HeI <sub>$\alpha$</sub>  UPS spectral profile [19, 21].

The Pn thin films were repeatedly exposed to 1-atm N<sub>2</sub> with a purity of 99.99995% (6N5) at RT (293 K) for a total exposure time of 20 h. Next, the film was exposed to 1-atm O<sub>2</sub> (6N5) for an additional 5 h at RT. This gas exposure procedure was repeated using Ar gas (5N5) on different samples. The effect of the N<sub>2</sub>-exposure on Pn thin film on a clean Au(111) single crystal surface (thickness=40 nm, RT deposition) was also evaluated. The gas exposures were performed by using a UHV-compatible gas inlet line connected to the preparation chamber.

The UPS measurements were performed at RT using an ultrahigh-sensitivity UPS apparatus with a hemispherical electron energy analyzer (MBS A-1) and a monochromatic XeI<sub>α</sub> ( $h\nu=8.437$  eV) radiation source with a LiF single crystal filter. The electrical wiring of the measurement system was carefully performed to minimize the background noises by positioning the electrical cables at appropriate positions. The accumulation time of the spectra was typically 40 min. Under these conditions, radiation damage effect [22] to the Pn films could be excluded [See Section I of the Supplementary Informations (SI)]. All UPS spectra were measured at normal emission with an acceptance angle of  $\pm 18^\circ$ , and a bias of -5 V was applied to the sample in order to measure the vacuum level (*VL*) (see Section II of SI). The energy resolution of the UPS system was set to 30 meV. The binding energy scale was relative to the substrate Fermi level.

Fig. 1(a) shows the XeI<sub>α</sub>-UPS spectra of the as-deposited and N<sub>2</sub>- (O<sub>2</sub>-) exposed Pn film (15 nm) in the cutoff and highest occupied molecular orbital (HOMO) regions [spectra (1)-(7)]. The HOMO band of the as-deposited Pn thin film consists of two main components [labeled  $H_1$  and  $H_2$  in Fig. 1(a)] with an energy separation of  $\sim 0.45$  eV. The two components correspond to the density of states (DOS) of the HOMO band in Pn thin film with an upright-standing molecular orientation and herringbone-like intermolecular packing [21, 23]. The  $H_1$  ( $H_2$ ) position was

determined by a least-square fitting of the HOMO-band UPS data using Gaussian functions (see Section III of SI). Following each N<sub>2</sub>-exposure, the  $H_1$  ( $H_2$ ) peak shifts towards low binding energies, while the vacuum level ( $VL$ ) moves upwards by the same amount. This N<sub>2</sub>-induced “rigid” energy shift almost saturates after a total exposure time of 20 h. Further exposure to O<sub>2</sub> (5 h) produces an additional energy shift [spectra (7)]. Interestingly, the ionization potential ( $IP$ ) of the as-deposited Pn thin film ( $IP=4.90$  eV) is unchanged upon the various gas exposure treatments. The  $IP$  of an organic thin film was reported to be strongly dependent on the molecular orientation [24] and molecular packing [21]. Therefore, the stability of the  $IP$  in the present case indicates that no large-scale structural rearrangement occurs. Similar results are obtained for the Ar-exposed Pn/SiO<sub>2</sub> thin film [spectra (8)], while no spectral shift is detected for Pn/Au(111) thin film after prolonged exposure (19 h) to 1-atm N<sub>2</sub> [spectra (9)].

Fig. 1(b) shows the expanded UPS spectra of the HOMO and gap energy region on log scale for the as-deposited, N<sub>2</sub>-exposed (total exposure time=20 h) and O<sub>2</sub>-exposed (total exposure time=5 h following the 20 h N<sub>2</sub> exposure) Pn thin film with the corresponding fitting curves (see Section III of the SI). The UPS spectrum of the SiO<sub>2</sub> substrate is shown for comparison. The DOGS of the as-deposited Pn film is very low, but it significantly increases after N<sub>2</sub>- and O<sub>2</sub>-exposure (the progressive increase in DOGS with gas exposure time is shown in Section IV of SI). Ar-exposure leads to a similar DOGS increase (not shown). In the gap state binding energy region (~0-0.5 eV), the DOS of the as-deposited Pn film and the SiO<sub>2</sub> substrate are comparable [(Fig. 1(b)]. Therefore, the SiO<sub>2</sub> DOS may overlap with the DOGS of the as-deposited Pn film in a way that depends on the electron mean free path in the Pn overlayer (see Section V of the SI). Once the substrate contribution is taken into account, the DOGS of the as-deposited film (~10<sup>16</sup> states eV<sup>-1</sup>

$\text{cm}^{-3}$ ) turns out to be comparable to that detected by electrical measurements for Pn on  $\text{SiO}_2$  [9, 12]. For the gas-exposed Pn films, the DOGS is  $\sim 10$  times larger than the contribution from the substrate, and can therefore be unambiguously related to the Pn film. In particular, for the  $\text{N}_2$ -exposed sample, an exponential-type DOGS [linear on the log scale of Fig. 1(b)] is clearly visible between the HOMO threshold energy  $E_T = 0.4$  eV (where the DOS starts deviating from a Gaussian line shape) and the Fermi level ( $E_F$ ). A different energy dependence is observed for the DOGS of the  $\text{O}_2$ -exposed sample. Post-annealing experiments ( $50^\circ\text{C}$  for 18 h) on  $\text{N}_2$ -exposed Pn films show a gradual recovery to the original  $VL$  and HOMO positions (i.e. before gas exposure). At the same time, a decrease in the DOGS is observed (see Section VI of the SI). Consequently, the DOGS of the gas-exposed sample can be ascribed to a slight intermolecular packing disorder resulting from prolonged gas exposure. These gap states may in turn affect the position of  $E_F$  within the energy gap [7]. Similar effect was observed for thinner Pn films (not shown). Note that no residual  $\text{N}_2$  is detected by X-ray photoemission spectroscopy in the gas-exposed film following re-introduction into UHV (see Section VII of SI). This supports the conclusion that the DOGS is not due to  $\text{N}_2$ -related states but rather to intermolecular packing disorder. The increase in DOGS and its different energy distribution upon  $\text{O}_2$  exposure can probably be ascribed to (i) a more effective penetration of  $\text{O}_2$  molecules into the Pn film (the penetration of a gas into organic systems strongly depends on its chemical properties and size [16]) and/or (ii) chemical interaction between  $\text{O}_2$  molecules and Pn molecules [11, 25]. However, it is worth noting that a prolonged  $\text{N}_2$  exposure of Pn films prepared at RT on single crystalline Au(111) does not induce any detectable change in the DOGS or spectral shift [Fig. 1(a) and (c)]. Pn films deposited on Au(111) was reported to exhibit larger crystallites [size $\sim 200$  nm] and significantly fewer grain boundaries than those on  $\text{SiO}_2$  [26, 27],



suggesting that grain boundaries play a crucial role in the penetration of gas molecules and in the changes of the intermolecular packing geometry as depicted in Fig. 2. According to the UPS data [Fig. 1(b)], the defect density is estimated to be in the range of  $10^{16}$ - $10^{18}$   $\text{cm}^{-3}$ , corresponding to a defect-to-molecule ratio of  $10^{-5}$ - $10^{-3}$ , which is hardly detectable via structural diffraction techniques [28]. The hypothesis that the DOGS is mediated by structural defects in the Pn film is also supported by theoretical calculations by Kang et al. [17]. They showed that (i) sliding defects along the Pn long axis create shallow gap states and (ii) the HOMO levels at the defect sites are distributed over a range of up to 100 meV from the HOMO of the unperturbed molecules.

According to this model, the DOS in the HOMO (gap state) binding energy region is expected to decrease (increase) with the density of defects. To verify this point, the evolution of the UPS intensity upon gas exposure is carefully evaluated. First, the  $\text{XeI}_\alpha$ -UPS spectra of as-deposited,  $\text{N}_2$ -exposed and  $\text{O}_2$ -exposed Pn thin films are aligned to the position of the HOMO band maximum ( $H_2$ ) [Fig. 3(a) and (b)]. Next the ratio between the UPS spectra of the gas-exposed and the as-deposited samples is evaluated for each gas-exposure step [Fig. 3(c)]. For long exposure times ( $\geq 2$  h), the increase in the UPS intensity in the gap state energy region (spectral ratio  $> 1$ ,  $E > E_T$ ) corresponds to a reduction in the HOMO band intensity (spectral ratio  $< 1$ ) within  $\sim 0.2$  eV from the threshold position. This result is in qualitative agreement with the theoretical prediction [17]. In the high intensity region of the HOMO band ( $\sim 0.5$  eV) the slight increase of the electronic states and/or the small broadening in the HOMO lineshape, as due to structural disorder induced by gas exposure [18], results in the slight increase of the spectral ratio (observed at  $\sim 0.5$  eV).

Finally, we comment on the impact of the gas exposure on the observed molecular level

shift, i.e. the shift of the HOMO level towards  $E_F$  (see Fig. 1(a) and also Section VIII of SI). We suggest that the lowest unoccupied molecular orbital (LUMO) of Pn also gives rise to a distribution of (unoccupied) gap states resulting from imperfections in the intermolecular packing [17]. The energy distributions of the HOMO- and LUMO-derived DOGS are not symmetric because the corresponding wave functions have different spatial spreads [17]. Such disorder-induced-, non-symmetric DOGS (tailing states) affect the position of  $E_F$  within the gap of organic semiconductors. Depending on the DOGS and their energy distribution,  $E_F$  may lie closer to the pristine LUMO or HOMO band [18]. With increasing structural disorder (as induced, for example, by gas exposure)  $E_F$  is expected to lie even closer to the HOMO, as observed in the present work (see Fig. 1(a) and Section VIII of SI).

In conclusion, ultralow background, high-sensitivity UPS allowed us to directly measure the DOGS in pristine Pn thin films grown on  $\text{SiO}_2$  and to determine values of the order of  $10^{16}$  states  $\text{eV}^{-1} \text{cm}^{-3}$ , comparable to those obtained by electrical measurements. Striking effects due to gas exposure are that: (i) exposure to 1-atm of inert gas ( $\text{N}_2$  or Ar) produces a rise in gap state density, as does exposure to  $\text{O}_2$ ; (ii) these gap states push the Fermi level closer to the HOMO; and (iii) the gap states originate from small imperfections in the Pn packing structure induced by gas molecule penetration into the film, presumably through the crystal-grain boundaries. Such imperfections remain even after removal of the gas molecules to yield gap states that are responsible to control the  $E_F$  position within the gap. The present findings demonstrate the significant impact of slight structural disordering on the electronic properties of organic thin films. Furthermore, they reveal that complete control of the organic film structure is a requisite for producing organic devices with the desired properties. Finally, they clearly demonstrate that,

contrary to a widely held assumption, processing of organic films such as Pn in inert atmosphere is not without negative impact on the electronic structure of the material.

### **Acknowledgements**

The authors acknowledge the support from the G-COE program at Chiba University (G-03, MEXT), Grand-in Aid for Scientific Research [(A) JSPS Grand No. 24245034 and (B) JSPS Grand Nos.23360005 and 23360006]. Work in Princeton was supported by a grant of the National Science Foundation (DMR-1005892).

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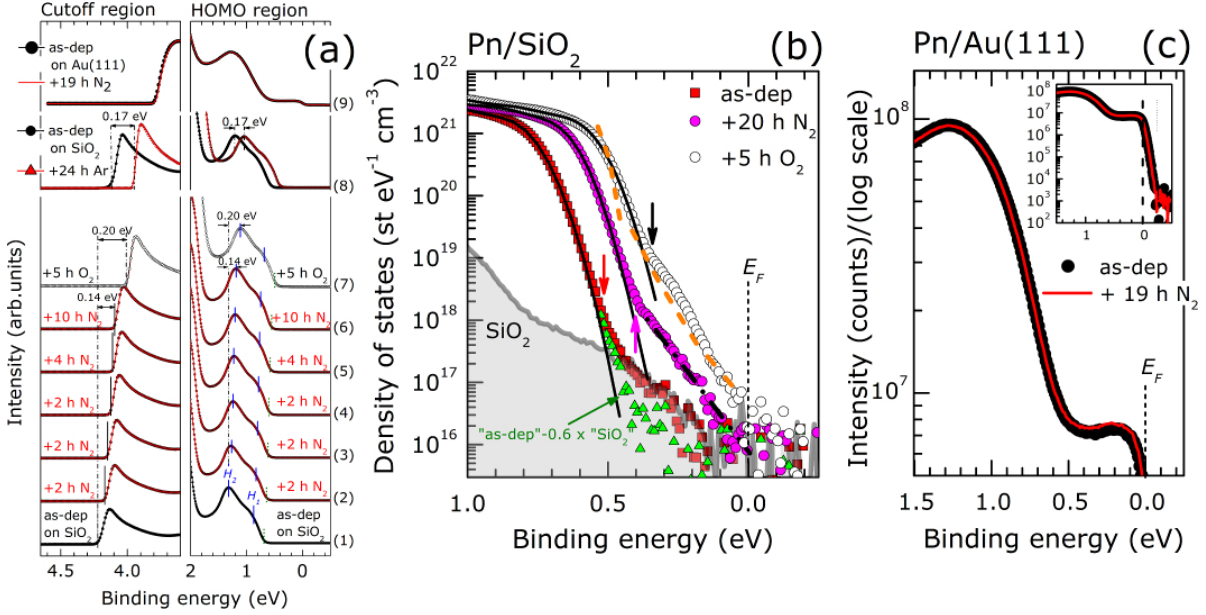
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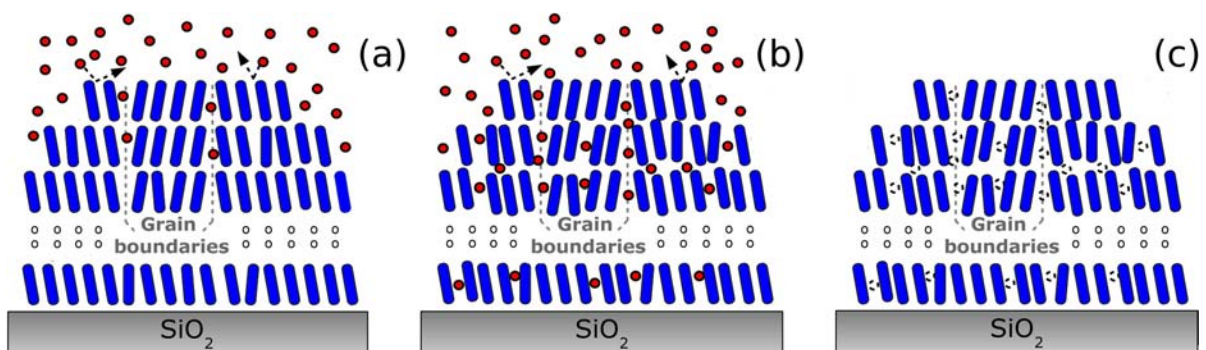
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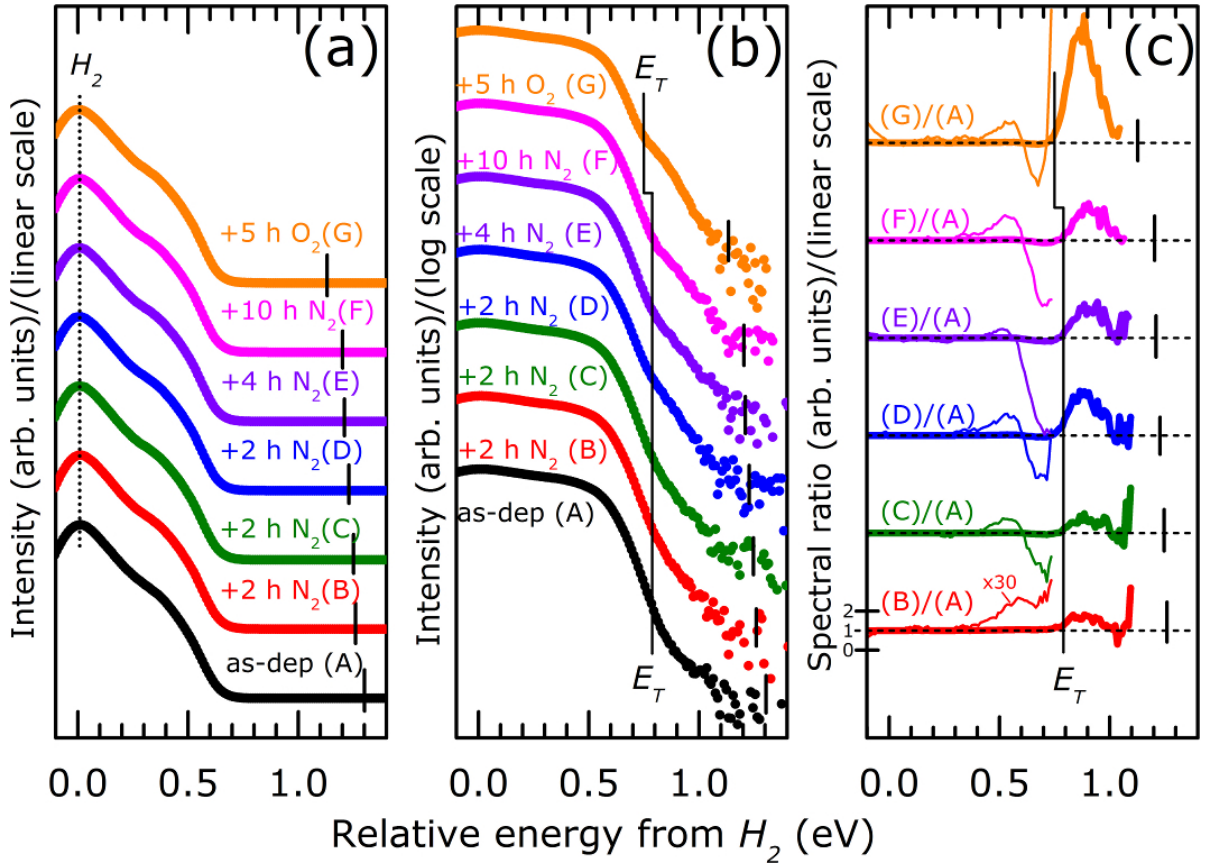
**Figure 1** (color online). (a) Xel $\alpha$ -UPS spectra of as-deposited [spectrum (1)], N<sub>2</sub>-exposed [spectra (2)-(6)], O<sub>2</sub>-exposed [spectra (7)] and Ar-exposed [spectra (8)] Pn thin film (15 nm) on SiO<sub>2</sub> substrate. Spectrum (9) includes the UPS data of as-deposited and N<sub>2</sub>-exposed Pn/Au(111) thin film (40 nm) acquired at RT. The positions of the  $V_L$  and HOMO derived bands ( $H_1$  and  $H_2$ ) are indicated by vertical (continuous) bars. The difference between the  $V_L$  (HOMO) positions of the Pn/SiO<sub>2</sub> thin films in the “N<sub>2</sub>” and “Ar” experiments reflects the difference between the initial SiO<sub>2</sub> work functions. (b) DOS (log scale intensity plot) of as-deposited (filled (red) square symbols), N<sub>2</sub>-exposed (20 h, filled (magenta) circles) and O<sub>2</sub>-exposed (5 h, open circles) Pn thin film on SiO<sub>2</sub>. Continuous (black) lines are the cumulative fitting curve of the HOMO band (see Section III of SI). DOS values were extracted from the UPS data, as described in Ref. [23]. SiO<sub>2</sub> data are rescaled to preserve, in the DOS scale, their relative intensity with respect to the as-deposited Pn data. Vertical arrows indicate the threshold energy position ( $E_T$ ) where the DOS distribution deviates from the cumulative fitting curve and DOGS starts to appear. The dashed line indicates the DOGS of the Pn thin film as determined by transport measurements. Data are adapted from ref. [12]. (c) Xel $\alpha$ -UPS spectra of as-deposited Pn thin film on Au(111) (40 nm)

before and after N<sub>2</sub> exposure. The Fermi edge of the Au(111) substrate is clearly visible (see also inset). No spectral change was detected upon gas exposure.





**Figure 2** (color online). Schematic representation of the gas penetration and mediated imperfections in Pn thin film on SiO<sub>2</sub>. During exposure [panel (a)], gas molecules progressively penetrate into the Pn film, where they *locally alter* the original intermolecular packing geometry [panel (b)]. The gas penetration proceeds through the grain boundaries of the film. Because of the weak N<sub>2</sub>-Pn interaction, N<sub>2</sub> molecules are easily removed once the film is put back in UHV. The result is a weakly disordered film [(panel (c))].



**Figure 3** (color online). (a)  $\text{XeI}\alpha$ -UPS data of as-deposited,  $\text{N}_2$ -exposed and  $\text{O}_2$ -exposed  $\text{Pn}/\text{SiO}_2$  thin film in the HOMO band region. The energy scale is referred to the  $H_2$  position (dotted line) where the HOMO band reaches the maximum intensity. The vertical, short bars on each plot indicate the position of the Fermi level. The  $\text{SiO}_2$  substrate signal was not removed from the as-deposited sample spectra. (b) Same as panel (a), but plotted on a log scale. The continuous (black) line indicates the position of the threshold energy ( $E_T$ ) from which the gap state energy distribution starts to appear. (c) Spectral ratio between the data of gas-exposed film and as-deposited film (see text for details).