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Formation of sharp metal-organic semiconductor interfaces: Ag and Sn on CuPc

V.Yu. Aristov[1,2], O.V. Molodtsova[1], V.M. Zhilin[2], Yu.A. Ossipyan[2], D.V. Vyalikh[3], B.P. Doyle[4], S. Nannarone[4,5], and M. Knupfer[1,a]

[1] IFW Dresden, 01069 Dresden, Germany
[2] Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow Distr. 142432, Russia
[3] Institute of Solid State Physics, TU Dresden, 01069 Dresden, Germany
[4] TASC-INFM Laboratory, Area Science Park – Basovizza, 34012 Trieste, Italy
[5] Dipartimento di Ingegneria dei Materiali ed Amb., Università di Modena e Reggio Emilia, Italy

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Abstract. A detailed investigation of the chemistry and electronic structure during the formation of the interfaces between thin films of the archetypal organic molecular semiconductor copper phthalocyanine (CuPc) and Ag or Sn deposited on it was performed using photoemission and near-edge X-ray absorption spectroscopies with synchrotron light. Our study demonstrates the formation of sharp, abrupt interfaces, a behavior which is of particular importance for applications in organic devices. Moreover, for Ag on CuPc we demonstrate that this interface is free from any reaction, whereas there is slight interface reaction for Sn/CuPc.

PACS. 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc. – 68.35.-p Solid surfaces and solid-solid interfaces: Structure and energetics – 73.20.-r Electron states at surfaces and interfaces

1 Introduction

State-of-the-art technology based on organic semiconductors is envisaged to provide novel electronic devices, and together with a relatively low cost of fabrication promises to offer the next technological breakthrough in mobile and foldable displays [1]. Moreover, latest research activities reveal that peculiar optical and electronic properties of organic semiconductors give rise to a new generation of light-emitting devices: organic semiconductor lasers with very stable performance with respect to usual inorganic laser diodes, which opens wide perspectives for optical communication and sensor applications [2]. In this respect, prospective commerce as well as basic scientific interest inspire and motivate studies in the field of molecular organic semiconductors.

Key elements in the architecture of micro- and nanoelectronic devices are organic-organic or organic-metal interfaces. Therefore, to make further progress in the development of such organic devices [3,4] one requires both the understanding and the tailoring of the physical, chemical and transport properties of the metal-OMTF (organic molecular thin film) interfaces [5]. Moreover, development and production technology of different organic based electronic devices require the production of different types of metal/organic thin film interfaces and contacts. The case of deposition of organic semiconductors onto metals has recently initiated considerable research activity and now some progress has been achieved as regards basic interfacial properties of such organic on metal contacts [5,6]. Despite its technological importance the opposite case, metal deposition onto organic films, is comparatively much less studied [5,7–9].

In recent years, we have focused on the investigation of the evolution of the electronic structure of copper phthalocyanine (CuPc) films at metal deposition and on interface formation during this process. CuPc belongs to the family of the phthalocyanines (archetypal organic molecular semiconductors), which play an important role among other OMTF's. Their potential technological applications [10] are a good reason for researcher to pay attention to these materials. Moreover, Pc's demonstrate good compatibility with ultra high vacuum (UHV) and can be successfully grown as thin, ultra-clean, well ordered films on various substrates in standard ultra high vacuum spectrometers. These films then possess excellent and well defined electronic properties [10] and can be studied in situ under UHV conditions by means of modern techniques. Studying the interface formation upon deposition

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[a] e-mail: `M.Knupfer@ifw-dresden.de`

of different metals on CuPc thin films, we have revealed different types of metal-organic interfaces. In this communication we present the observation of sharp interfaces for Ag/CuPc and Sn/CuPc systems.

2 Experimental

The preparation of the CuPc films, the Ag and Sn deposition and the soft X-ray photoemission (PE) spectroscopy measurements were performed in the ultra high vacuum electron spectrometers at high energy resolution dipole beam lines: the BEAR line [11] of the synchrotron ELETTRA (Trieste) and the Russian-German line [12] of the Berliner Speicherring für Synchrotronstrahlung (BESSY). These beam lines provide continuous radiation with distribution over a wide photon energy (E_{ph}) ranges (30–1500 eV) and (30–1500 eV) correspondently. Besides, they are especially suited for studies of fragile organic materials, which potentially could be damaged under X-ray irradiation. The pressure in the experimental systems during data acquisition was always in the range of (1.5–3) $\times$ 10^{-10} Torr.

As substrate for CuPc film deposition, we used the (100) surface of a gold single crystal. The surface was prepared by repeated sputtering and annealing cycles after which a 5 × 20 surface reconstruction was observed using low energy electron diffraction, while no remaining contamination was detected in the core level photoemission spectra. The CuPc films were grown by sublimation of phthalocyanine powder at about 500 °C from an effusion cell in a sample preparation chamber (base pressure of 2.5×10^{-10} Torr). The latter was directly connected to the analyzer chambers. The deposition rate, monitored by a quartz microbalance, was about 1–2 Å/min, while the total thickness of the CuPc films was about 70 Å thick. This thickness appears to be large enough to minimize contributions from the gold substrate in the PE spectra, and small enough to as much as possible avoid charging effects.

Ag and Sn were deposited onto the CuPc films from resistively heated tungsten baskets without detectable pressure increase during deposition. The deposition rates controlled by a quartz thickness monitor were 0.5–1 Å/min. In addition, the total amount of metal accumulation at each step of deposition was evaluated from a comparison of the relative intensities of the Ag $3d$, Sn $3d$, and C $1s$ or N $1s$ core level signals. The sensitivity factors of the core-levels for the corresponding photon energies were taken from tabulated cross-sections and the throughput of the analyzer [13].

The PE measurements: valence band and Sn 4d core level taken at $E_{ph} = 110$ eV, and Sn $3d$, Ag $3d$, C $1s$, N $1s$, Au $4f_{7/2}$ core-levels taken at $E_{ph} = 600$ eV were carried following each metal deposition step. The total instrumental resolution in PE studies (full width at half maximum, FWHM) also accounting for the thermal broadening was about 130 meV for the VB and Sn 4d core levels, and about 240 meV for Sn $3d$, Ag $3d$, C $1s$, N $1s$ and Au $4f_{7/2}$ ($E_{kin} \sim 502$ eV) core levels. The Fermi level (E_F) position in the spectra was determined after each move of the monochromator by measuring the Fermi edge and/or the Au $4f_{7/2}$ electron emission from a gold foil in electrical contact with the CuPc film.

The near-edge X-ray absorption spectra (NEXAFS) were recorded at the ELETTRA synchrotron radiation facility using soft-X-ray light emitted by the BEAR dipole beam line in the total electron yield mode and normalized to the incident photon flux. The resolution for the NEXAFS measurements is determined exclusively by the performance of the beam line and was varied from 80 meV to 90 meV FWHM when going from C $1s$ (~283 eV) to the N $1s$ (~400 eV) thresholds respectively, and was about 100 meV for the Cu $2p$ threshold (~930 eV). The acquired spectra were energy calibrated using the photoionization spectra of Ar and N2 gases [14]. In the NEXAFS experiments the photon incidence angle was selected to be 35° relative to the sample surface normal. We have chosen this angle to explore simultaneously both: the $1s - \pi^*$ and $1s - \sigma^*$ transitions. The pressure in the experimental systems during data acquisition was always better than 1.5×10^{-10} Torr.

Other experimental details, concerning UHV electron spectrometers, Au(100) substrate preparation with following verification of surface reconstruction and cleanness, CuPc film deposition on the gold substrate, its characterization including evaluation of the organic film thickness, etc can be found elsewhere (see e.g. Ref. [15]).

3 Results and discussion

In order to evaluate the degree of Ag and Sn chemical reactivity with CuPc thin films we will compare our present results with those for K and In deposition, which were studied recently [15,16]. For these two systems we have observed strong diffusion of the metal atoms deeply into the CuPc films and a concomitant formation of electronic states within the energy gap of CuPc. These are due to charge transfer and a chemical reaction between the intercalated metal atoms and the organic molecules.

The bottom curves of both panels of Figure 1 present the top of the valence band (TVB) spectra of pristine CuPc thin films. The Figure additionally shows the TVB spectra evolution with silver (left panel) and tin (right panel) deposition and demonstrates, that Ag and Sn reveal significantly less chemical reactivity with CuPc thin films.

From these figures it is evident that the shape of the HOMO (highest occupied molecular orbital) peak, which is located at smallest binding energies, practically does not change, we only observe a small shift to higher energies for smallest metal coverage. Upon increasing metal deposition the energy positions essentially stay constant. Furthermore, there is no sign of the formation of additional electronic states within the gap of CuPc. Thus, from these measurements we already can conclude, that Ag/CuPc and Sn/CuPc interfaces are abrupt. The observed energy shifts most likely are due to the formation of a short range interface dipole at these contacts.

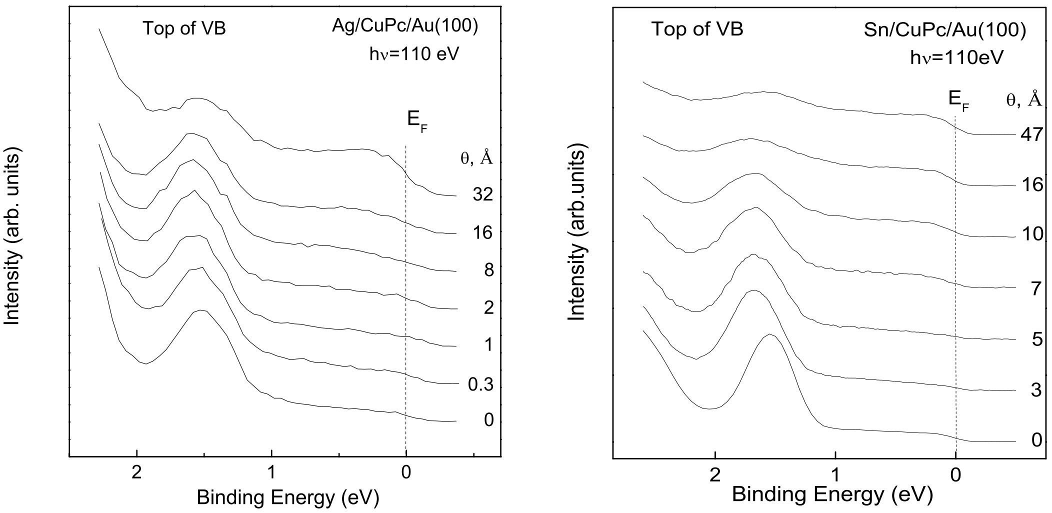

Fig. 1. Top of the valence band measured using photoemission spectroscopy, as a function of Ag (left panel) and Sn (right panel) deposition on CuPc films at room temperature. The nominal coverage of the metal layers is indicated.

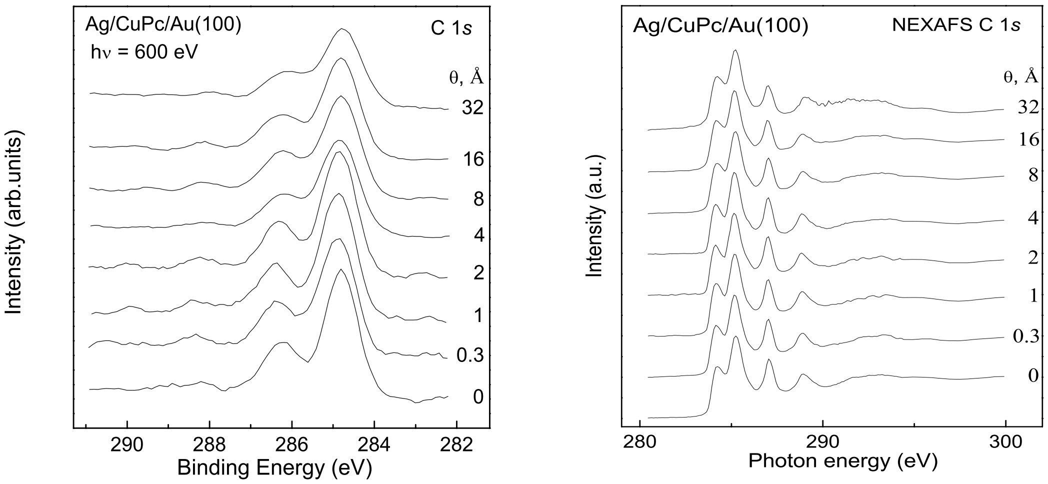

Fig. 2. Ag 3*d* (left panel) and Sn 3*d* (right panel) core level photoemission and as a function of Ag (Sn) deposition on CuPc films at room temperature. The nominal coverage of the metal layers is indicated.

Our core level photoemission studies corroborate these conclusions. While for K and In deposition onto CuPc the core level photoemission data reveal charge transfer from these metal atoms intercalated into CuPc film and strong chemical interactions, Figure 2 (left panel) demonstrates that from the first stage of Ag deposition onto CuPc films the Ag 3*d* core level emission appears at a binding energy consistent with metallic silver and exhibits a narrow spin-orbit doublet. No indication of the presence of other Ag 3*d* core-level components is observed in accordance with the formation of a non-reactive and abrupt Ag/CuPc interface.

For tin deposition onto CuPc films, the Sn 3*d* core levels as depicted in Figure 2 (right panel) show essentially the same behavior. The only differences one can observe is the very small additional shoulder at about 1.6 eV above the Sn 3*d* feature and an energy shift as a function of Sn thickness. The former indicates that a small fraction of Sn atoms weakly reacts with organics molecules, but the majority remains unaffected. From the intensity of the additional shoulder we can estimate that about 1/3 of the Sn atoms in the first monolayer react with CuPc molecules. This slight interface reaction will be discussed further below in the context of the core level data from the CuPc molecules. We attribute the energy shift to the formation of Sn islands for small coverages and the appearance of closed Sn layers for thicker metal overlayers only.

In Figure 3 we present the C 1*s* core level photoemission data (left panel) as well as the corresponding C 1*s* NEXAFS data (right panel) as a function of Ag deposition on CuPc. The C 1*s* core level data in the left panel exhibit a characteristic fine structure with maxima at 284.8, 286.24 and 288.2 eV. This fine structure is a direct consequence of the inequivalent carbon sites in a CuPc molecule and satellites related to C 1*s* emission. Also, it is well documented and discussed in the literature [17,18] and will

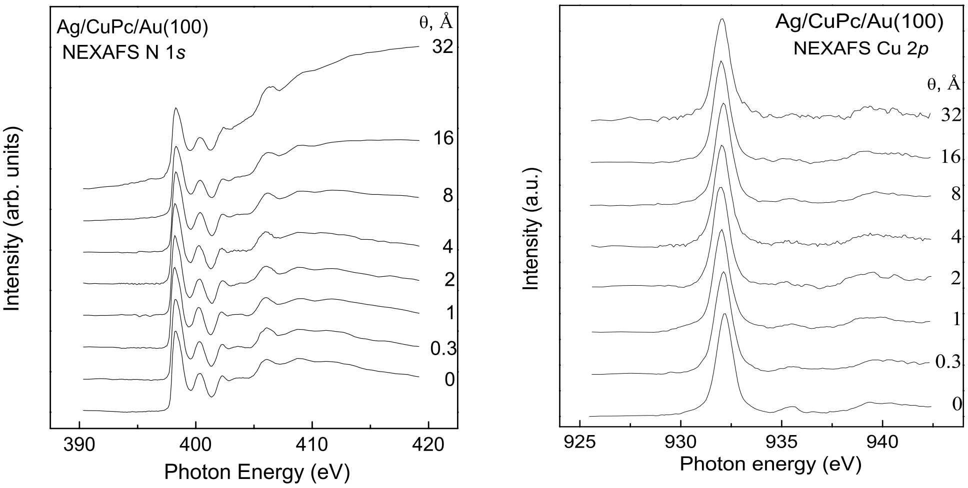

Fig. 3. Left panel: C 1*s* core level photoemission data as a function of Ag deposition on CuPc films at room temperature. The nominal coverage of the Ag overlayer is indicated. Right panel: NEXAFS data taken at the C 1*s* absorption edge for the same sample.

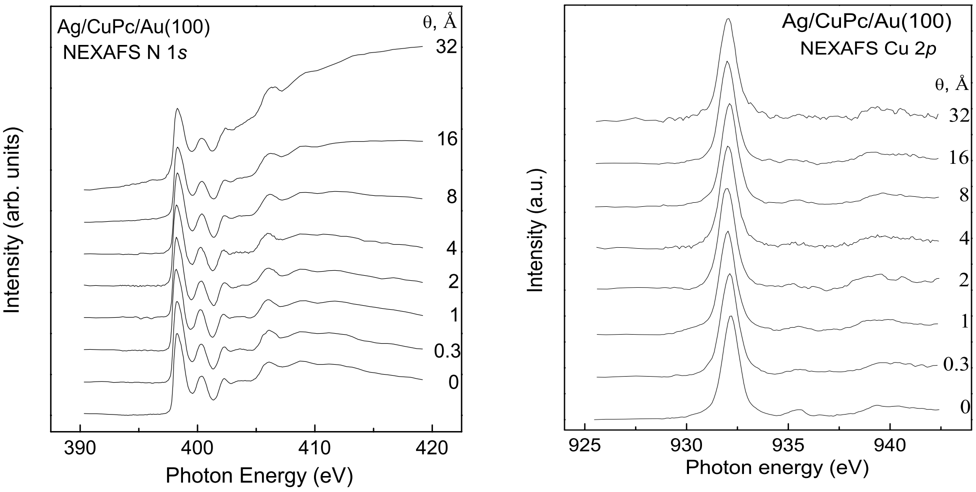

Fig. 4. NEXAFS data taken at the N 1*s* (left panel) and at Cu 2*p* (right panel) absorption edges as a function of Ag deposition on CuPc films. The nominal coverage of the Ag overlayers is indicated.

therefore not be considered further in this contribution. Figure 3 demonstrates that there is no change of the C 1*s* core level spectral shape, independent of the Ag coverage. For initial silver deposition, we observe a small shift in energy, which is related to the interface dipole as mentioned above, later on also the energy positions remain constant. Thus this measurement confirms the conclusion above, that the Ag/CuPc interface is sharp and without any sign of chemical reaction.

This is further corroborated by the NEXAFS signal of CuPc molecular thin films as a function of silver deposition. It is common to describe X-ray absorption in closed-shell molecules within an orbital approximation as one-electron transitions from a core level into the unoccupied molecular orbitals that are derived from the same contributing atom where the electron excitation occurs. Thus, for the molecules under consideration NEXAFS spectra contain information about the site and element specific density of unoccupied electronic states. The latter gives the chance not only to obtain information on chemical interaction between CuPc molecule and intercalated metal atoms in general, but to specify the atoms of the molecule involved in the interaction if any. Therefore the NEXAFS data of CuPc molecular thin films were obtained for all types of contributing atoms (C 1*s*, N 1*s* and Cu 2*p* edges). In addition, the soft X-ray absorption spectra are more bulk sensitive than the photoemission response, because they were recorded in the total electron yield mode, where the majority of the signal comes from the secondary electrons.

The NEXAFS spectra of CuPc as a function of Ag deposition are presented as follows: in the right panel of Figure 3 — at the C 1*s* absorption edge between 280 eV and 300 eV photon energy; in the left panel of Figure 4 — at the N 1*s* absorption edge between 390 eV and 420 eV; and in right panel of Figure 4 — at the Cu 2*p*3/2 absorption edge between 926 eV and 945 eV. The lowest spectra in all 3 panels are recorded from a pristine CuPc film.

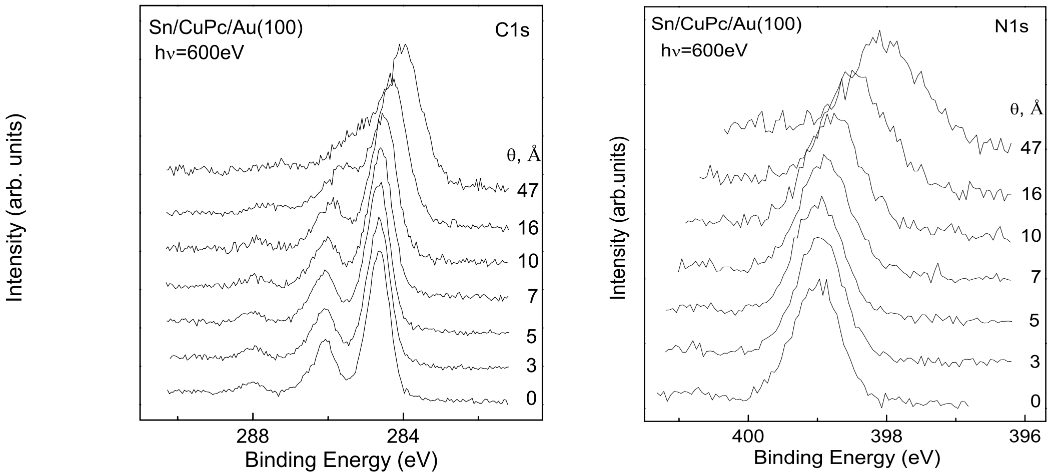

Fig. 5. Left panel: C 1*s* core level photoemission data as a function of Sn deposition on CuPc films at room temperature. The nominal coverage of the Sn overlayer is indicated. Right panel: N 1*s* core level photoemission data for the same samples.

Recently [19] the electronic structure of the unoccupied electronic states of pristine copper phthalocyanine was fully described. In this investigation the combined experimental and theoretical study allowed to identify the contributions from different parts of the pristine CuPc molecule to the unoccupied DOS and the measured spectra. Therefore we will not describe all details of the NEXAFS spectra of pristine CuPc here. We rather concentrate on the analysis of potential changes in the NEXAFS spectra of CuPc upon silver deposition. It is clearly seen from our experimental measurements, that none of the series of the NEXAFS spectra, recorded as a function of Ag deposition onto CuPc thin films at the C 1*s*, N 1*s* and Cu 2*p* absorption edges shows any spectral shape variation. Therefore we can conclude, that Ag atoms do not interact neither with carbon atoms of benzene or pyrrole rings nor with nitrogen atoms of pyrrole rings or with those linked to the central Cu atom and they do not interact with Cu as well. Consequently, the CuPc molecules are not affected by the formation of the Ag contact on top, and there is no diffusion of Ag into the CuPc film.

The situation changes going to Sn/CuPc as indicated in Figure 2 (right panel) above and in Figure 5, where we show both C 1*s* (left panel) and N 1*s* (right panel) core level photoemission data as a function of Sn coverage on CuPc. While both data sets reveal no spectral changes for the first steps of Sn addition, there is a shift of the spectral features to lower binding energy and broadening for larger Sn overlayer thicknesses. Taking into account the mean free path of the photoelectrons in Sn, which is of the order of this thickness, the data in Figure 5 for larger Sn thickness stem from the CuPc molecules very close to the metal/organic interface. This means that the molecules at the interface experience a different chemical environment, most likely due to some chemical reaction restricted to a thin interfacial region. We therefore infer that the Sn/CuPc interface also is abrupt, but that there is some interaction only within the first monolayer of Sn with CuPc molecules at the very top of the CuPc film.

4 Summary

Recently, there have been a few photoemission studies concerning Ag or Sn deposition onto various organic semiconducting thin films, or the deposition of metals onto phthalocyanine films. In the majority of cases, such interfaces are characterized by a diffusion of the metal atoms into the organic layers and by a chemical reaction between the two contact materials [20–28]. Our results clearly demonstrate that it is possible to achieve well defined, abrupt and nonreactive contacts by deposition of metals with a moderate work function onto phthalocyanine organic semiconductors. This is an important information in regard of electron injection contacts where the metal work function should not be too high in order to avoid large injection barriers. In the case of Sn, we presented the first observation of the formation of an abrupt interface with an organic semiconductor, while for deposition of silver onto CuPc, our data corroborate those obtained previously by valence band photoemission studies [27].

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References

1. J.K. Borchardt, Materials Today **7**, 42 (2004)
2. I.D.W. Samuel, G.A. Turnbull, Materials Today **7**, 28 (2004)
3. R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Bredas, M. Lögdlund, W.R. Salaneck, Nature (London) **397**, 121 (1999)

4. G. Margaritondo, A. Franciosi, Ann. Rev. Mat. Sci. **14**, 67 (1984)
5. A. Kahn, N. Koch, W. Gao, J. Polymer Science: Part B: Polymer Physics **41**, 2529 (2003)
6. M. Knupfer, H. Peisert, Phys. Stat. Sol. (a) **201**, 1055 (2004)
7. Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, Appl. Phys. Lett. **68**, 217 (1996)
8. N.J. Watkins, L. Yan, Y. Gao, Appl. Phys. Lett. **80**, 4384 (2002)
9. C. Shen, A. Kahn, J. Schwartz, J. Appl. Phys. **90**, 6236 (2001)
10. S.R. Forrest, Chem. Rev. **97**, 1793 (1997), references therein
11. S. Nannarone, F. Borgatti, A. DeLuisa, B.P. Doyle, G.C. Gazzadi, A. Giglia, P. Finetti, N. Mahne, L. Pasquali, M. Pedio, G. Selvaggi, G. Naletto, M.G. Pelizzo, G. Tondello, AIP Conference Proceedings **705**, 450 (2004)
12. S.I. Fedoseenko, D.V. Vyalikh, I.E. Iossifov, R. Follath, S.A. Gorovikov, R. Püttner, J.-S. Schmidt, S.L. Molodtsov, V.K. Adamchuk, W. Gudat, G. Kaindl, Nucl. Instr., Meth. in Phys. Res. A **505**, 718 (2003)
13. X-ray Photoelectron Spectroscopy (XPS) Database, V. 3.4, `http://srdata.nist.gov/xps/`
14. T.K. Sham, B.X. Yang; J. Kirz, J.S. Tse, Phys. Rev. A **40**, 652 (1989)
15. V. Yu. Aristov, O.V. Molodtsova, V.M. Zhilin, D.V. Vyalikh, M. Knupfer, Phys. Rev. B **72**, 165318 (2005)
16. O.V. Molodtsova, V.M. Zhilin, D.V. Vyalikh, V.Yu. Aristov, M. Knupfer, J. Appl. Phys. **98**, 093702 (2005)
17. T. Schwieger, H. Peisert, M.S. Golden, M. Knupfer, J. Fink, Phys. Rev. B **66**, 155207 (2002)
18. H. Peisert, M. Knupfer, J. Fink, Surf. Sci. **515**, 491 (2002)
19. V.Yu. Aristov, O.V. Molodtsova, V.V. Maslyuk, D.V. Vyalikh, V.M. Zhilin, Yu.A. Ossipyan, T. Bredow, I. Mertig, M. Knupfer, Appl. Surf. Sci., in press
20. Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic, S.R. Forrest, Phys. Rev. B **54**, 13748 (1996)
21. I.G. Hill, A. Rajagopal, A. Kahn, J. Appl. Phys. **84**, 3236 (1998)
22. C. Shen, A. Kahn, J. Appl. Phys. **90**, 4549 (2001)
23. S. Park, T.U. Kampen, T. Kachel, P. Bressler, W. Braun, D.R.T. Zahn, Appl. Surf. Sci. **190**, 376 (2002)
24. N.J. Watkins, L. Yan, Y. Gao, Appl. Phys. Lett. **80**, 4384 (2002)
25. L. Lozzi, S. Santucci, S. La Rosa, J. Vac. Sci. Technol. A **22**, 1477 (2004)
26. T.U. Kampen, A. Das, S. Park, W. Hoyer, D.R.T. Zahn, Appl. Surf. Sci. **234**, 333 (2004)
27. M. Gorgoi, D.R.T. Zahn, Appl. Surf. Sci. **252**, 5453 (2006)
28. M. Gorgoi, D.R.T. Zahn, J. Phys. IV **132**, 337 (2006)