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Growth of Organic n-Conductors on Thin Polymer Films for Use in Organic Field Effect Transistors

W. Michaelis,[1] *C. Kelting,*[2] *A. Hirth,*[2] *D. Wöhrle,*[2] *D. Schlettwein*[1]

[1] Physical Chemistry 1, University of Oldenburg, P.O.Box 2503, 26111 Oldenburg, Germany
[2] Institute of Organic and Macromolecular Chemistry, University of Bremen, P.O.Box 330440, 28334 Bremen, Germany

Summary: Thin films of different polymers - poly(styrene) (PS), poly(methylmethacrylate) (PMMA), poly(vinylcarbazole) (PVCz), poly(vinylchloride) (PVC) and poly(vinylidene fluoride) (PVDF) - were deposited by spin-coating or by vapor deposition. On these polymers, thin films of (hexadecafluorophthalocyaninato)-oxovanadium ($F_{16}PcVO$) were prepared by physical vapor deposition. The growth of these films was monitored in situ by optical spectroscopy. The optical absorbance spectra were analyzed based on the coupling of transition dipoles to obtain information on the intermolecular arrangement of chromophores in the films. In all of these samples, the molecules are oriented with their molecular plane preferentially perpendicular to the substrate surface. This gives the desired overlap of the π-systems for electric conductance parallel to the substrate. Differences in the interactions were detected when deposition temperatures below or above the glass transition temperature of a given polymer were compared. The morphology of the polymer films and the deposited semiconductors were investigated by atomic force microscopy and scanning electron microscopy. The influence of the chosen substrate on the film structure is determined. The optical and electric properties of the films could thereby be influenced and the applicability of such films as active layers in organic thin film transistors is discussed.

Keywords: molecular semiconductor; n-conduction; phthalocyanines; polymer thin films

Introduction

The growth of molecular semiconductor films on polymer substrates is investigated because the polymer can also be used as gate insulators in devices following an all-organic approach. Such an approach allows to avoid high temperatures and thereby ensures a high flexibility with regard to the chosen substrates. Also, it opens the way towards low production costs of envisaged electronic devices.

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The intermolecular arrangement of organic semiconductors in thin films is decisive for their use in electronic devices, such as organic field-effect transistors or diode structures, since it should determine both the charge carrier mobility and optical properties of such films.[1-3] Recently, molecular n-conducting materials like $F_{16}PcVO$ have attracted special interest.[4-9]

Optical absorbance spectroscopy is used as a method to probe the chromophore interactions of the semiconductor molecules.[10] In the present experimental setup these spectra were measured in situ during the growth of the semiconductor films. Aside from the intermolecular arrangement, the morphology of films determines the effective mobility of charge carriers and is probed by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Experimental

The films of PS, PMMA, PVC and PVCz were prepared by spin-coating from a methylcyclohexanone solution on an ITO substrate. The film thickness was determined as 270-300 nm (PMMA, PVCz), 600 nm (PVC) and 700 nm (PS) by using a DEKTAK profilometer. The films of PVDF were prepared by thermal decomposition of PVDF in a crucible, evaporation of the fragments and re-polymerization on the substrate, a process performed in analogy to PVD at a pressure of 10^{-3} Pa and an evaporation rate of 0,5 nm/min on a glass support. The thickness of these films was determined as 110 nm.

$F_{16}PcVO$ was synthesized as described earlier.[11] This compound was purified by temperature gradient sublimation in a three zone-oven (Lindberg).

Thin films of this material were then prepared by PVD under high vacuum conditions (10^{-3} Pa). The evaporation rate was 0.5 - 1 nm/min. The films were grown at two temperatures (at about 323 K or 393 K). Optical absorbance spectroscopy was performed with a light beam perpendicular to the substrate surface using a diode array spectrometer, Ocean Optics PC 2000 with a tungsten lamp HL 2000 LL, which was coupled to the deposition vacuum chamber by optical fibers. To heat the substrates, they were mounted on ITO coated glass, which was used as a resistive heater. The spectra were measured in situ during the film growth.

After deposition and optical analysis, these films were characterized ex situ by AFM (MT-MDT Smena A) in resonant mode and by SEM (Zeiss DSM 940).

Results and Discussion

AFM-measurements of the polymer films made by spin coating showed very smooth surfaces with an average roughness in the range of only a few nanometers (Fig. 1). The PVDF films prepared by PVD had a higher roughness of about 30 nm.

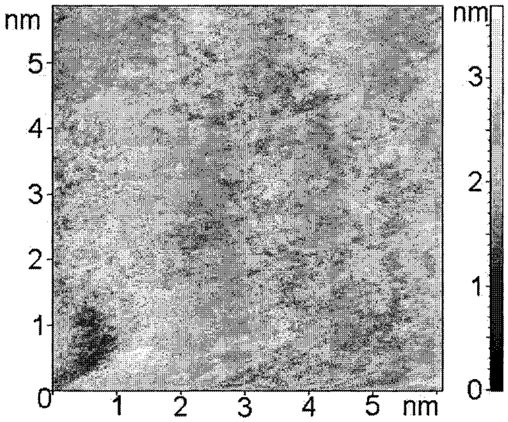

Figure 1: AFM-measurement of a spin-coated PVCz-film on ITO

When $F_{16}PcVO$ was deposited on these polymer films, two different characteristics could be observed depending on the temperature of the substrate during the evaporation. On cold substrates (~ 323 K), the smooth surface of the polymer substrate could be widely preserved during deposition of $F_{16}PcVO$, with a roughness in the range of about 20nm. Generally, these films are too smooth to be measured in SEM in contrast to the films that were prepared at elevated temperature (~ 393 K; Fig.2).

For these films of $F_{16}PcVO$ film morphology could be detected by SEM. In the case of PVCz, small islands have been seen. The same behavior has been found for films prepared on glass at a comparable temperature. On PMMA and PVC, needle-like structures were found that are similar to those reported earlier for films on SiO_2.[12] The film on PS showed a texture that, aside from crystals as on PVC, suggests a growth of $F_{16}PcVO$ that often started from new marked crystallization seeds. A widely homogeneous surface of PS with, however, a few marked defects was thereby indicated when compared with the other polymer surfaces. The formed islands are not so well defined as on PMMA or PVC, but they showed a similar crystalline shape.

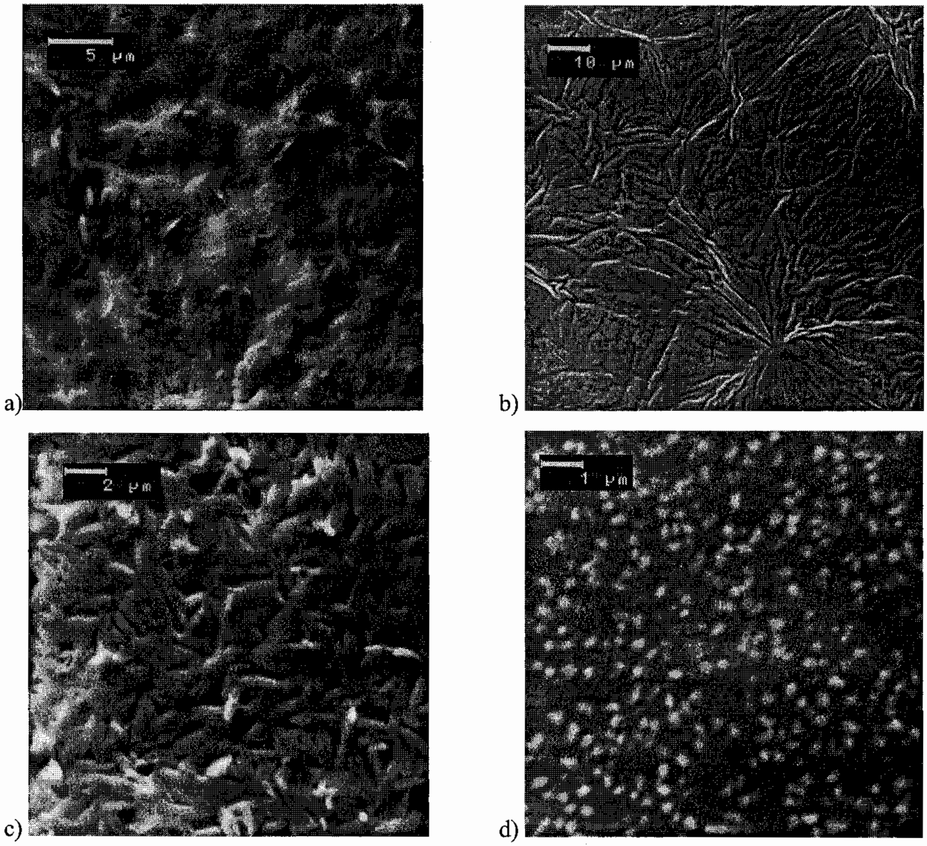

Figure 2: SEM images of F_{16}PCVO deposited on different polymer substrates at 393 K, a) on PMMA, b) on PS, c) on PVC, d) on PVCz

Optical absorption spectra are used to study relative molecular interactions in the films. Spectra of 40 nm F_{16}PcVO on glass, PMMA, PVC, PS, PVCz, and PVDF are depicted in Figure 3. These films were prepared at 323 K. The development of all bands in the spectra was continuous. All spectra were dominated by an absorption band shifted to the blue (~ 670 nm) relative to that of the individual uncoupled molecules in solution (707 nm). A slightly red-shifted band at about 745 nm accompanied this. On glass at elevated temperature (393 K) an additional band appeared at about 830 nm (Fig. 4). This band did not appear on PS and was generally weaker on the other polymer substrates when compared with the film on glass. A transition of the polymers to their visco-elastic state seemed to suppress this band of $F_{16}PcVO$ since it was not detected on the polymer of the lowest glass transition temperature (PS) but it was most clearly detected on those polymers, which were at 393 K still well below their glass transition temperature.

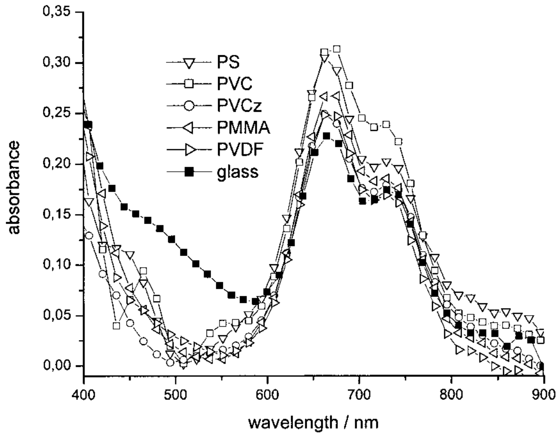

Figure 3: Absorbance spectra of 40 nm $F_{16}PcVO$ films prepared at 323 K

Although small spectral shifts can occur due to different polarizable environments in solids when compared with solvents, the present shifting and splitting of the absorption bands relative to the position in solution could be interpreted within a model based upon the dipole-dipole interaction of the transition dipoles.[10,13] In this model the red shift means a head-to-tail arrangement of the chromophores (J-aggregate), the blue shift a cofacial arrangement (H-aggregate). So it is clear that in all studied films a cofacial orientation of adjacent molecules was dominating. This was accompanied by smaller contributions from a head-to-tail interaction. Since we have observed the individual bands separately in earlier experiments,[14] and since their relative ratio changes even in the present study, we conclude that a mixture of different crystalline phases of $F_{16}PcVO$ was present in the films. The shoulder above 800 nm is caused by a band at 830 nm that has been detected earlier for unsubstituted phthalocyanines and stands for a strongly coupled crystalline phase in which a head-to-tail-arrangement clearly dominates [13].

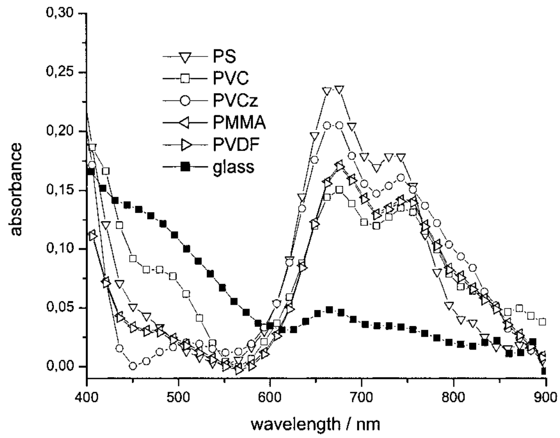

Figure 4: Absorbance spectra of 40 nm $F_{16}PcVO$ films prepared at 393K (on glass only 10 nm $F_{16}PcVO$ on glass)

All films showed a low integral absorbance when normalized to the deposited amount of $F_{16}PcVO$ and when compared with earlier results on alkali halide (100) surfaces [14]. The observed small absorbance for the electric field vector of the incoming light (parallel to the surface) leads to the conclusion that the molecules were essentially standing upright on the surface, because the main transition dipole lies in the molecular plane, so that there was only a weak interaction between the transition dipole and the electric field vector of the light.

Conclusions

Smooth polymer films were obtained by spin coating as well as by vapor deposition that were vacuum-compatible and could serve as a suitable substrate for the growth of thin films of organic semiconductors. The polymers provided a uniform surface for the deposition of phthalocyanines, which then led to the formation of smooth uniform layers of the latter. This was shown in detail for the organic n-conductor $F_{16}PcVO$. By variation of the deposition temperature relative to the glass transition temperature of the polymer, details of the intermolecular coupling and film morphology could be adjusted.

The molecular orientation in the semiconductor films was found in an "edge-on" or "standing" orientation with the molecular plane perpendicular to the substrate surface. This is a highly desired orientation since it offers the possibility of good intermolecular overlap of the aromatic π-systems and thereby provides a fundamental prerequisite for an attractive mobility within the semiconductor film. Regarding possible gate insulators, such a "standing" orientation of $F_{16}Pc$ has been found before only for depositions on amorphous SiO_2. In the present work it is shown that suitable polymer films also provide an interaction that promotes this orientation. They represent promising insulator layers because they can be easily processed, causing minimum thermal stress on device substrates, and thereby allow an all-organic approach to thin film transistors.

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