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Pentacene-gate dielectric interface modification with silicon nanoparticles for OTFTs

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Abstract

We report on the properties of pentacene layers and OTFTs (Organic Thin Film Transistors) deposited on semiconductor-gate insulator interfaces covered with silicon nanoparticles (SiNPs) monolayer prepared by the Langmuir-Blodgett method compared to a reference sample (without SiNPs) prepared in an otherwise identical way. To analyse the structural quality, micro-Raman spectroscopy was employed and the correspondence between thin and bulk phase of the integral intensities peaks ratio (α) at 1154 and 1158 cm^{-1} ($\alpha = Int_{1154} / Int_{1158}$) was evaluated. The AFM analysis of the pentacene layers reveals that the different surface treatment of SiO_2 gate insulator (hydrophobic or hydrophilic) before SiNPs monolayer deposition has a distinct influence on the formation of different pentacene grain size and morphology. We demonstrate the higher time stability of pentacene OTFT and increasing of saturation current ($\sim 2.5 \times$) behavior after storage time if the semiconductor-gate insulator interface is modified using a SiNP monolayer.

1. Introduction

Organic semiconducting thin films have been intensely studied due to their potential applications in organic electronics [1-4]. Pentacene, as one of the most investigated organic semiconductors, is regarded to be one of the leading candidates for the active semiconductor in organic thin film electronics. This is mainly due to its high

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intrinsic charge carrier mobility, the ambipolarity of the charge carrier transport, the excellent interface properties with different organic dielectrics, and the controllable growth of crystalline pentacene thin films. It is well known that the growth process and the quality of pentacene thin films are highly sensitive to the choice of the substrate material, the deposition rate, the substrate temperature, the film thickness, and the purity of the source material. The results show that the morphology, crystal structure and molecular ordering of the first organic monolayer(s) at the pentacene/dielectric interface are essential determinants of carrier transport phenomena. It has been shown that carrier transport is mostly limited by space-charge effects [5]. Therefore, the charge accumulated on the semiconductor-gate insulator interface has great influence on device properties. Many theoretical studies have been carried out to clarify the device physics of OTFTs [6, 7]. Their results call our attention to the control of the accumulated charge below the electrodes and in the channel region, which is crucial for carrier transport properties. One possibility to control accumulated charge is to use silicon nanoparticles (SiNPs) as was demonstrated by Weis [8]. These NPs serve as trapping centers and by design of their density it is possible to control the trapped charge, which has a strong impact on the carrier transport properties.

In this paper, we report on the properties of pentacene layers deposited on semiconductor-gate insulator interfaces covered with SiNP monolayer prepared by the Langmuir-Blodgett (LB) method. We will also demonstrate the behavior of pentacene OTFT where the semiconductor-gate insulator interface is modified using SiNP monolayer. All characteristics are compared to a reference sample (without SiNPs) prepared in an otherwise identical way.

2. Experiment

For studying the growth of pentacene layers on SiNPs we used two different types of samples, A and B. The substrate treatment before SiNPs deposition (before pentacene growth) differs for both samples. In both cases heavily doped silicon wafers were used with a 40 nm thick thermally grown silicon dioxide insulating layer (Supplier: ON Semiconductor). Prior to SiNPs deposition one substrate has the oxide surface cleaned for 10 min with UV light and ozone to obtain a hydrophilic surface (sample B), while the other substrate was treated in Hexamethyldisilazane (HMDS) vapor for 50 hours (sample A), resulting in different conditions for LB deposition. On both substrates the monolayer of SiNPs (Meliorum Technologies, Rochester, NY) stabilized with sodium n-dodecylbenzenesulfonic acid (DBSA) and with size of 5 nm (shown in Fig. 1a), was deposited by the LB method before pentacene evaporation. Because the nanoparticles are covered with DBSA film approximately 2.5 nm thick we have modified (thinned away) this SiNPs cover with UV light for different times (5, 10 and 15 minutes). Pentacene films with a thickness of 40 nm were deposited on top of the SiNPs by thermal evaporation at a pressure of 10^{-3} Pa at 30 °C with a deposition rate of 0.030 nm/s, monitored by a quartz crystal microbalance. No further purification was performed for the commercially available pentacene material (Acros Organic). For device demonstration in the experiments we used top-contact pentacene OTFTs (see Fig. 1b). For these devices after the deposition of pentacene, gold electrodes (source and drain electrodes) with a thickness of 40 nm were deposited on the semiconductor surface. The designed channel length (L) was 20 μm and 50 μm, respectively. The gate width (W) was 2.5 mm for all samples. For comparison, the reference sample C (OFET without SiNPs) was prepared in an otherwise identical way.

Structural properties of the layers were characterized by micro-Raman spectroscopy (Jobin Yvon HR800) at room temperature in backscattering geometry using He-Ne (633 nm) and Nd: YAG (532 nm) lasers. Standard AFM investigations were done using a Park System XE100 in non-contact mode with conductive Cr-Au cantilevers to study the surface morphology and the thickness of the pentacene layers. XRD measurements were carried out using a GE reflectometer (Cu Kα1 radiation). Structural properties of the prepared layers were compared with the reference sample (sample C).
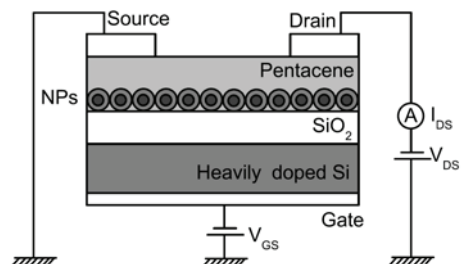

FIG. 1. Schematic illustration of top-contact pentacene OFET with DBSA-stabilized SiNPs of size ~5 nm (distance of nanoparticles ~10 nm).

3. Results and discussion

The structure of pentacene layers is usually characterized by the presence of the thin-film and the bulk phase [9]. To analyze the structure, micro-Raman spectroscopy was employed. The evaluation of the ratio (α) of the integral peak intensities at 1154 and 1158 cm^{-1} (α = Int$_{1154}$ /Int$_{1158}$) provides information on the thin film and bulk phase across the scanned area of pentacene layer. If this ratio is close to 1, the structure is normally suitable for the preparation of OTFTs with high carrier mobility. A ratio of about 0.5 reflects a low fraction of the thin-film phase in the pentacene layer, hence usually low channel mobility in OTFTs. The Raman measurements of our samples where the semiconductor-gate dielectric interface was modified with SiNPs show that the average value of α is between 0.8 and 1.0. We have tested if UV ozone treatment changes α. Fig 2 shows maps of α on a 10×10 μm^2 area for 40 nm pentacene layer grown on the hydrophilic surface of SiO$_2$ gate insulator layer covered with SiNPs monolayer. α depends on SiNP treatment before pentacene deposition as is visible from Fig 2. Using 5 min UV ozone treatment we have obtained pentacene layers with slightly lower α but better structural homogeneity.

X-ray scattering data (not shown) confirm that the films are well-ordered, with well-defined Bragg reflections and narrow rocking widths (0.1 degrees and below), as well as pronounced Kiessig interferences [3, 4].

The AFM analysis of the pentacene layers reveals that the different surface treatment of SiO$_2$ gate insulators (hydrophobic or hydrophilic) before SiNPs monolayer deposition has a distinct influence on the surface morphology as shown in Fig.3a-d. In Fig. 3a and 3b the typical surface

Fig. 2. Raman spectra intensity ratio mapping of 40 nm thick pentacene layer grown on hydrophilic semiconductor-gate insulator (SiO$_2$) surface covered with SiNPs monolayer a) as deposited b) with UV and ozone pretreatment for 5 minutes.

morphology of the 40-nm thick pentacene layer grown on hydrophobic and hydrophilic surface is shown. The formation of large grains suggests preferable 3D pentacene step growth for hydrophobic surface with shallow valleys between grains while for hydrophilic surface the spilled grains are distinctive. The pentacene layers grown on the surface with SiNPs treated by UV and ozone (Fig. 3c, d) shows strongly bound grain peaks and deeper valleys due to the UV ozone treatment in comparison with pentacene layers grown on as deposited SiNPs. The results are comparable with Raman spectral intensity mapping as shown in Fig.2a, b.
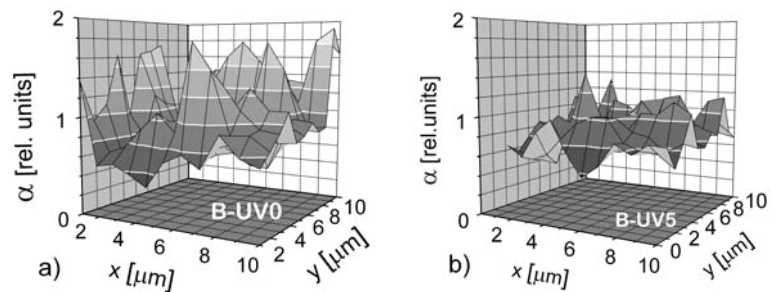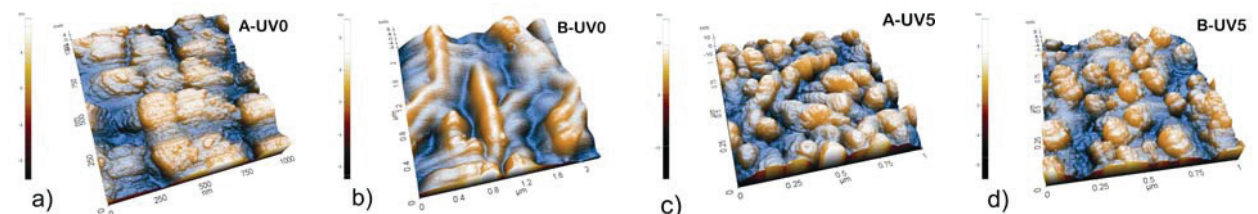

Fig. 3. AFM image of 40 nm pentacene layer grown on the semiconductor-gate insulator (SiO$_2$) interface covered with SiNP monolayer. In Fig. 3a and 3c SiNPs were deposited on a hydrophobic SiO$_2$ surface and in Fig. 3b and 3d SiNPs were deposited on a hydrophilic SiO$_2$ surface. Before pentacene deposition SiNPs were treated for 10 min in UV and ozone (Fig. 3b and 3d) while samples in Fig. 3a and 3c were without this treatment.

Fig. 4 shows the dependence of the saturation current and output characteristics (for U$_G$ = -20 V) as a function of storage time of the top contact OTFT where the pentacene layer was grown on a semiconductor-gate dielectric interface modified with SiNPs (sample A) and without SiNPs (sample C). The samples were measured after storage under ambient conditions for 54 and 85 days, respectively. The saturation current for sample C measured after processing shows 2 times higher saturation current in comparison with sample A after UV treatment (Fig 4a).

Interestingly, saturation current of OTFTs with SiNPs is increasing ($\sim 2.5 \times$) with storage time (85 days) in comparison to OTFTs without SiNPs, which decrease similarly after 54 days (Fig. 4b).
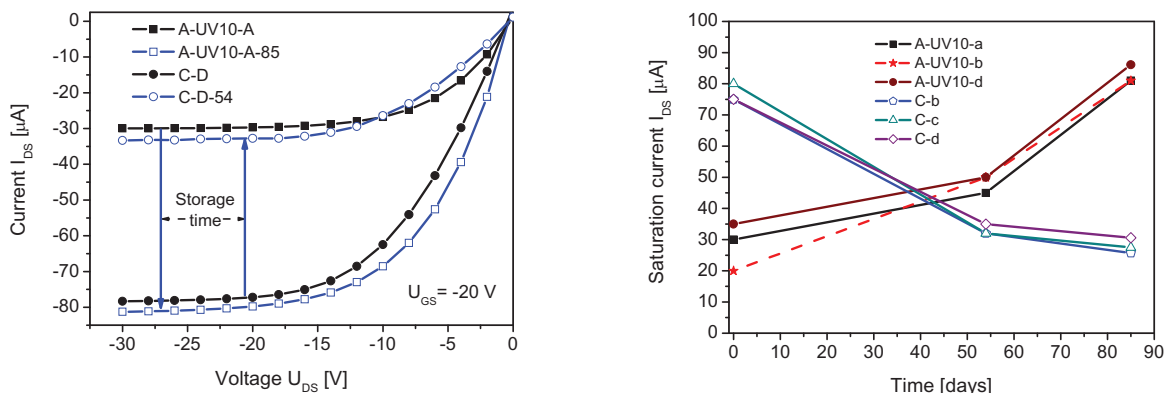

Fig. 4. Time dependence comparison of top-contact pentacene OFET with DBSA-stabilized SiNPs (sample A-UV10) and without SiNPs (sample C) respectively a) output characteristics b) saturation current characteristics.

The reason of higher time stability and increasing of saturation current behavior of pentacene OTFT after storage time where the semiconductor-gate insulator interface is modified using SiNP monolayer may be interpreted by the higher structural quality and possibly the presence of charged defects at the interface. The detailed analysis is presently underway.

4. Conclusion

We have for the first time investigated the structural and electrical properties of pentacene OTFT deposited on the semiconductor-gate insulator interface covered with silicon nanoparticles (SiNPs) monolayer prepared by the LB method and compared these to a reference sample (without SiNPs). The micro-Raman, AFM and XRD measurements confirmed that the pentacene layer deposited on the semiconductor-gate insulator interface covered with SiNPs monolayer on both hydrophobic and hydrophilic surfaces improves crystalline quality. The Raman measurements shows that the average value of α is between 0.8 and 1.0. The improved structural quality of pentacene leads to better OTFTs electrical characteristics mainly saturation current of OTFTs with SiNPs increasing ($\sim 2.5 \times$) with storing time (85 days) in comparison to OTFTs without SiNPs, which decrease similarly after 85 days.

Acknowledgements

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