

University of Groningen

Ordered Semiconducting Self-Assembled Monolayers on Polymeric Surfaces Utilized in Organic Integrated Circuits

Gholamrezaie, Fatemeh; Mathijssen, Simon G. J.; Smits, Edsger C. P.; Geuns, Tom C. T.; van Hal, Paul A.; Ponomarenko, Sergei A.; Flesch, Heinz-Georg; Resel, Roland; Cantatore, Eugenio; Blom, Paul W. M.

Published in:
 Nano Letters

DOI:
[10.1021/nl9032268](https://doi.org/10.1021/nl9032268)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2010

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gholamrezaie, F., Mathijssen, S. G. J., Smits, E. C. P., Geuns, T. C. T., van Hal, P. A., Ponomarenko, S. A., ... de Leeuw, D. M. (2010). Ordered Semiconducting Self-Assembled Monolayers on Polymeric Surfaces Utilized in Organic Integrated Circuits. *Nano Letters*, 10(6), 1998-2002. DOI: 10.1021/nl9032268

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Ordered semiconducting self-assembled monolayers on polymeric surfaces applied in organic integrated circuits

Fatemeh Gholamrezaie, Simon G. J. Mathijssen, Edsger C. P. Smits, Tom C.T. Geuns, Paul A. van Hal, Sergei A. Ponomarenko, Heinz-Georg Flesch, Roland Resel, Eugenio Cantatore, Paul W.M. Blom and Dago M. de Leeuw

Supporting Information

Contact Angle

We determined the contact angle before and after SAM formation on an oxygen plasma treated polymer surface. In Figure S1a and S1b optical micrographs are presented of a water droplet deposited on an oxygen plasma treated polymer surface before and after SAM formation respectively. From these pictures we deduce an increase of the contact angle with respect to water from 30 degrees to 90 degrees that confirms the SAM formation.

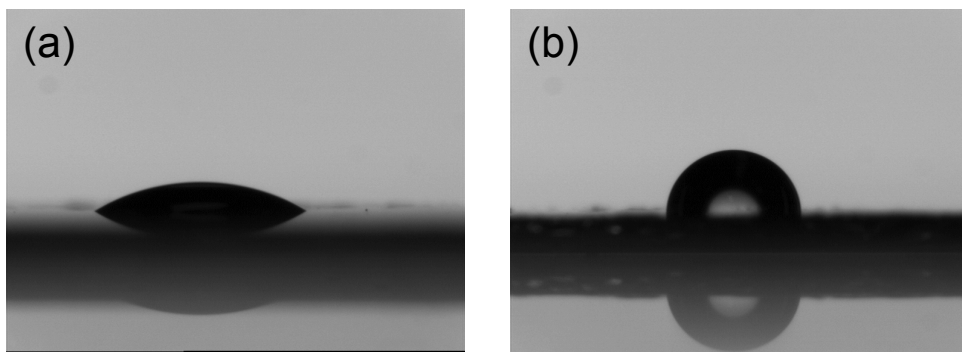


Figure S1. Optical micrograph of water droplet on an oxygen plasma treated polymer substrate before (a) and after (b) SAM formation.

X-ray Photoelectron Spectroscopy (XPS)

The presence and thickness of the monolayer on the polymer dielectric is studied with X-ray Photoelectron Spectroscopy (XPS) before and after deposition of the SAM. Figure S2 shows the peaks for C1s, Si2p and S2p for both samples. Measurements at duplicate positions on each sample are similar.

The XPS spectrum of the reference sample, *i.e.* the oxidized polymer dielectric, shows only peak intensities for C and oxidized C(C-O, C=O and O-C=O) of the polymer dielectric. At small angle more oxygen is found at the surface than at large angle due to the oxygen plasma treatment at the outer surface of the polymer. Additionally, in the C1s-spectrum of the reference sample an electron loss peak is visible, typical for aromatic rings present within the polymer. Si and S peaks are not detected.

After deposition of the SAM on the polymer, the XPS spectrum shows besides C also the Si (organic) and S (R-SH, thiophene) peaks. The C1s electron loss peak characteristic for the aromatic rings of the polymer dielectric is no longer detectable. At both angles, we find much less oxidized C in the C1s-spectrum. Hardly any oxygen is present. The detection of Si and S together with the reduced amount of oxidized C demonstrates the presence of the SAM on the polymer dielectric.

The concentrations C (C-H), S (thiophene), and Si (organic Si) in the SAM on polymer are 82, 14 and 2 at% in agreement with the theoretical values for the SAM. To model the XPS data, we used a stack consisting of two layers: oxidized polymer-layer (C-H, C-O, C-Ox) / SAM layer (C-H, S, Si). A quantitative analysis of the XPS showed that the layer thickness of the SAM is 2.9 nm assuming a densely packed monolayer in agreement with the calculated length of the molecule.

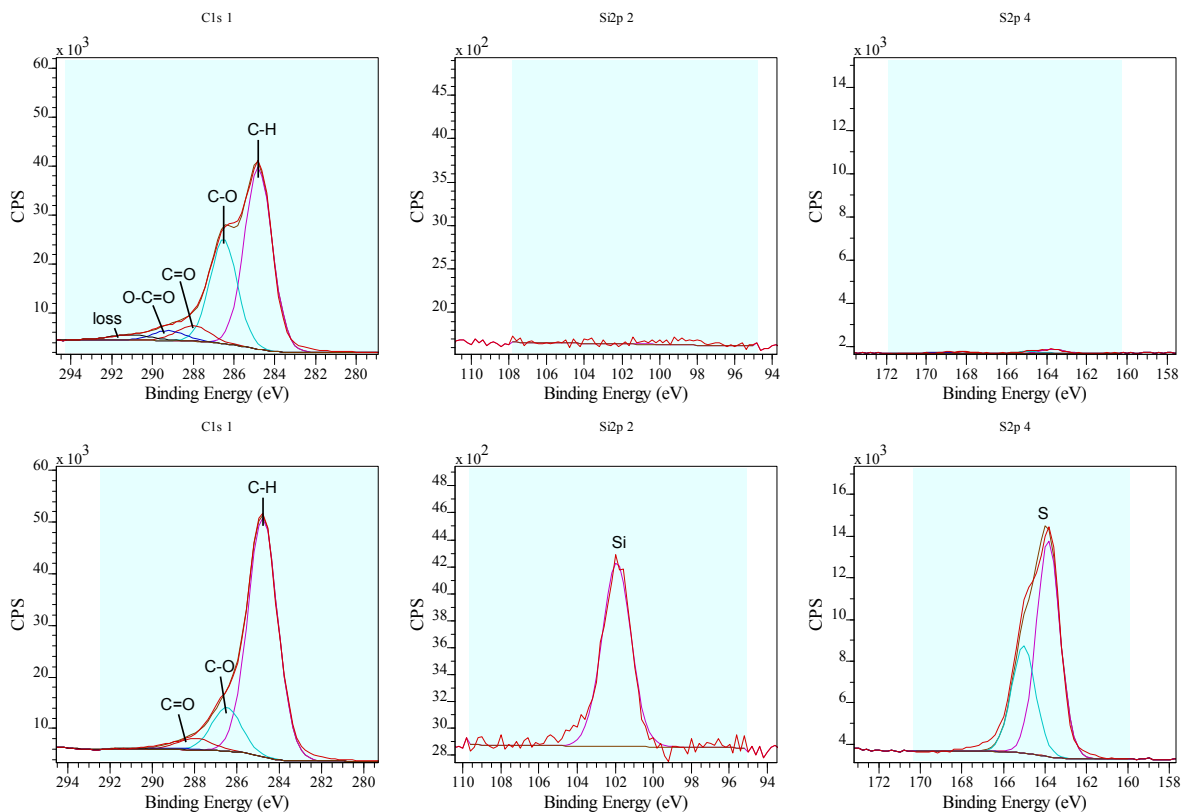


Figure S2: XPS spectra measured at a take-off angle of 75° of an oxygen plasma treated polymer substrate before (upper row) and after (lower row) SAM formation; corresponding spectra are plotted with the same vertical scale. From left to right spectra are shown of the C1s-peak, the Si2p-peak and the S2p-peak. The C1s-peaks have been decomposed into five components, corresponding to four chemical environments; the fifth C1s-component at 291.2 eV is an electron loss effect typical for aromatic bonds. In the S2p-spectrum in the lower row the doublet structure of this peak is visible (doublet distance 1.18 eV).

X-ray reflectivity

To probe the electron density profile in the SAM, X-ray reflectivity measurements were performed, which reveal a smooth and homogeneous layer that corresponds in thickness to one monolayer of the SAM molecule. The reflected X-ray intensity is presented in Fig. S3 as a function of wavevector transfer q_z . The long-wavelength oscillations with maxima at about 0.14 and 0.30 \AA^{-1} originate in the SAM layer. The signal is smeared due to low contrast in electron density between the photoresist substrate and the monolayer. Nevertheless a model assuming lower electron density near the substrate corresponding to the alkyl spacer groups and a second region with higher electron density for the semiconducting thiophene backbone fits the data reasonable well. The critical angle of the photoresist is clearly visible at small q_z . The thickness of the photoresist is beyond the upper resolution limit of the machine and could not be resolved.

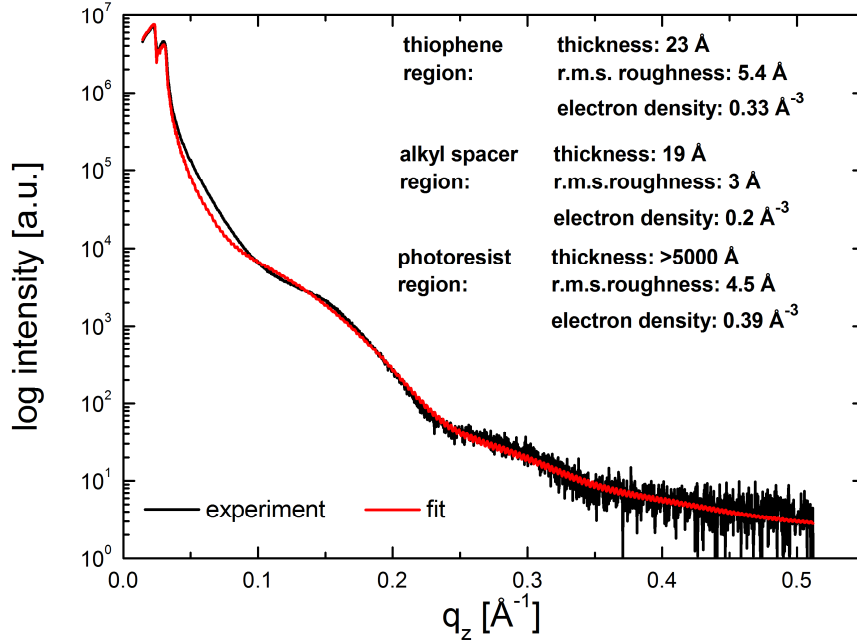


Figure S3: X-ray reflectivity of the SAM measured on the polymer photoresist substrate. The thickness of the substrate is too large for the experimental resolution. The figure gives thickness, r.m.s. roughness and mean electron density of the layers. The signal is smeared due to the strong signal from the substrate.

The X-ray reflectivity measurements have been performed on a Bruker D8 Discover laboratory machine in Bragg Brentano setup using CuK α radiation and a secondary side graphite monochromator. The simulation of the XRR experiments is based on the recursive algorithm of Parratt [1] and the roughness model of Nevot and Croce [2].

Grazing-incidence scattering experiments have been performed at the beamline ID 10b, ESRF Grenoble under technical assistance of F Zontone. The wavelength of the experiment is 1.535Å. A position sensitive 1D detector with vertical soller slits has been used. The angle of incidence for the experiment is carefully chosen and optimized below the critical angle of the polymer substrate at $\alpha_i=0.13^\circ$ to suppress scattering from the amorphous photoresist. However the critical angles of the SAM and the polymer are close to each other which causes a strong background scattering signal. The signal is detected using a position sensitive 1-dimensional detector.

[1] L. G. Parratt, *Phys. Rev.* **95**, 359 (1954).

[2] L. Nevot and P. Croce, *Rev. Phys. Appl.* **15**, 761 (1980).