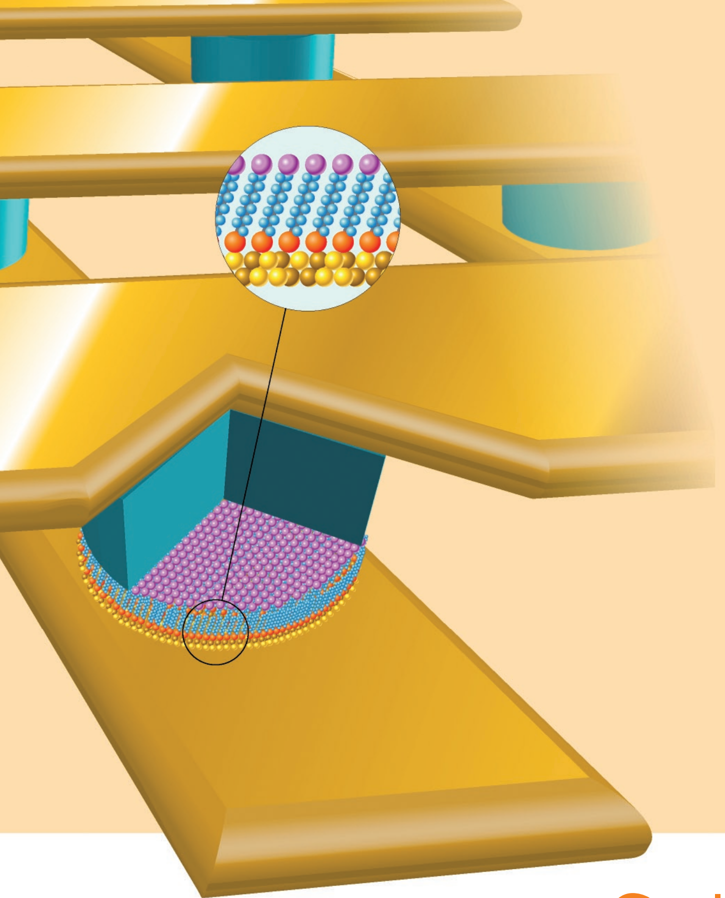

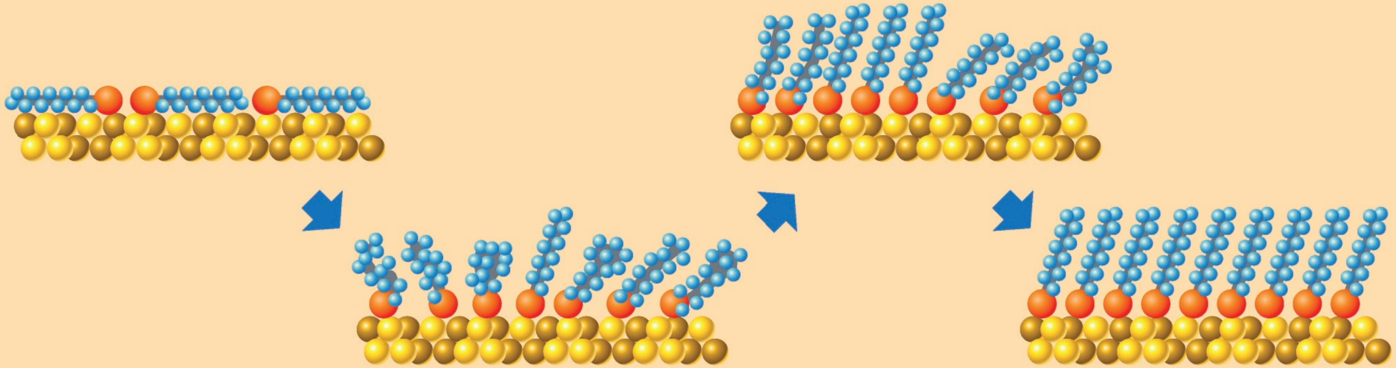

Self-assembled monolayers

a closer look with X-ray Photoelectron Spectroscopy

Self-Assembled Monolayers (SAMs) are used in the area of molecular recognition, surface engineering, micro-contact printing and molecular electronics. The ultimate objective of molecular electronics is to combine different types of functional molecules into integrated circuits. This process of combination should be autonomous by self-assembly. A crucial aspect in the fabrication of molecular electronics is the formation of a high quality self-assembled monolayer. Characterization of different SAMs on gold has been investigated in detail using X-ray Photoelectron Spectroscopy (XPS).

MiPlaza

PHILIPS

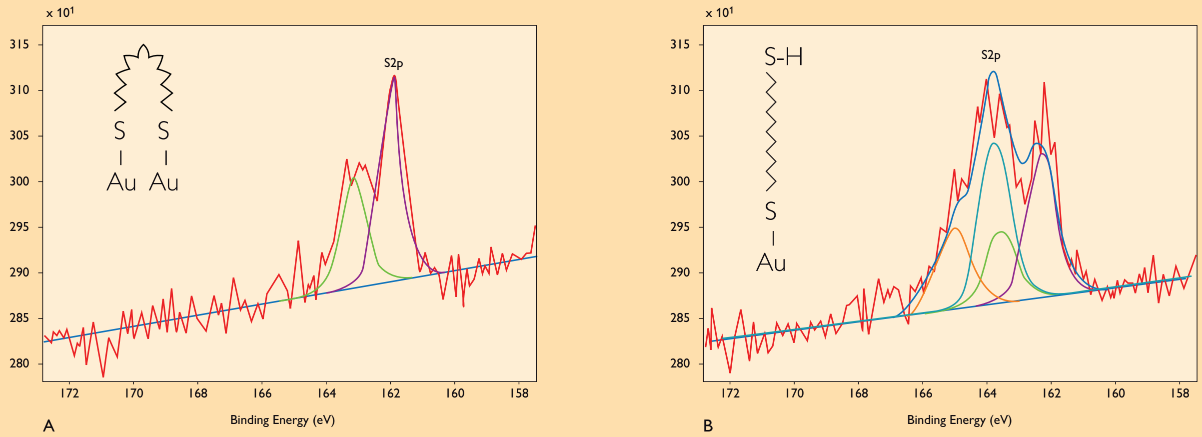

Fig. 1: XPS spectra of the sulphur S2p peak for SAM of alkane-di-thiol made at different concentrations of (A) 0.3 mM and (B) 30 mM.

MiPlaza Materials Analysis
offers a full range of analytical methods and expertise to support both research and manufacturing, serving customers by taking an integral, solution-oriented approach.

World-class expertise – working for you

For more information:
Tel./fax: +31 -40-2748044/42944
E-mail: materials@miplaza.com
www.miplaza.com/materials

Application Note 26
November 2008

Self-assembled Monolayers

A self-assembled monolayer consists of molecules having an anchoring group, a backbone and an end-group. The end-group determines the surface properties of the monolayer and can be used as target molecule for specific recognition. The anchor group of the SAM is attached to the surface of the substrate.
In this context self-assembly means the autonomous organization of components into patterns and structures without human intervention. The spontaneous formation of an array of molecules on a substrate is the ultimate technology for mass production of molecular electronics. This spontaneous formation is achieved by simply submerging a substrate into a solution containing the SAM-molecules dissolved.
A crucial parameter for the performance of molecular electronics is the formation of this self-assembled monolayer onto a metal bottom electrode (see frontpage graphics).

The self-assembled monolayer acts as an isolator and should be densely packed, i.e. defect free, to prevent electrical short circuits. In general, a self-assembled monolayer (SAM) of alkane-di-thiols on gold is used within molecular electronics. The thiol (-SH) group anchors to the gold to form a gold-thiolate (S-Au). XPS provides insights on the SAM formation of alkane-di-thiols on gold.

X-ray Photoelectron Spectroscopy

When irradiating a sample with X-rays, photoelectrons are generated. The generated electrons are collected in a detector and an XPS spectrum is obtained. From the XPS spectrum, raw concentrations of the elements present are obtained. A self-consistent model interprets these raw concentrations. The model gives information of the layer thickness, the composition and the coverage of the SAM on gold.

Alkane-di-thiol formation on a gold electrode

Alkane-di-thiols have two -SH groups. Therefore, two different phases can be formed during the self-assembly process: the looping phase with both –SH anchored to the gold, and standing-up phase having only one -SH attached to gold (schematics in Fig 1). XPS discriminates between the different chemical environments of an element. S bonded to gold (C-S-Au) has a different binding energy than an unbound S (C-S-H). Hence, we are able to distinguish between the looping and standing-up phase of alkane-di-thiols on a gold electrode.
Figure 1 shows XPS results for 1,14-tetradecanedithiol (HS-$C_{14}H_{28}$-SH) on Au for two different concentrations. Low concentration solutions result in the looping phase as we observe only S-Au bonds at 162 eV (1 doublet: 2 peaks). High concentration solutions show the standing-up phase, as both S-Au and C-SH peaks at 162 and 163.5 eV (2 doublets: 4 peaks) are observed. In the latter case the signal emanates from the desired, densely packed monolayer. This packing density can be quantified from the concentrations measured. Further understanding of the self assembly process is obtained by investigating aspects such as cleaning of the metal substrate, variation of SAM preparation and changes in SAM-composition. In conclusion, fabrication of junctions in molecular electronics using alkane-di-thiols can successfully be characterized and optimized using XPS analysis.