Fullerenes C_{60} self-assembled on functionalized surfaces

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Memory devices play an important role in electronics market leading to a growing research interest in the next generation of non-volatile memory cells. Numerous groups [1,2] work on top-down memory cells based on fullerenes C_{60} that are generally embedded in insulating polymers where they act as storage sites. Beside these studies, a reaction path between amines and fullerenes [3] may be used to covalently bind C_{60} on an amine-functionalized surface. Such an approach is interesting since it involves self-assembled monolayers (SAM) [4,5] which constitute a promising strategy to build molecular nano-devices. For applications compatible with microelectronics technology, it is very important to control first the formation of amine-terminated SAMs grafted on silicon, second the grafting of a C_{60} monolayer on top of these SAMs. In this work, we studied these two steps in order to build memory cells using a bottom-up approach based on organic SAMs.
As substrates, we used silicon covered with its native oxide, and Au(111) for scanning tunnelling microscopy (STM) experiments. Surface modification is observed by contact angle measurements, ellipsometry, UV-visible and FTIR spectroscopy, and AFM/STM microscopy. Surface functionalization is performed using aminopropyltrimethoxysilane (APTMS) molecules for Si/SiO_2 surfaces, and aminothiophenol or aminoethanethiol for Au(111). We developed two methods to build APTMS SAMs on Si/SiO_2 substrates. Using APTMS in methanol solution, SAM formation was analyzed in order to obtain the right parameters leading to a single amine-functionalized monolayer. A second original way was studied using a dry deposition method. In the latest, freshly prepared clean substrates are exposed to APTMS vapor under a nitrogen flux, leading to the formation of APTMS SAM. This deposition method allowed us to show there is a minimum waiting time of ~4 hours under our conditions for the monolayer to be grafted on Si/SiO_2. APTMS SAM formation could be monitored using ATR-FTIR spectroscopy. Particularly, the increase of OH absorption band at ~3253 cm^{-1} (Fig.1(a)) may be attributed to the formation of methanol due to the reaction between methoxysilane heads and silicon oxide. Moreover CH_2 band narrowing (Fig.1(b)) indicates the monolayer order is increasing during the grafting process. Fullerenes are then grafted from a toluene solution on these amine-functionalized SAMs. Two deposition conditions are compared: at room temperature and at high temperature under solvent reflux. AFM/STM experiments allowed monitoring fullerene deposition by either imaging (Fig.2) or I-V characteristics (Fig.3). Further studies are addressed such as thermal deposition of fullerenes [6], Surface Enhanced Raman Scattering on fullerenes grafted on nanostructured amine-modified gold substrates, and electronic transport properties of those C_{60} SAMs via evaporated metallic contacts.

References:

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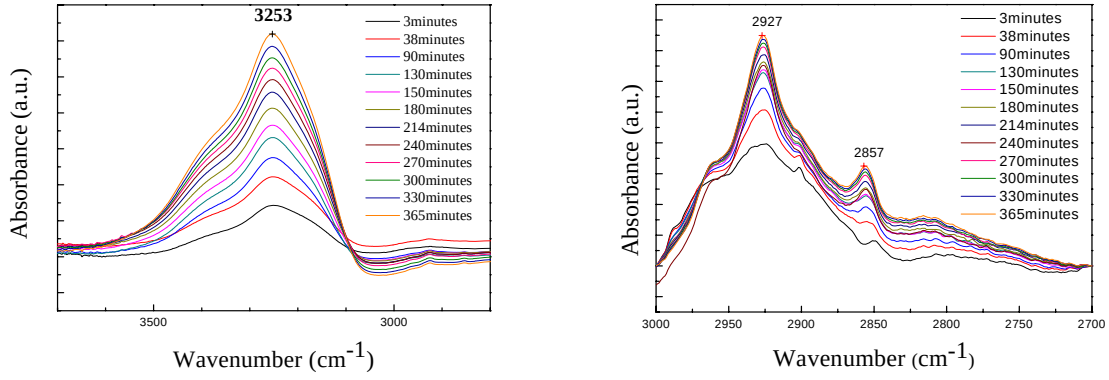
Figures:



(a) (b)

Figure 1. ATR-FTIR spectra of dry-deposited APTMS SAM showing (a) the increase of OH absorption band,(b) the CH_2 band narrowing with time.

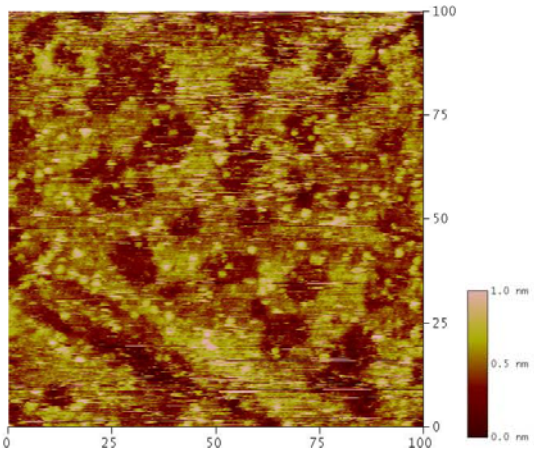


Figure 2. STM (100nmx100nm) image of C_{60} molecules grafted under reflux during 24 hours on NH_2 (aminoethanethiol) functionalized Au(111).

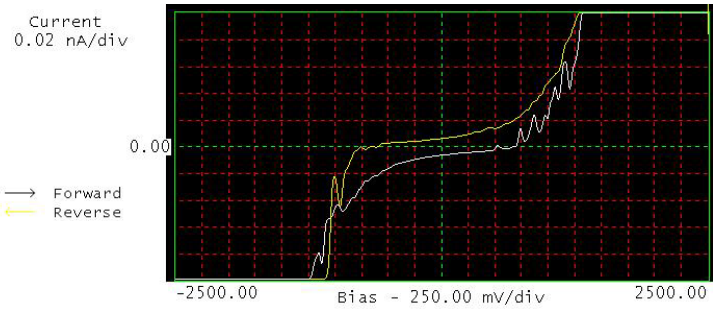


Figure 3. STM I-V characteristic of C_{60} molecules grafted under reflux during 24 hours on NH_2 (aminoethanethiol) functionalized Au(111).