ROLE OF LABILE BONDING IN STOCHASTIC SWITCHING OF MOLECULAR CONDUCTANCE STUDIED BY STM

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Due to miniaturization of CMOS devices new memory cells with high density and low-power consumption are investigated. Molecular switches are likely to be among the most basic and important components of future molecule-based electronic devices. In the literature, on-off switching effect has been reported with phenylene-ethynylene oligomers bonded to gold via S-Au, using nanopore junctions [1] and scanning tunneling microscopy (STM). In these STM studies, molecules of interest have been inserted in an alkylthiol self-assembled monolayer (SAM). The observed stochastic conductance switching has been explained by conformational changes through aromatic ring rotation [2] or molecular hybridization changes at the interface with gold [3]. However, independent STM studies on SAMs on gold have reported similar stochastic switching effects for thiol molecules which cannot exhibit any conformational changes [4]. A thiol bond breaking/reforming mechanism was invoked, due to the labile nature of thiol bonding. Potential use of such conductance switching for molecular memory cells requires determining whether it is intrinsic to specific molecules or due to a bond fluctuation mechanism. For this purpose, comparative experiments need to be carried out on molecules more strongly bonded to the substrate. In this work, we compare the influence of S-Au labile bond versus C-Si stronger covalent one in obtaining a stochastic conductance switching of terthiophene molecules (3T). First we prepared binary SAMs of small bundles of 3T dispersed in dodecyl (DD) matrix, both on Au(111) using thiol-ended molecules and on hydrogenated silicon surface H-Si(111) with molecules bearing a vinyl reactive head. For this purpose, terthiophene-thiol and terthiophene-allyl molecules were synthesized. If obtaining binary SAMs on Au(111) is well known [5], growth of binary SAMs on H-Si(111) was studied using ellipsometry, contact angle measurements and scanning probe microscopy in order to obtain the right conditions giving isolated 3T molecules in DD. Then, we performed STM experiments on these binary SAMs, using the apparent molecular height of 3T above DD matrix as a measure of electronic conductance. We observed stochastic switching events for S-Au bond as reported in the literature. A statistical analysis of molecular blinking was carried out. However we show that stochastic switching is hindered in the case of C-Si bond. These results allow attributing the origin of published stochastic switching observations to a bond fluctuation mechanism. Moreover this work shows that silicon is a suitable substrate for developing molecular memory cells both avoiding stochastic switching and being compatible with microelectronics technology.

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