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Effect of Doping on Electronic Transport through Molecular Monolayer Junctions

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Modern electronics is based on the ability to dope semiconductors, that is, to purposely introduce small amounts of impurities to control the electronic properties of the material. A similar approach is used in organic electronics, although impurity concentrations are generally significantly higher than those used for materials such as Si and GaAs. The approach to molecular electronics that we investigate uses molecular monolayers, rather than a single molecule, between electrodes. In such systems, both properties of individual molecules and collective properties come into play, but an unspoken criticism is that transport, measured across the monolayer, may well be dominated by uncontrolled defects in the monolayer. One way to unambiguously address this issue is to explore "doping" such monolayers, so as to measure changes in charge transport after introducing defects or impurities. However, this process can only work if electronic transport across the original layer is not dominated by defects; that is, the monolayer has sufficiently low defect and impurity density.

Recently, we reported transport measurements through alkyl monolayers bound to oxide-free Si and contacted by Hg on their other end. These monolayers have sufficiently high structural and electronic quality that they act as ideal insulators in this MIS-like structure.[1] This is clearest with *n*-Si. Then, as predicted by MIS theory,[2] transport at reverse or low forward bias is dominated by thermionic emission (TE) over the barrier of the Si and by tunneling across the molecular monolayer at higher forward bias.[1] In particular, transport via TE, more than any other common characterization method tried so far,[3] was found to be extremely sensitive to the monolayer quality.

Alkanes are well-known to be affected by X-ray, UV, and electron irradiation,[4−9] and indeed, we found from UV photoemission spectroscopy (UPS), inverse photoemission spectroscopy (IPES), and near-edge-X-ray absorption fine structure (NEXAFS)[10] that alkyl monolayers are also changed by such irradiations. In UPS, this is reflected by the appearance of electronic states between the highest occupied molecular orbital (HOMO) of the adsorbed alkyls and the Fermi level, E_F. The NEXAFS results point to C═C formation in the alkyl chains as one of the irradiation-induced effects, in agreement with what is known for alkanes and similar systems.[11−16] Here we demonstrate the effect of these changes in the monolayer on the electronic charge transport through $Si-CH_2-(CH_2)_{12}-CH_3$//Hg junctions.

The alkyl chain monolayers were prepared, as described previously,[3] on *n*-Si(111) 1−15 Ω·cm. The changes in the monolayer were induced by a 10 min irradiation with 100 eV electrons (from an electron flood gun) at a current density of ~0.8 μA/0.1 cm^2, either in a Kratos AXIS-HS XPS instrument at the Weizmann Institute or in a home-built UPS system at Princeton University. Detailed conditions were described elsewhere.[3,10] In both cases, the ultrahigh vacuum prevented contamination of the sample during irradiation and also allowed in situ characterization, before and after irradiation. Current−voltage ($I-V$) measurements on the molecular monolayer were done, ex situ, as described elsewhere,[3] after contacting the layer with a 99.9999% pure Hg drop. Figure 1 shows the effect of irradiation on the C KVV Auger spectrum. Before electron irradiation, the spectrum shows two well-defined features at ~257 and ~263 eV. After irradiation, these two peaks merge and a broadened spectrum is obtained, with a ~2 eV shift of its edge toward higher kinetic energy. This phenomenon was already interpreted in terms of disorder in the monolayer[15] which, in our case, is presumably due to the formation of intramolecular[11] C═C and intermolecular[12] C−C bonds. We can interpret the tail shift in the Auger KVV transition as a shift of the valence density of states and, thus, as the emergence of new states near the top of the valence band, consistent with previous UPS results.[10]

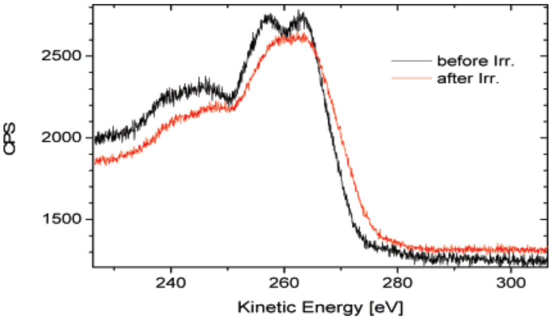

Figure 1. The X-ray-induced C KVV Auger spectrum of a *n*-$Si-C_{14}H_{29}$ sample, before (black) and after (red) electron irradiation, measured with Al Kα X-ray source.

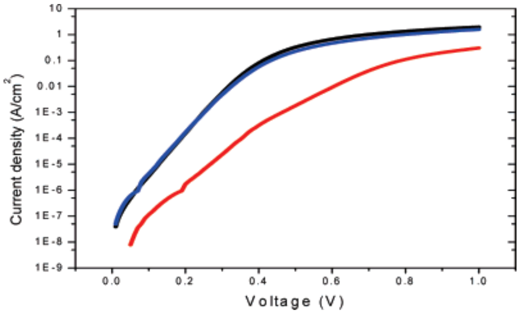

Figure 2. $J-V$ curves for *n*-$Si-C_{14}H_{29}$/Hg junctions, (red) nonirradiated monolayer, (black) freshly irradiated, (blue) irradiated monolayer remeasured after 1 week. Bias is applied to the Si, and the Hg drop is grounded. The measurements start at 0 V. A complete curve, including the reverse bias range, is given in the Supporting Information.

$I-V$ characteristics, taken before and after irradiation, are compared in Figure 2, where nominal current density, J, based on the geometric contact area, is plotted against applied voltage. Note that all of the curves are obtained on the same sample, only part of which was irradiated. Before irradiation, the sample is highly uniform over its entire area (1 × 1 cm^2) in terms of $I-V$

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10.1021/ja071960p CCC: $37.00 © 2007 American Chemical Society

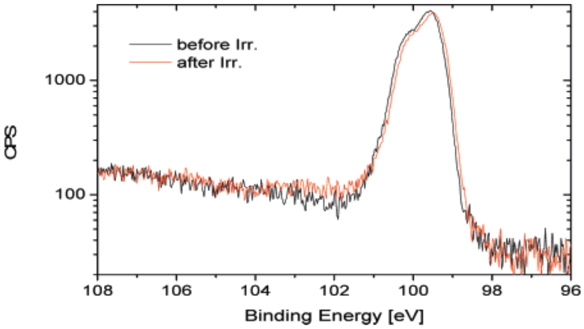

Figure 3. The XPS Si2p line of a n-Si−$C_{14}H_{29}$ sample, before (black) and after both irradiation and electrical transport measurement (red). Note the semilogarithmic scale and the minute amount of SiO_x at ∼103 eV.

characteristics. After irradiation, the nonirradiated part of the sample retains the $I-V$ characteristic expected for a high quality monolayer of C14 alkyls.[3] However, the irradiated part shows a 1−2 orders of magnitude enhancement of the current in the voltage range, where TE dominates transport in nonirradiated samples, and 1 order of magnitude increase in the voltage range, where tunneling dominates transport. These changes scale with irradiation time. We ascribe these changes to defects created in the monolayer by irradiation. If the samples are stored in inert atmosphere for up to 7 days, these characteristics do not change.

Figure 3 compares the Si2p XPS lines of a fresh and an irradiated sample, where the latter was used for electrical transport measurements (with Hg contact) as well. The spectrum from the fresh sample does not show any significant oxide, consistent with our earlier report on high quality layers.[3] Following electron irradiation and exposure to ambient (for the electrical transport measurements with Hg as contact), only a minute amount of silicon oxide is detected (102−104 eV) on the irradiated areas where the Auger C KVV spectrum is broadened. This amount is too small to account for the changes in electrical transport, based on the shape of the $I-V$ characteristic, which is very different from those obtained on samples with oxide.[3] Considering the treatment on the sample, this result shows that irradiation does not significantly affect the density of the monolayer because the interface is still well protected from the ambient. Consequently, not all molecules are affected; that is, we are "doping" the monolayer. The very slight (∼0.1 eV) shift to lower binding energies of the Si2p core level after irradiation (Figure 3) indicates a change in band bending, the implications of which will be discussed in detail elsewhere.

The $I-V$ characteristics of the irradiated samples can be analyzed and compared with those of the nonirradiated samples. In the low voltage range, where TE over the barrier of the Si dominates, transport through a nonirradiated sample yields a barrier height (BH) and an ideality factor (n) of 0.90(±0.01) eV and 1.5(±0.1), respectively. These values are quite similar to those deduced earlier for virgin high quality monolayers.[3] If we assume that after irradiation the dominant transport mechanism in this voltage range does not change, the BH and n values calculated from the data are 0.84(±0.01) eV and 1.1(±0.1), respectively. An ideality factor so close to 1 (in an MIS structure) indicates a nearly negligible voltage drop in series with the space charge layer (e.g., over the monolayer).[17]

As mentioned above, the previously reported irradiation-induced changes in the UPS, on the one hand, and the changes in NEXAFS spectra[10] and the shift in the C KVV threshold (Figure 1), on the other hand, show that new electronic states are formed between the electrode Fermi level and the HOMO and LUMO of the molecule, respectively. These states, which are attributed in part to C═C bond formation, based on the NEXAFS results,[10] can explain the observed current enhancement for both transport regimes. In the TE regime, the current increases with a steeper slope than for the virgin sample, corresponding to an ideality factor close to unity. Assuming that irradiation does not significantly reduce the thickness of the monolayer, the decrease in the ideality factor can be explained by an increase in the number of interface states with energy levels within the Si gap.[17] In the voltage range where transport is dominated by tunneling (in virgin samples), the current enhancement is presumably due to an increased density of states between the HOMO and LUMO of the molecules throughout the monolayer. Such an increase facilitates transport mechanisms such as hopping, trap-assisted tunneling, or TE, an issue that we are currently investigating. Disordering of the monolayer, though possible, cannot account for the observed current increase since electron transfer through disordered hydrocarbon chains is less efficient than through ordered ones.[18,19]

In conclusion, irradiation-induced effects, most likely C═C bonds and C−C cross-links in relatively defect-free alkyl monolayers, introduce new states between the HOMO and LUMO gap of the alkyl chain. These states strongly affect electronic transport through the monolayer. This doping effect (see Supporting Information for discussion of the use of the doping concept here) can clearly be distinguished from effects due to defects in as-prepared layers, which in turn suggests that the overall layer density is not affected. Our results suggest, therefore, a way to extend significantly the use of monolayers in molecular electronics.

Acknowledgment. We thank E. Umbach (Wuerzburg University) and A. Salomon (WIS) for stimulating discussions, the Israel Science Foundation (Jerusalem), the Minerva Foundation (Munich), and the Kimmel Centre for Nanoscale Science and, at Princeton, the National Science Foundation (DMR-0408589) and NSF MRSEC (DMR-0213706) for partial support. D.C. holds the Schaefer Energy Research chair.

Supporting Information Available: Reverse bias $J-V$ characteristics, complete ref 10, and the concept of doping. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA071960P