Understanding the Assembly of $\pi$-Conjugated Dithiol Molecules on GaAs

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Introduction

The assembly of alkane-based molecular layers on metals (e.g. Au, Ag, Pt)\textsuperscript{1-4} and, to a smaller extent, on semiconductors (e.g. GaAs, Si)\textsuperscript{4-6} has been investigated in detail. Such chemistries, although potentially valuable in surface engineering and patterning\textsuperscript{7,8}, cannot facilitate charge transport on the molecular level due to their backbone saturation. On the other hand, $\pi$-conjugated systems are capable of intramolecular charge transport and are therefore potential candidates for molecular wires and electronic devices whose electrically-active component consists of a single molecule\textsuperscript{9-11}. Assembly of such molecules, however, has been challenging and not thoroughly investigated. Here, we report solvent and substrate effects on the assembly of n-phenyldithiols ($n = 3, 4$). The coverage and the average molecular orientation on Au are not sensitive to solvent composition. In sharp contrast, the quality of the molecular assembly on GaAs varies drastically with solvent type.

Experimental

As synthesized, the n-phenyl-containing molecules ($n =$ number of phenyl rings along the backbone) are protected by thioacetyl endgroups. The protected molecules are first dissolved in either tetrahydrofuran (THF), ethanol (EtOH), or a THF/EtOH mixture at 50 µM. A small excess of ammonium hydroxide (NH$_4$OH) is then added to facilitate an acid/base reaction with the acetyl endgroups, resulting in thiol (-SH) termini. Au-coated silicon wafers (with a Ti strike layer) or freshly-etched GaAs substrates are subsequently immersed in the solution. Assembly is carried out over a period of 24 hours in a nitrogen atmosphere ($< 0.1$ ppm O$_2$ and H$_2$O) to prevent oxidation of the thiol endgroups. While EtOH is the most common solvent for assembling thiol molecules, the longer n-phenyldithiols ($n = 4$), in their protected forms, are virtually insoluble in EtOH. In contrast, all of the protected molecules ($n = 1 \ldots 4$) are soluble in THF. THF, however, is a poor solvent for the deprotecting agent, NH$_4$OH. In light of such a solubility conflict, we chose to investigate the assembly of the n-phenyldithiols from EtOH/THF co-solvents.

Results and Discussion

To verify molecule/substrate bonding, X-ray Photoelectron Spectroscopy (XPS) was carried out on freshly-assembled molecular layers on Au and GaAs. High-resolution scans were collected in the S 2p (155-170 eV), Ga 2p (1110-1125 eV), As 3d (30-50 eV), O 2p (525-540 eV), Au 4f (80-95 eV), and C 1s (280-295 eV) regions. As expected, we observe two doublets in the S 2p region attributable to at least two distinct sulfur environments: sulfur bonded to the substrate, and free thiol endgroups. In fact, the high-resolution S 2p spectra for molecular assemblies on both Au and GaAs are qualitatively similar. Quantitative analysis, however, indicates that the doublet assigned to the sulfur-substrate bond is broader for molecular layers on GaAs. This observation suggests that the number of non-equivalent bonding sites is higher on GaAs than on Au, which can be attributed to the presence of both S-Ga and S-As bonds. Permanent chemical bonding at the molecule/substrate interface is further
corroborated by the presence of additional peaks, assigned to Ga-S and As-S, in the Ga 2p and As 3d regions, respectively.

Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy was employed to examine the surface coverage and molecular orientation on Au and GaAs. High-resolution c-edge spectra reveal that the molecules assembled on Au from THF, EtOH, and co-solvents exhibit similar molecular coverage, thereby suggesting that assembly on Au is insensitive to solvent composition. In contrast, the molecular coverage on GaAs monotonically decreases with increasing amounts of THF in the assembly solvent mixture. While the exact origin of this observation is still under investigation, we believe it can be attributed to the reactivity of freshly-etched GaAs substrates.

NEXAFS spectra collected at multiple x-ray incident angles reveal that both tri- (n = 3) and quater-phenyldithiol (n = 4) are well-ordered on Au having molecular orientation independent of solvent type. In fact, fitting our data to a geometrical model suggests that TPDT and QPDT on Au are on average tilted ~32° and ~30° from the substrate normal, respectively. In contrast, the lateral order in the molecular layers on GaAs decreases with increasing amounts of THF in the assembly solvent. In particular, TPDT regresses from a well-ordered layer with the molecules tilted on average ~34° from the substrate normal to a laterally disordered layer as we change the assembly solvent from pure EtOH to pure THF. Similar trends are observed for QPDT.

Our XPS and NEXAFS results show that the assembly of n-phenyl dithiols (n=3, 4) on Au is independent of solvent composition, suggesting that low solubility of NH₄OH in THF does not impact molecular assembly. In sharp contrast, the molecular assembly on GaAs is extremely solvent-sensitive; the quality of these assemblies varies from very well ordered (with an average molecular axis tilt of ~30° from the substrate normal) to completely disordered depending on the solvent type.

References