## FUNCTIONALIZED SILOXY-ANCHORED MONOLAYERS WITH EXPOSED AMINO, AZIDO, BROMO, OR CYANO GROUPS Natarajan Balachander and Chaim N. Sukenik\*

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Summary: The creation of new, uniformly functionalized, surfaces has been achieved with mono layers bearing  $NH_2$ ,  $N_3$ , Br, or CN functional groups.

The use of trichlorosilyl terminated amphiphiles to form stable, ordered, self-assembled, monolayer films is well established<sup>1</sup>. Functionalization of the exposed face of such surfaces is an important problem with many potential ramifications<sup>2</sup>. Incorporation of reactive functionality, like amines, is particularly desirable and correspondingly difficult. We report herein the creation of such monolayer surfaces by a combination of self-assembly and subsequent in-situ modification.

Bromide I is made from commercial  $\omega$ -undecenyl alcohol in >40% overall yield. Reaction of I with SiCl<sub>3</sub>H (neat, cat H<sub>2</sub>PtCl<sub>6</sub>) yields II in 70% yield. Displacement of the Br in I with CN (NaCN/DMSO, 73%) and treatment of the unsaturated nitrile with SiCl<sub>3</sub>H (as above, 82%) yields III. All yields are for distilled materials<sup>3</sup>.

 $\begin{array}{c} C_{11}H_{21}OH & \frac{1)MesC1 & 2)LiBr}{3)Mg, & C_{5}H_{10}Br_{2}} > H_{2}C=CH-C_{13}H_{26}-CH_{2}-Br & \frac{SiCl_{3}H}{H_{2}PtCl_{6}} > SiCl_{3}-CH_{2}-CH_{2}-C_{13}H_{26}-CH_{2}-Br \\ II & II \\ I & II \\ I & \frac{NaCN}{II} > H_{2}C=CH-C_{13}H_{26}-CH_{2}-CN & \frac{SiCl_{3}H}{H_{2}PtCl_{6}} > SiCl_{3}-CH_{2}-C_{14}H_{28}-CH_{2}-CN \\ III \\ I$ 

Deposition of these surfactants as self-assembled monolayer films was done from 0.02 M solutions in dicyclohexyl. All surfaces on which monolayers were formed had been pre-cleaned by an Argon plasma. To provide a well studied reference system for our new films, we used monolayer films of octadecyltrichlorosilane (OTS, commercial).<sup>1,4</sup>

Monolayer characterization was based on wetting properties, IR, and ESCA measurements. Whereas OTS (deposited on glass or on Si ATR crystals) gave films with contact angles to water  $>110^{\circ}$  and which were completely oleophobic, water contact angles for II were  $81-84^{\circ}$  and for III were  $69-74^{\circ}$ . Neither of these new films was oleophobic. ATR-FTIR spectroscopy showed comparable intensity polymethylene stretches (2920 and 2850 cm<sup>-1</sup>) for monolayers made of II and III, and the expected (weak) band at 2247 cm<sup>-1</sup> for the CN group of films made from III. ESCA analysis of these monolayers showed the expected bromine signal for monolayers of II and nitrogen signal for monolayers of III (72 and 403 ev respectively<sup>5</sup>).

The monolayer packing of II could be assessed by reduction to the OTS-like hydrocarbon

using LiAlH<sub>4</sub>/Et<sub>2</sub>O. This resulted in the appearance of the IR band expected for a terminal methyl group (2960 cm<sup>-1</sup>), as is seen for OTS. Moreover, this new (reduced) surface has greatly increased contact angles with water and is oleophobic. These changes argue for efficient reduction of the terminal bromide and that the close-packing of the bromide-terminated monolayer is comparable to that of OTS.

Monolayers of II and III were used to create surfaces with pendant amino groups. The nitrile groups of films derived from III were reduced either with  $BH_3/THF$  or with  $LiAlH_4/Et_2O$ . The cyano IR band dissappears and the water contact angle on the reduced surfaces is 52-60°. NaN<sub>3</sub>/DMF treatment of the bromide terminated surface from II, results in the appearance of an IR band for an alkyl azide at 2098 cm<sup>-1</sup>, disappearance of the Br ESCA signal, and a water contact angle of 70-71°. Reduction of this azido-surface with LiAlH<sub>4</sub>/Et<sub>2</sub>O results in disappearance of the azide IR band and generation of a surface with water contact angles of 55-60°. Comparable nitrogen ESCA signals are obtained from the amino-surfaces whether derived from II or from III. The close-packing of II, coupled with ESCA and IR monitoring of the bromide to azide to amine sequence, is strong evidence for efficient functional group interconversion and for the integrity and packing of these amino-surfaces.

An additional advantage of II and III is their ability to self-assemble on Ge crystals. A limitation of the functionalizable amphiphile  $\omega$ -hexadecenyltrichlorosilane (HTS)<sup>2a</sup> is that its  $\pi$ -bond prevents efficient self-assembly on the surface of germanium<sup>4a</sup>. II and III are deposited on Ge to yield ordered monolayer films comparable to those described above<sup>6</sup>. This bodes well for the construction of thin film microelectronic devices on Ge wafers.

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