Supporting information for

Structure of thiol self-assembled monolayers commensurate with the GaAs (001) surface

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Discrete tilts.

In order to achieve the same orientation of all the molecular headgroups on a flat surface (the assumption usually made to fit experimental IR data) while preserving the densest packing of thiols, only discrete values of tilt and twist angles are allowed. This is similar to the discrete adsorption site spacing allowed to achieve thiol chains interlocking (i.e. dense packing), obtained in the fixed-surface approach.

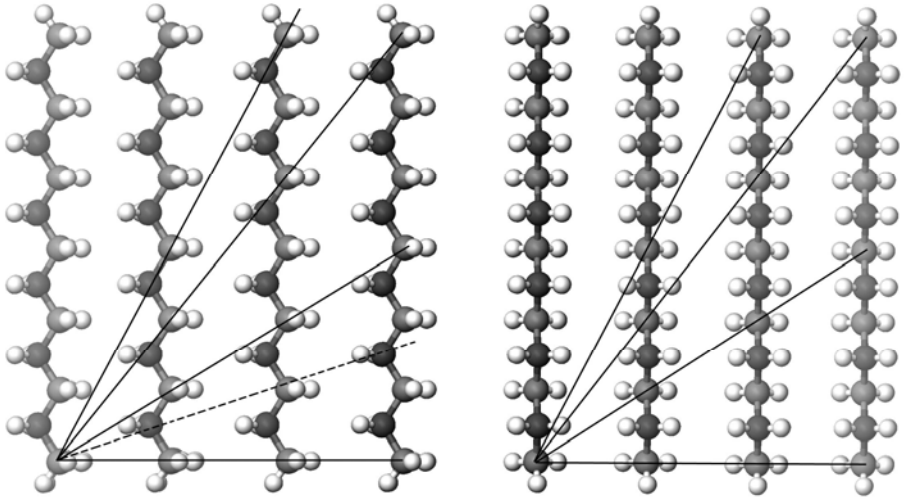

Figure 1. Tilt angles leading to the flat-surface condition for the monoclinic bulk alkanes structure. Solid lines indicate the position of the surface providing the same orientation of all head-groups, dashed line – changing the headgroup orientation of every second molecule.

To achieve the flat surface condition, every next row of thiols should be shifted by equal amount of carbons (or cut by a plane through them, as in Fig. 1). In order to achieve the same orientation of all headgroups this amount should be even. Otherwise, the headgroups would successively change their orientation from row to row, as shown by dashed line. Only the tilts along directions perpendicular to the translation vectors of the crystal structure are allowed, i.e. 22° twist (Fig. 1a) and 90° twist (Fig. 1b), and their vector sum. This results in allowed tilts of 32°, 52°, 62°, … for both 22° and 90° twists, and 36°, 47°, 50°, 55°, 59°, 61°, 65°, … for combinations of tilts in these two directions, with the twist angle varying with tilt.

Estimation of the GIXRD peak directions for model structures.

The GIXRD peaks are formed along directions where Bragg diffraction condition is satisfied, i.e. where distinct planes formed by carbon atoms of the SAM are present.

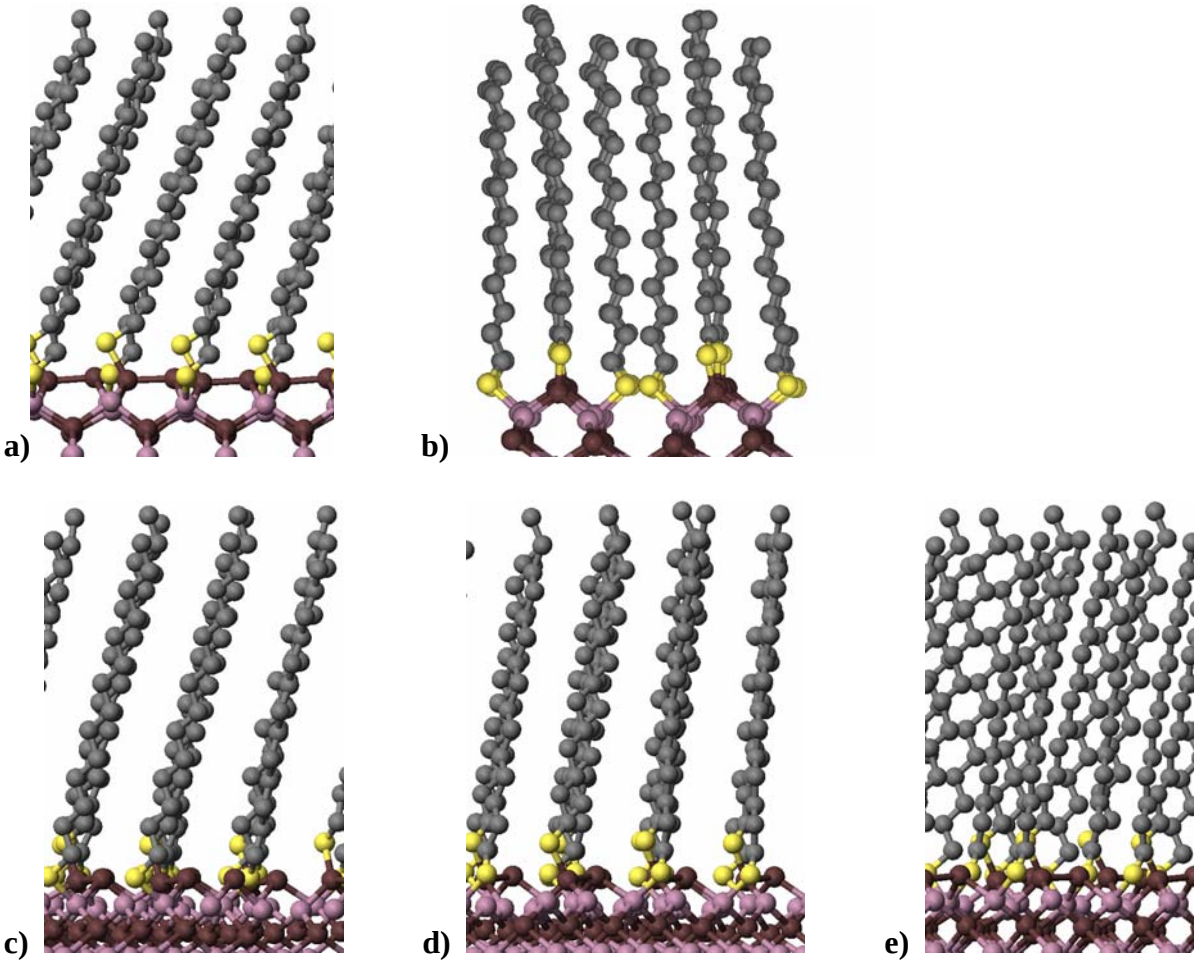

Figure 2. View through SAM along different directions parallel to the GaAs surface: a) 0° azimuth (along [-110] GaAs direction), b) 90° azimuth – potentially possible peak direction, however, not observed experimentally, probably, due to broken periodicity in this direction, c) and d) equivalent ±57° azimuths, e) 40° azimuth as an example of the direction without distinct carbon planes and, as a result, producing no GIXRD peak.