Electronic Supplementary Information for:

Simple, Robust Molecular Self-Assembly on Germanium

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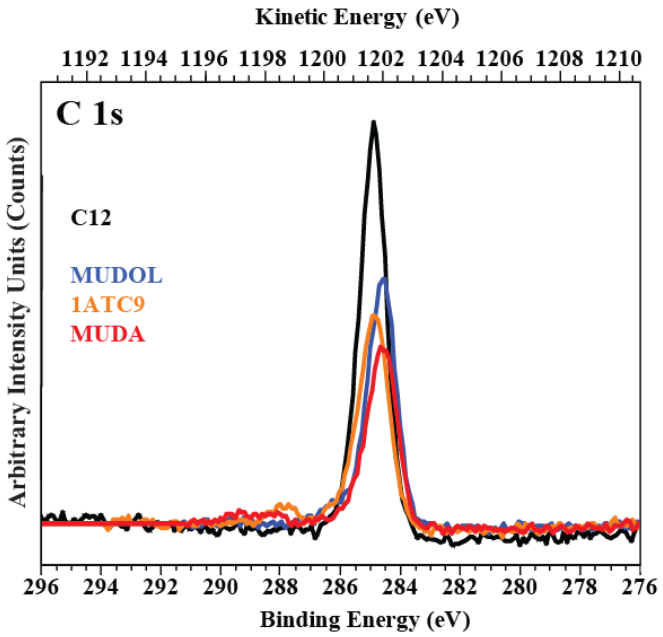

Fig. S1 Overlay of high-resolution XPS spectra for the C 1s regions of 1-dodecanethiol (**C12**), 1-mercaptoundecanol (**MUDOL**), 3-mercapto-*N*-nonylpropionamide (**1ATC9**), and 11-mercaptoundecanoic acid (**MUDA**) deposited on Ge(100) at 25 °C. Absolute integrated peak intensity is similar for each SAM, but **1ATC9**, **MUDOL**, and **MUDA** show consistently lower carbon signal intensity relative to **C12**.

Table S1 Elemental composition of C12 SAMs on Ge(100) surface by XPS.

		As received (eV)	Oxide Removed (eV)	C12 Monolayer (eV)
C 1s		285.9 287.2	285.1	284.9
S 2p	$S\ 2p_{3/2}$ $S\ 2p_{1/2}$			162.4 (66.67 %) 163.6 (33.33%)
Ge 2p	$Ge\ 2p_{3/2}$ $Ge\ 2p_{1/2}$ GeO_2	1218.2 1249.2 1220.9 1252.0	1217.9 1249.0 1219.4 1250.9 1235.3	1217.9 1249.0 1219.4 1250.9 1235.8
Ge 3d	$Ge\ 3d_{5/2}$ $Ge\ 3d_{3/2}$ GeO_2	30.0 30.6 33.2	29.8 30.4	29.8 30.4
O 1s		532.5 (100 %)	531.4 (42 %)	531.1 (17 %)

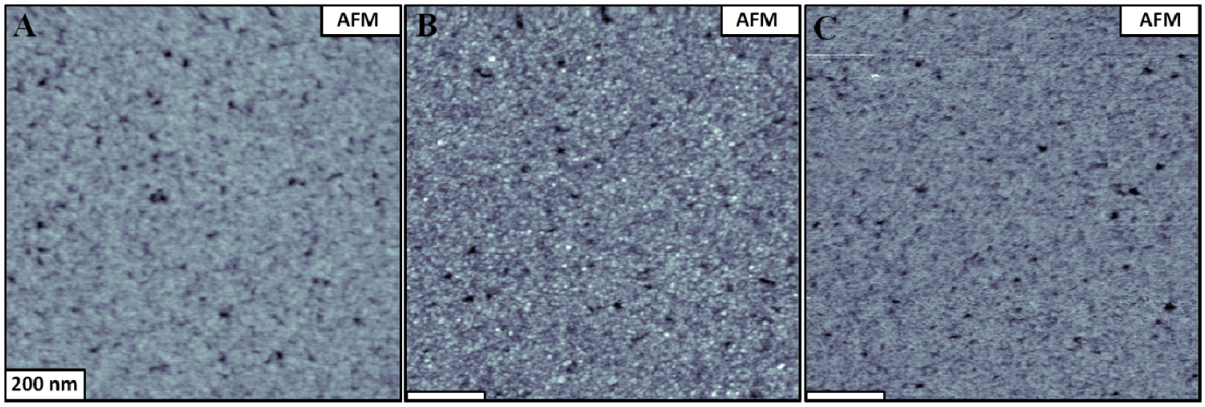

Fig S2 Progression of Ge(100) surface topography during and after SAM deposition, monitored by atomic force microscopy (AFM) in intermittent contact mode. A) Untreated Ge(100) wafer, used as received. B) The native germanium oxide is removed by holding in 1:1 water/ethanol solution overnight. C) Wafer held in 0.5 mM **C12** in 1:1 water/ethanol solution for 24 hours. Water etches the germanium surface only slowly, so there is no discernable difference in roughness for all three samples, nor any obvious trends (measured 2 Å RMS roughness). Features appear slightly rounded in the etched sample (B), after SAM deposition the surface is returned to its original flatness.

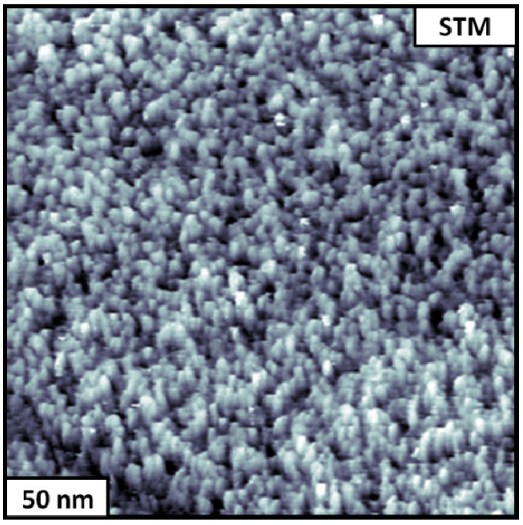

Fig S3 Scanning tunneling micrograph of Ge(100) surface modified by a **C12** monolayer, showing the atomic-scale roughness and grainy appearance of the surface. Image recorded at -1 V (sample bias) and 1 pA.

Stability of SAMs on Germanium

Self-assembled monolayers on germanium prepared by the described one-pot method display an overall stability similar to those reported previously.[1] Monolayers begin to degrade after 24 hours of exposure to air. There are several hypotheses for the degradation of the monolayers. First, insoluble GeO remaining on the surface after SAM deposition could act as nucleation sites for the reoxidation of the surface. Once the degradation process begins, the protection against oxide formation afforded by the SAM is eliminated. From its maximum contact angle, the measured angle will decrease over the course of several days, until it is ultimately indistinguishable from the as-received germanium wafers. Exposure to ambient light has also been implicated as a factor in speeding the degradation of SAMs.[1] Finally, the atomic scale roughness of the surface and lack of long range molecular order provides atmospheric oxygen access to the germanium interface.

Fig. S4 illustrates the decline in advancing contact angles for **C12** SAMs on Ge(100), Ge(110), and Ge(111) that are exposed to the laboratory environment after their deposition. Monolayers were deposited at room temperature (~50% coverage), 60 °C (100% coverage), and for long deposition periods (1-2 weeks). Light, deposition temperature, and deposition time seem to have no consistent effect on the lifetime. The experiments shown in Fig. S4 are representative; we observed on several occasions samples with anomalously long lifetimes (up to a week), but have not identified the factors that lead to that improved stability. Absolute interface roughness is variable and is uncontrolled by our methods; we suspect that improving the interface quality will likewise improve SAM stability.

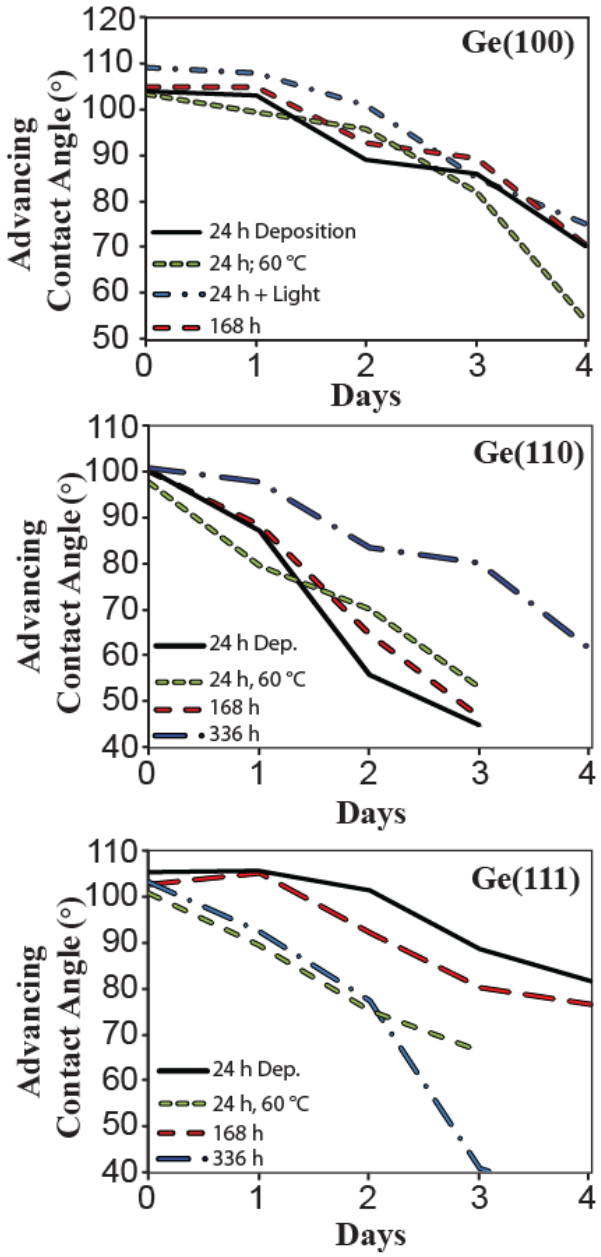

Fig. S4 Representative examples of **C12** SAM stability on germanium wafers, as a function of deposition conditions. Most samples begin to degrade rapidly after 24 hours from deposition. Samples typically degrade at the same rate; light exposure and deposition conditions do not reliably alter SAM stability. Contact angle measurements collected at 24 h intervals.

References and Notes

1. P. Ardalan, C. B. Musgrave and S. F. Bent, *Langmuir*, 2009, **25**, 2013-2025.