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Work Function Control of Germanium through Carborane-Carboxylic Acid Surface Passivation

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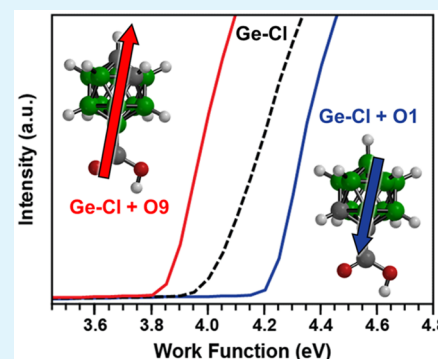
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Supporting Information

ABSTRACT: Self-assembled monolayers (SAMs) of carborane isomers with different dipole moments passivate germanium to modulate surface work function while maintaining chemical environment and surface energy. To identify head groups capable of monolayer formation on germanium surfaces, we studied thiol-, hydroxyl-, and carboxyl-terminated carboranes. These films were successfully formed with carboxylic acid head groups instead of the archetypal thiol, suggesting that the carborane cluster significantly affects headgroup reactivity. Film characterization included X-ray and ultraviolet photoelectron spectroscopies as well as contact angle goniometry. Using these carboranes, the germanium surface work function was tailored over 0.4 eV without significant changes to wetting properties.

KEYWORDS: germanium, self-assembled monolayers, ultrathin film, work function, carborane, ligand



Recent advances in interface engineering for semiconductors have contributed to significant improvements for electronic devices, such as transistors, photovoltaics, and sensors.^{1–9} Many of these architectures require precise control of energy levels at the interface between materials. Alignment of these energy levels provides low-resistance contacts, whereas large misalignment causes band bending that generates internal electric fields. This internal field can be helpful for preventing electron–hole recombination in heterojunction photovoltaics. Band engineering can be accomplished by controlling surface work functions (WFs), which has been demonstrated by passivating surfaces with covalently bound organic monolayers possessing different dipole magnitudes and orientations.^{2,3} However, these monolayers also often alter surface energy, adding complications to the device fabrication process by changing wetting or adhesive properties at the material interface.^{7–9} The ability to tune energy level alignment with a simple and reliable method without influencing surface energy and wetting will greatly reduce complications across industries.¹⁰

Recently, our group modified gold and silver surfaces with carboranethiols to tune band alignment and thus interfacial charge-transfer resistance between metal contacts and a polymer semiconductor with minimal effects on surface energy and wetting at the interface.¹⁰ By changing both placement of carbon atoms within the cluster and headgroup position on the carborane cage, it is possible to tune dipole moment magnitude and orientation while leaving the chemical environment

identical between isomers.^{11–14} This feature makes carboranes an attractive option for tuning surface WFs. Translating the carborane system from metal to semiconductor systems would aid in rapid-prototyping of semiconductor devices by enabling precision band engineering with minimal impact on processing.¹⁵

Germanium is a promising candidate for semiconductor-based technologies because of its small band gap (0.67 eV) and high electron and hole mobilities, $\sim 2.5\times$ and $\sim 4\times$, respectively, those of silicon. These properties are useful for faster devices and an absorption spectrum that extends into the infrared. Unfortunately, germanium's defect-rich, intrinsic oxide keeps it from having significant impact on today's devices.¹⁶ Researchers have investigated methods for removing germanium's oxide layer, commonly through etching, and then depositing an organic monolayer to suppress oxide formation. Maboudian and co-workers demonstrated this removal by etching the oxide with HF and simultaneously passivating the surface with hydrogen. Monolayers of 1-octadecanethiolate were subsequently formed by displacing surface hydrogens.¹⁷ Bent and co-workers applied this alkanethiol deposition to halogenated Ge(111) and Ge(100) surfaces.¹⁸ They removed germanium oxide by H₂O₂ and HCl or HBr etches, leaving behind halogen-passivated surfaces. The halogen layer was then displaced by

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octanethiol or octadecanethiol, resulting in organic monolayers that are stable in ambient conditions for several days. Many head groups have been explored for Ge, however, thiol passivation remains a prominent wet chemical method for organic self-assembled monolayer (SAM) formation.¹⁹

While exploring headgroup–surface interactions, Bent and co-workers revealed a significant difference in halogen and sulfur concentrations between Ge(100) and Ge(111) surfaces, which they attributed to the unique characteristics of the Ge(100) surface.^{18–20} To reduce the number of dangling bonds, the Ge(100) surface reconstructs into a 2×1 structure, resulting in the creation of surface dimers. The major difference in surface reactivity is attributed to the nucleophilic top Ge atom and the electrophilic bottom Ge atom. This reactivity difference has been studied with other possible headgroup chemistries on sputter-cleaned surfaces in ultrahigh vacuum. For example, alcohols and carboxylic acids were found to chemisorb selectively to Ge(100), and not Ge(111), through hydrogen dissociation and reaction between the oxygen and the electrophilic bottom atom in the surface dimer.^{21,22}

Herein, we investigate deposition of icosahedral carboranes with different head groups on Ge(100) surfaces using an H_2O_2 and HCl pretreatment. Specifically, boron clusters with thiol, hydroxyl, and carboxylic acid head groups attached at various vertices were studied in order to determine suitable headgroup chemistries for chemisorption of carborane monolayers on germanium with the ultimate goal of tuning the WF with minimal perturbations to surface energy. While there are established methods for germanium SAM formation using thiol head groups,^{16–19} our work indicates these are not suited for the carborane system and instead present evidence for carboxylic acid binding to the germanium surface. Figure 1A

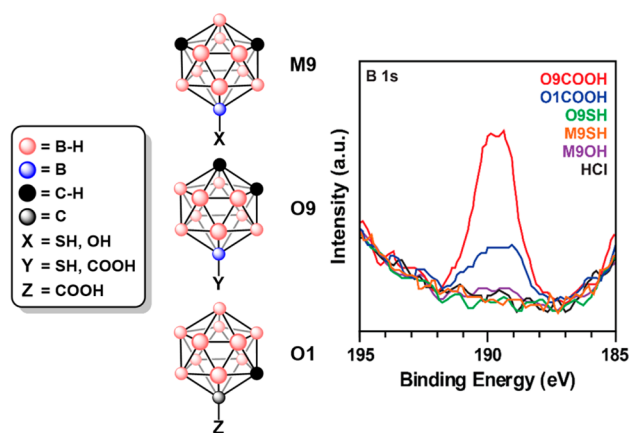


Figure 1. Schematic representation of 9-*m*-carborane (M9) with thiol and hydroxyl head groups (M9SH and M9OH, respectively), 9-*o*-carborane (O9) with thiol and carboxylic acid head groups (O9SH and O9COOH, respectively), and 1-*o*-carborane (O1) with a carboxylic acid headgroup (O1COOH). X-ray photoelectron spectra of the B 1s electron indicates only the presence of O9COOH and O1COOH on Ge(100).

contains a schematic depicting the various head groups and carborane isomers used in this study. Initial experiments focused on binding positions where the headgroup was bound to boron vertices, specifically, 9-*o*-carborane (O9) and 9-*m*-carborane (M9), as this would reduce lateral dipole–dipole interactions that could aid in assembly and instead enable focus on headgroup surface reactivity.

Single-side polished, undoped Ge(100) wafers were cleaned by sonication in acetone and then rinsed with deionized water. The substrate was prepared for molecular deposition using an etch cycle of H_2O_2 and HCl that was repeated 3 times. After the last etch, samples were quickly dried under a nitrogen gas stream, and immediately transferred to a nitrogen glovebox with oxygen content ~ 0.1 ppm. The effects of the $\text{H}_2\text{O}_2/\text{HCl}$ pretreatment are shown in Figure S9. All carborane films were formed using 1 mM concentrations of functionalized carboranes dissolved in anhydrous benzene and deposited at room temperature for approximately 24 h. Modified germanium surfaces were held in solution until just before analysis, and immediately rinsed in benzene only or benzene followed by anhydrous isopropanol (*vide infra*), and dried with a nitrogen gas stream.

X-ray photoelectron spectroscopy (XPS) was used to investigate head groups binding on germanium surfaces by taking high-resolution spectra of B 1s (Figure 1B) and S 2p (Figure S10). For both 9-SH-*m*-carborane (M9SH) and 9-SH-*o*-carborane (O9SH), the lack of peaks in both the B 1s and S 2p spectra indicate that neither bind. Expanding to the two other possible head groups, (hydroxyl and carboxylic acid), we find that 9-OH-*m*-carborane (M9OH) did not show any evidence for binding, however, presence of boron for 9-COOH-*o*-carborane (O9COOH) suggests ultrathin film formation.

With the success of O9COOH, we examined its isomer 1-COOH-*o*-carborane (O1COOH), where the headgroup is bound to a carbon vertex instead of boron. This isomer also shows evidence of monolayer formation; however, the relative quantity of boron signal observed on the surface by XPS analysis was lower than what was observed for O9COOH (Figure 1B). We hypothesize that a strong vertically oriented dipole moment might facilitate multilayering through head–tail attraction. To test this possibility, we rinsed O1COOH and O9COOH Ge surfaces with a polar solvent, isopropanol, after the benzene rinse to disrupt dipole–dipole interactions. This procedure resulted in decreases in B 1s signal for O9COOH (Figure 2A) so that both O1COOH and O9COOH are present in similar quantities, consistent with our multilayering hypothesis. After extensive rinsing with both polar and nonpolar solvents, the presence of boron suggests that the carborane carboxyl film is likely chemisorbed, through deprotonation analogous to work reported previously.^{23–25}

High-resolution XPS spectra of carboxylic acid carborane films on germanium, shown in Figure 2, highlight the regions for (A) B 1s, (B) Cl 2p, (C) C 1s, (D) O 1s, and (E) Ge 2p. Ge(100) surfaces modified by HCl (black trace), O9COOH (red trace), and O1COOH (blue trace) are all shown for comparison, with fitted peak positions (ST1) and relative elemental concentrations (ST2) shown in the Supporting Information. These data show that the $\text{H}_2\text{O}_2/\text{HCl}$ pretreatment successfully leaves a relatively oxide-free surface by etching away germanium oxide and passivating the germanium surface with chlorine atoms.

Figure 2B highlights the chlorine region, showing that after deposition chlorine is still present on the surface, with Cl 2p_{1/2} and 2p_{3/2} XPS features at 198.6 and 200.3 eV, respectively. Note that there is overlap between Cl 2p peaks and the Ge 3s plasmon peak (fitted with purple dotted line). The chlorine peak decreases upon O1COOH and O9COOH film formation, relative to the Ge 3s plasmon background, while the chlorine peak position remains unchanged. This reduction in signal could be a result of the displacement of chlorine ions with

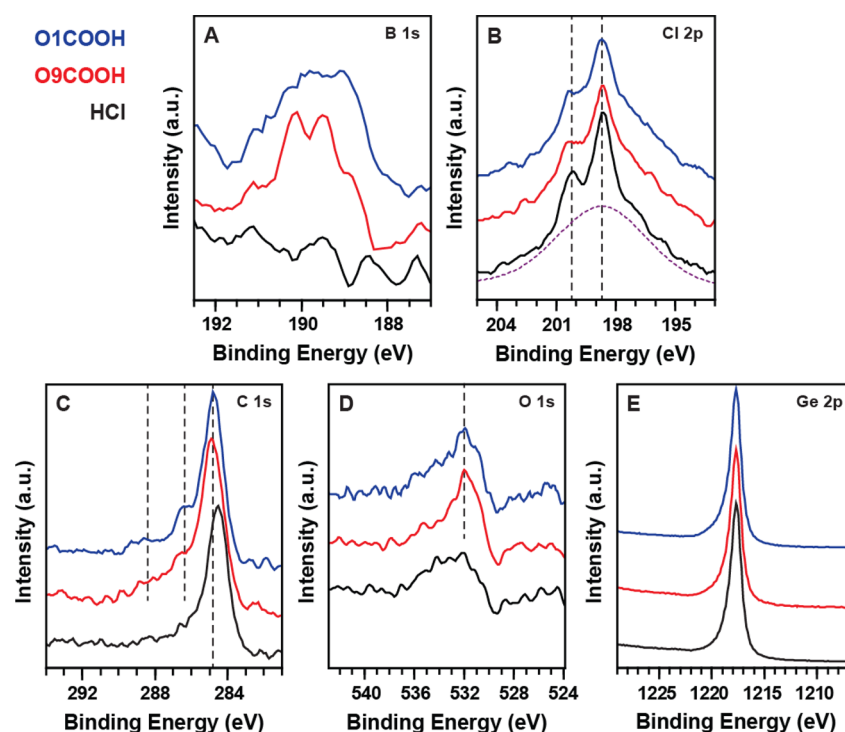


Figure 2. X-ray photoelectron spectroscopy of 1-COOH-*o*-carborane (O1COOH, blue trace), 9-COOH-*o*-carborane (O9COOH, red trace), and HCl etched (black trace) on Ge(100), highlighting the (A) B 1s, (B) Cl 2p, (C) C 1s, (D) O 1s, and (E) Ge 2p regions. Dotted purple line (B) outlines the Ge plasmon peak. Dotted black lines highlight specific peak positions.

carboxylate groups, attenuation from the monolayer, or a combination of both.

The C 1s spectra (Figure 2C) indicate multiple carbon species on the surface. Presence of carbon on the HCl-treated sample is attributed to C–C/C–H bonds from adventitious carbon (284.5 eV). A similar carbon signal, slightly shifted to higher binding energies (284.8 eV), is observed for both carborane isomers, which may be due to the higher electropositive nature of carboranes. In addition, the peaks at 286.4 and 286.5 eV for O1COOH and O9COOH, respectively, correspond to a C–B bond from the carborane cage.²⁶ The slight difference in binding energy between isomers may be a result of different bonding configurations. Peaks at 288.5 and 288.2 eV for O1COOH and O9COOH, respectively, are a result of the presence of the carboxylate functional group (O–C=O) on the surface. This small difference correlates to electronegativity difference between isomers, with the C–C bond in O1COOH increasing binding energy and C–B bond in O9COOH decreasing binding energy.

Both carborane systems change the O 1s spectra (Figure 2D) from the chlorine-passivated system in a similar fashion. The HCl-etched control sample shows a small amount of residual oxygen. After assembly of carborane films, there are increases in peak intensity at 531.7 and 531.6 eV for O1COOH and O9COOH, respectively, due to the presence of the carboxylate groups.²³ There is a prominent, but asymmetric Ge 2p peak at 1217.7 eV, corresponding to elemental Ge and possibly Ge–Cl (Figure 2E). The O1COOH and O9COOH samples show a slight shift in the peak onset to higher binding energy (Figure S11) indicating Ge–O bond formation.^{23,27} However, it is difficult to deconvolute peaks due to the small energy separation between oxidation states and the high concentration of bulk Ge.

Previous work with 11-mercaptoundecanoic acid has shown that the thiol group binds to Cl-terminated Ge(111) surfaces preferentially over the carboxyl group.^{18,28} Preference of carboxylate over thiolate binding here may be the result of interplay between several factors, including the presence of surface dimers on the Ge(100) surface,^{16,18,20,23,24} the electronic nature of the carborane cage,^{29,30} the reduction in steric hindrance due to the size of the carboxylate group relative to the size of the carborane cage, and a more energetically favorable Ge–O bond. To assess the contributions between these possible mechanisms, we deposited O1COOH on Ge(111) using similar surface preparation procedures, and characterized samples with XPS. The Ge(111) surface has a 1 × 1 structure, and therefore does not contain surface dimers. High-resolution spectra show (Figure S12) that both boron and chlorine are still present on the Ge(111) surface, indicating surface dimers are not responsible for carboxylate binding.

Ultraviolet photoelectron spectroscopy (Figure 3A) was used to determine WF changes on the Ge(100) surface through the chemisorption of carborane carboxylic acid. The WF is calculated using eq 1, where $h\nu$ is the excitation energy of the He I photon (21.2 eV) and E_{cutoff} is the high binding energy (BE) cutoff of the spectrum.¹ This sharp intensity drop in the spectrum corresponds to the energy level at which electrons can no longer escape.

$$WF = h\nu - E_{\text{cutoff}} \quad (1)$$

The total WF change is a summation of both chemical bonding and molecular dipole effects, but due to the similarity of the binding between O1COOH and O9COOH isomers, we can directly compare how the molecular dipole affects surface WF. Using density functional theory (Supporting Information, ST3) with B3LYP functional,¹⁰ we determined dipole magnitudes and orientations to be 3.24 D oriented toward the headgroup

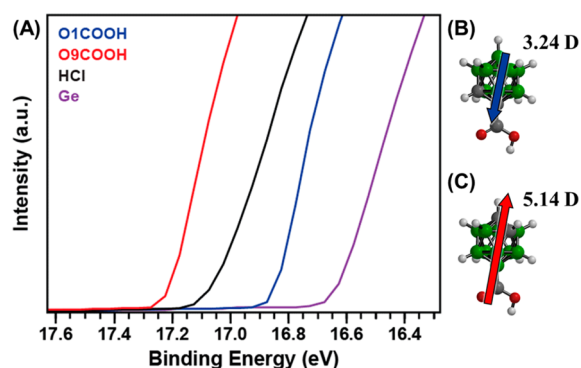


Figure 3. (A) Ultraviolet photoelectron spectroscopy of Ge(100) surfaces modified by 1-COOH-*o*-carborane (O1COOH, blue trace), 9-COOH-*o*-carborane (O9COOH, red trace), and chlorine (HCl, black trace), and Ar-ion-etched Ge(100) surface (Ge, purple trace). Surface modification by O1COOH and O9COOH show a shift of ± 0.2 eV from chlorine passivated Ge with both shifted lower from germanium's native work function. Schematic representations of (B) O1COOH and (C) O9COOH with calculated dipole magnitudes and orientations.

for O1COOH (Figure 3B) and 5.14 D oriented away from the headgroup (Figure 3C) for O9COOH. These differences in dipole moment manifest themselves in a 5.22 pK_a difference between O1COOH and O9COOH, with O9COOH having a more electron-rich and O1COOH a more electron-poor headgroup.³⁰ Although the net dipole of the molecules chemisorbed on the Ge surface will change, these values are useful in making qualitative comparisons.

All surface treatments (O1COOH, O9COOH, and HCl) examined here cause increases in the low-energy cutoff region of the spectra due to the strong effect that chemical binding has on the Ge WF.³ For reference, clean Ge(100) surface and hydrochloric acid-etched Ge(100) surface exhibit a WF of 4.56 eV (BE of 16.65 eV) and 4.13 eV (BE of 17.08 eV), respectively. Upon modifying the hydrochloric acid-etched Ge(100) surface with O1COOH and O9COOH films, the WF increased to 4.39 eV (BE of 16.82 eV) and decreased to 3.99 eV (BE of 17.22 eV), respectively. This result shows that the different dipoles of the carborane isomers influence the WF of the germanium surface in a similar fashion as on Au and Ag.¹⁰ Relative to the Ge–Cl surface, the vertical component of O1COOH's dipole moment points into the surface increasing the WF by 0.26 eV, whereas the vertical component of the O9COOH's dipole moment points away from the surface decreasing the WF by 0.14 eV. These data indicate that the WF can shift by approximately ± 0.2 eV relative to the Ge–Cl surface WF. The WF change with carborane dipole direction agrees with past work of carboranethiol SAMs on Au and Ag.¹⁰ Additionally, following that work, these data suggest that a mixed monolayer of carborane carboxylates could tune the WF of Ge over a 0.4 eV range centered around 4.19 eV. Lastly, correlation between dipole orientation and WF change offers further verification that these carboranes are tethered to the surface through carboxylic acid head groups.

Advancing and receding contact angles for O1COOH and O9COOH (shown in Table 1), indicate that the wetting properties and surface energy of the two are not significantly different. The O1COOH has the smaller contact angle and a smaller molecular dipole of the isomers used, consistent with data for M1 and M9 thiol on gold. Monolayers of M1 thiol on gold have a smaller dipole moment (1.06 D) relative to

Table 1. Advancing and Receding Contact Angles for 1-COOH-*o*-Carborane (O1COOH), 9-COOH-*o*-Carborane (O9COOH) on Ge(100) surfaces

	advancing θ	receding θ
O1COOH	$56.8 \pm 5.5^\circ$	$39.9 \pm 3.6^\circ$
O9COOH	$59.5 \pm 4.6^\circ$	$42.3 \pm 6.9^\circ$

monolayers of M9 (4.08 D) thiol on gold, corresponding to static contact angles found to be 77.7° and 85.8°, respectively.¹⁰ The reduced contact angle observed for the O1COOH and O9COOH may be due to substrate roughness (discussed in more detail in the Supporting Information), lower molecular packing density, or differences in molecular orientation.^{23,24} The nonpolar solvent hexadecane was used as well, and similarly to the carboranethiol-Au system, the surface was completely wetted and no contact angle was attainable.¹⁰

In summary, carborane carboxylate monolayers were formed on germanium surfaces to modify surface WF with minimal effects to surface energy. We find that the carborane cluster affects headgroup binding, where carboxylic acid tethers successfully assemble and thiol and hydroxyl groups do not. This affinity for carboxylic acid is hypothesized to be induced by several factors, including steric effects, the unusual electronic character of the carborane cluster, and thermodynamic favorability. Carborane monolayers on Ge present the opportunity for the surface WF to be tailored over a 0.4 eV range while the integrity of surface properties, such as wetting and adhesion, are maintained. Potential challenges for carborane films on Ge, such as air and thermal stability, will be the focus of future research. Additionally, how binding angle may influence surface properties and stability, as well as whether this angle can be controlled with an annealing phase are areas for further exploration.^{23,24} Results presented herein motivate future experimental and theoretical investigations to understand how carborane clusters affect headgroup–surface binding chemistries, and whether other headgroup chemistries may be affected. Additionally, with the successful WF modulation presented here, it is worth exploring how carboranes may benefit other semiconductor device systems, such as silicon and metal oxides.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b10596.

Figures and experimental details describing molecule synthesis, surface preparation, molecular dipole simulations, further analysis of Ge(100) using XPS, UPS, and contact angle, and XPS analysis of Ge(111) surfaces (PDF)

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Notes

The authors declare no competing financial interest.

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