Cycloaddition-like reactions at germanium (100) surfaces:
Adsorption and reaction of 1,5-cyclooctadiene

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Received 7 August 2007; accepted for publication 6 November 2007
Available online 17 November 2007

Abstract
The adsorption and reaction of 1,5-cyclooctadiene with the Ge(100) surface has been investigated. The subsequent surface reactions are followed by photoelectron spectroscopy and temperature programmed desorption. The bonding configuration is determined with photoelectron spectroscopy and compared with ab initio calculations. 1,5-Cyclooctadiene reacts with surface Ge dimers to form a four-membered ring structure at the surface at room temperature. Heating this surface results in some molecular desorption of 1,5-cyclooctadiene and the remaining surface species decompose at higher temperatures and desorb as either hydrocarbon species or molecular hydrogen.

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Keywords: 1,5-Cyclooctadiene; Germanium; X-ray photoelectron spectroscopy; Ultraviolet photoelectron spectroscopy; Adsorption

1. Introduction
The surface chemistry of Group IV materials, including Si, Ge and C (diamond), is of interest for a number of developing technologies. One area receiving increased attention is the attachment of organic molecules to the (100) surfaces of crystalline silicon [1–15], germanium [16,17], and diamond [18] by cycloaddition-like reactions. Experimental and theoretical studies have examined the interaction of hydrocarbons with clean Si(100). However, there are relatively few studies examining the interaction of hydrocarbons with the Ge(100)-2 × 1 surface. The study of simple
organic molecules like ethylene, on Ge(100)-2 × 1 was reported by Lal et al. [27]. These experiments were performed using multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and temperature programmed desorption (TPD). They showed that ethylene chemisorbs molecularly on the Ge(100)-2 × 1 surface at room temperature and that C2H4 is bonded across a Ge dimer. Lal and co-workers suggested that the major thermal pathway in the ethylene/Ge(100)-2 × 1 system is molecular desorption. No carbon was left on the surface after thermal desorption as observed by Auger electron spectroscopy (AES).

Lee et al. [16] investigated the adsorption and reaction of two of cyclic unsaturated hydrocarbons, cyclopentene and cyclohexene, with the Ge(100) surface. The experiments were performed using scanning tunneling microscopy (STM), ultraviolet photoelectron (UPS), X-ray photoelectron (XPS) and FTIR spectroscopies. STM images of cyclopentene at high coverages on the germanium surface revealed that the molecules packed along the Ge∥Ge dimer rows. Cyclopentene and cyclohexene reacted with surface dimer bonds forming a four-membered ring at the surface containing two carbon and two germanium atoms. The FTIR spectra showed no alkene C–H stretching modes after exposure of cyclopentene or cyclohexene to Ge(100) at room temperature. The photoelectron spectroscopy results also supported reaction of the π-bond.

The interaction of organic molecules containing more than one alkene group with germanium has been reported by Lee et al. [17]. The adsorption and reaction of 1,3-cyclohexadiene with the Ge(100)-2 × 1 surface was examined. High-resolution electron energy loss spectroscopy (HREELS) and UPS were used to follow the surface reaction. The authors showed that 1,3-cyclohexadiene reacted with the Ge(100)-2 × 1 surface. The HREELS experiments and frequency calculations support the conclusion that 1,3-cyclohexadiene reacts with the germanium surface to form predominately a [4 + 2] cycloaddition-like product.

Other organic molecules reported to have interactions with the germanium surface include 1,3-buta diene and 2,3-dimethyl-1,3-buta diene. Teplyakov et al. [28] studied the reaction using temperature-programmed reaction/desorption (TPR/D) and MIR-FTIR. Both butadienes reacted with the dimers of the Ge(100)-2 × 1 surface forming Diels–Alder like adducts. This assignment was made partly based the absence of a terminal vinylic CH2 stretch in the MIR-FTIR studies. In thermal desorption studies, the [4 + 2] reaction product of 1,3-buta diene decomposed to yield 1,3-buta diene, in a retro-Diels–Alder transformation. This observation is in contrast to Si(100)-2 × 1, where the thermal reaction pathway for butadiene, is dehydrogenation. No carbon was detected on the Ge(100)-2 × 1 surface after the retro-Diels–Alder reaction of the butadienes. These studies nicely show that while similar adsorption/reaction chemistry can be observed on Si and Ge surfaces, different thermal behavior is observed on the two surfaces.

Organic molecules with more complicated structures are also of interest. 1,5-Cyclooctadiene (1,5-COD) is a nonconjugated cyclic diene. It is expected that the organic molecule can bond to the germanium surface using a single π-bond and surface reaction could occur over a single Ge dimer. The interactions of 1,5-cyclooctadiene with the Si(100)-2 × 1 surface have been studied by several investigators. Hovis and co-workers [2] identified the bonding configuration of the carbon atoms utilizing XPS, STM and FTIR after saturation exposures of 1,5-COD. 1,5-COD produced well-ordered monolayers on Si(100) at 373 K. The XPS data indicated that there are three chemically different carbon atoms in each surface-bound 1,5-COD molecule; the two carbon atoms bonded to the silicon surface (binding energy 283.7 eV), the four alkane-like carbons (binding energy 284.4 eV) and the two alkene-like carbon atoms (binding energy 284.8 eV). The FTIR data supported the conclusion of 1,5-COD being bound to the surface by reaction of one double bond. Jolly et al. [3] also studied this system by using XPS and NEXAFS. The results supported the conclusions of Hovis and co-workers. Upon adsorption at room temperature, the valence-band spectra showed that the Si dimers were involved in the reaction (expected when forming a di-σ bound species). From NEXAFS spectra, they suggested that only one of the C=C bonds in 1,5-COD was involved in bonding with Si dimer. A number of recent organic systems have been reviewed by Filler and Bent [29] and by Loscutoff and Bent [30].

In this work, we investigate the interactions of 1,5-COD with the Ge(100)-2 × 1 surface. It is our desire to better understand the reaction of germanium dangling bonds upon exposure to increasing amounts of 1,5-cyclooctadiene and to study the stability of the organic layers formed as a function of annealing temperature. Ultraviolet and X-ray photoelectron spectroscopies, in combination with temperature programmed desorption (TPD), have been used to characterize the organic layer on the germanium surface. Density functional theory with the B3LYP functional [31,32] and split valence 6-31 G* and 6-31 + G* [33] basis sets have been used to explore several possible adsorbate structures of this hydrocarbon with the Ge(100) surface.

2. Experimental

The experiments are performed in a stainless steel ultrahigh vacuum (UHV) chamber that is described in detail elsewhere [34]. Briefly, the chamber is equipped with a double-pass cylindrical mirror analyzer for Auger electron and photoelectron spectroscopies, a differentially pumped ultraviolet discharge lamp, twin X-ray source, ion gun, and quadrupole mass spectrometer for both temperature programmed desorption and secondary ion mass spectrometry. The base pressure of the system is 6 × 10⁻¹¹ torr with a typical working pressure of 1 × 10⁻¹⁰ torr.

The 1,5-cyclooctadiene (99% purity) was purchased from Aldrich. It was further purified by several freeze–
pump–thaw degassing cycles and the purity of the gas was checked by mass spectrometry in situ. The resulting mass spectrum of 1,5-COD was carefully compared with reference spectra [35] prior to use in experiments. A 70 eV ionization energy was used. No fragment ions other than those due to 1,5-COD were detected, indicating no contamination of the 1,5-COD. The reagent was introduced into the chamber through a leak valve and directed onto the sample surface for a given pressure and time through a dosing tube. The actual pressure at the sample is higher than the chamber background pressure. Since they are proportional to one another, all exposures reported here are based on the pressure in the chamber as measured by the ion gauge and exposures are reported in Langmuir (L) (1 L = 1 × 10⁻⁶ torr s). The temperature ramp rate used in TPD experiments was 5 K s⁻¹.

The samples used in this work were cut into 0.8 × 2.5 cm long strips from p-type Ge(100) wafers purchased from Eagle–Picher (0.10–0.39 Ω cm, resistivity). Clean Ge(100) samples were prepared using a two part procedure [36]. The ex situ part of the procedure consists of a wet chemical treatment using solutions of HCl (HCl (36%)/H₂O 1:4) to remove the oxide layer, H₂O₂ (H₂O₂ (30%)/H₂O 1:10) to re-oxidize the sample, NH₂OH (NH₂OH (28%)/H₂O₂ (30%)/H₂O 1:2:20) to prepare the final oxide layer, and methanol (100%) as a rinse. The details of this procedure are given in Ref. [36]. For the in situ part of the procedure, the Ge samples were degassed for several hours at ~550 K at a pressure of less than 1 × 10⁻⁸ torr. The sample was then annealed to 850 K to remove the oxide layer. Ion sputtering with 2 keV Ar⁺ was used as needed. This procedure produces a clean surface with no impurities detected by AES. The temperature was followed by the chromel–alumel thermocouple attached to the back of the sample with Areemo 516 ceramic adhesive.

Ultraviolet photoelectron spectra are taken with HeI (21.2 eV) radiation from a He gas discharge lamp and the analyzer is operated with fixed pass energy of 25 eV. All the reported UPS binding energies are referenced to the Ge valence band edge, which is assigned as 0 eV binding energy.

X-ray photoelectron spectroscopy (XPS) experiments were performed using Al Kα radiation (hν = 1486.6 eV). The data presented here were obtained using a pass energy of 50 eV. For the annealing experiments, the substrates were heated to the selected temperature, cooled to room temperature, and the XPS spectra recorded.

The calculations reported here were carried out using a hybrid method in which the energy is first calculated at the Hartree–Fock level with the 6-31G* or 6-31 + G* basis set, and the B3LYP density functional [31,32] is then used to include electron correlation effects. Energy and derivative calculations have been carried out within the Gaussian 98 [33] suite of programs. The Ge(100)-2 × 1 surface was modeled using a dimer cluster consisting of nine Ge atoms and twelve H atoms. The top layer of the model is a dimer consisting of two Ge atoms, each with one dangling bond. The seven subsurface Ge atoms are terminated with twelve H atoms to maintain the sp³-hybridization of bulk Ge. Vibrational frequencies are calculated at the B3LYP/6-31G* level using the fully optimized B3LYP/6-31G* geometry.

3. Results and discussion

3.1. Adsorption of 1,5-cyclooctadiene at 100 K

Fig. 1 shows the He I UPS difference spectrum for 9 L of 1,5-COD condensed on the germanium surface at 100 K. This exposure is sufficient to generate about 5–7 molecular layers. A difference spectrum is made by directly subtracting the clean Ge(100) surface spectrum from the 1,5-COD exposed surface. A low binding energy peak is observed at 4.3 eV. Another broad peak is observed at 7.9 eV with a shoulder towards the lower binding energy side at 6.2 eV. Also shown on Fig. 1 is the gas phase spectrum of 1,5-cyclooctadiene [37]. The gas-phase spectrum has been shifted in energy to account for the difference in reference levels between the gas- and condensed-phase spectra. For both the gas-phase and condensed-phase spectra, the lowest binding energy peaks are observed with similar energy separations. When compared with the gas-phase spectrum, some solid-state broadening is present, as expected for a condensed-phase. Based on the similarity between the UPS spectrum at 100 K with the gas-phase spectrum of 1,5-COD, it is concluded that 1,5-COD physisorbs on the Ge(100) surface. A low binding energy peak at 4.3 eV is assigned to the π-bonds of the molecule and the peak at 6.2 eV is assigned to the σ-backbone of the cyclooctadiene ring.

Additional experiments to examine the condensed-phase of 1,5-COD were performed using XPS. Fig. 2 shows the C(1 s) region for Ge(100) exposed to 9 L of 1,5-COD at a surface temperature of 100 K. Along with the experimental data (dots) the results of an unrestricted fit of the data to two Voigt peaks are shown. The fit procedure yielded peaks at binding energies of 284.1 and 284.8 eV with integrated peak area ratios of 1.2:1.0, close to the expected ratio of 1:1. We assign the peak at 284.8 eV to alkene-like carbon and the peak at 284.1 eV to alkane-like carbon within the 1,5-COD molecule. These results are consistent with condensed molecular layers of 1,5-COD on the Ge(100) surface and with previous results on Si(100) [2].

3.2. Adsorption of 1,5-COD at 250 K

The UPS results for several different 1,5-COD exposures to Ge(100) at a surface temperature of 250 K are shown in Fig. 3. Several changes are observed at this higher adsorption temperature. The two peaks with the lowest binding energies are now observed at 4.1 and 5.6 eV. Increasing the exposure leads to further development of the peaks. For coverages greater than 2.7 L, no changes are observed in the UPS spectra. TPD experiments (not shown), follow-
ing a fragmentation ion for molecular 1,5-COD ($m/z = 54$ or 80), confirm that the surface is saturated for exposures greater than 2.7 L. The dotted spectrum in Fig. 3 is the 9.0 L exposure of 1,5-COD presented in Fig. 1. The observed changes in the spectrum indicate that a $\pi$-bond in 1,5-COD reacts with the Ge(100) surface at 250 K. The reaction product between 1,5-COD and germanium surface can be considered a substituted cyclooctene. For

Fig. 1. He I UPS difference spectrum of 9.0 L 1,5-COD exposed to the Ge(100) surface at 100 K. The gas-phase UPS spectrum of 1,5-COD [37] is shown for comparison.

Fig. 2. The C(1s) XPS spectrum of a 9.0 L exposure of 1,5-COD to Ge(100) at a surface temperature of 100 K.
Fig. 3. He I UPS spectra for various 1,5-COD exposures. The exposures are (a) 0.1 L, (b) 1.0 L, (c) 1.5 L, and (d) 2.7 L 1,5-COD at a Ge(100) surface temperature of 250 K. The dotted spectrum is the UPS difference spectrum of 1,5-COD from Fig. 1 (adsorption temperature of 100 K). The gas-phase spectrum of cyclooctene [37] is shown for comparison.

Fig. 4 shows the C(1s) XPS spectrum taken after exposing 2.7 L of 1,5-cyclooctadiene to the Ge(100) surface at a surface temperature of 250 K. The C(1s) XPS data indicate that there are three types of carbon on the surface. Since C has a greater electronegativity than Ge, it is expected to

comparison, the gas-phase UPS spectrum of cyclooctene [37] is shown directly below spectrum 3a. Based on these comparisons, we assign the peak at 4.1 eV to a $\pi$-bond and the peak at 5.6 eV to the $\sigma$-backbone in a ringed structure.
decrease the electron density of C atoms bound to it, and exhibit a lower C(1s) binding energy. We assign the peak at 283.5 eV to the two carbon atoms bound to the Ge dimer. The peak at 284.1 eV is assigned to the four alkane-like carbon atoms and the peak at 285.0 eV is assigned to two alkene-like carbon atoms. The peak area ratio of these three peaks is 2:4:2 which is the ratio of the three types of carbon atoms in the expected [2 + 2] cycloaddition-like reaction product.

To help identify the bonding configuration of 1,5-COD on Ge(100), a series of ab initio calculations were performed with the B3LYP functional [30,31] and the 6-31 + G* basis set using Gaussian 98 suite of programs [33]. The calculations predict that 1,5-COD is bound to the Ge(100) surface by forming a [2 + 2] cycloaddition-like product and it is stable by 60.8 kcal/mol with respect to the reactants. The optimized geometry of the cycloaddition-like product is shown as Fig. 5. The calculated Ge–C bond length is 2.01 Å. The C–C bond length stretches upon adsorption to 1.59 Å compared to 1.34 Å in molecular 1,5-cyclooctadiene. The longer bond can be explained as the C–C bond changes from a double bond to a single bond during the adsorption reaction. If we consider the Ge–Ge bond length, the optimized geometry shows that there is not a major change in bond length of Ge dimer upon adsorption. This result may be due to the less π character in Ge dimer. The optimized structure data are presented in Table 1. The optimized geometry is consistent with the XPS and UPS data after exposing Ge to 1,5-COD at 250 K. The results suggest that 1,5-cyclooctadiene attaches to the Ge(100) surface and forms a reaction product similar to a [2 + 2] cycloaddition reaction.

There is also the possibility that the reaction could occur over more than a single dimer. This possibility was not investigated computationally at this time. Studies are currently underway with clusters involved multiple surface dimers. However, the cluster models involving all germanium atoms are computationally intensive. Therefore, a mixed cluster in which multiple surface dimers contain germanium atoms, and the subsurface portion contains silicon atoms is being explored. This mixed cluster method has been used in a number of studies by Wang and co-workers [38].

### 3.3. Thermal behavior of 1,5-cyclooctadiene

Temperature programmed desorption (TPD) was used to help investigate the thermal behavior of the 1,5-COD exposed germanium surface. The TPD results from a 9 L exposure of 1,5-COD to Ge(100)-2 × 1 at a surface temperature of 250 K are shown as Fig. 6. This exposure was sufficient to produce a saturated surface. A molecular desorption state for 1,5-COD is observed at 340 K. We observe a small desorption peak at 485 K for m/z = 39 and a H₂ desorption peak at 560 K. The peak at 560 K occurs at the temperature normally observed for H₂ desorption from Ge(100) when using atomic hydrogen as the adsorbate. The presence of a desorption state for m/z = 39 at 485 K and for m/z = 2 at 560 K indicates that there is some decomposition of 1,5-COD upon heating. Based on desorption peak areas, at saturation about 80% of the 1,5-COD molecules desorb intact and the remaining 20% decompose to other volatile species.

A simple Redhead analysis [39] (assuming a preexponential factor of 10^{13} s^{-1}) of the molecular desorption state yields an energy of 20.6 kcal mol⁻¹, which is significantly lower than the calculated energy. This difference in energies may be due to the reaction occurring over adjacent dimers or may be a result of the basis set used for the calculation. These effects are currently being explored; yet do not alter the overall conclusions made in this study.

### Table 1

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<th>Ge bulk bond length (Å)</th>
<th>C–C (Å)</th>
<th>Ge–Ge (Å)</th>
<th>Ge–C (Å)</th>
<th>∠Ge–C–C (°)</th>
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The thermal stability of 1,5-COD on the Ge(100) surface was also examined by photoelectron spectroscopy. Fig. 7 shows He I UPS spectra for a sample exposed to 9 L of 1,5-cyclooctadiene at 250 K (Fig. 7a) and then annealed to 400 K (Fig. 7b) and 540 K (Fig. 7c). As previously discussed, the peak observed at 4.1 eV binding energy, is due to the remaining $\pi$-bond within the adsorbate. Heating the 1,5-COD covered surface from 250 K to 400 K (just past the molecular 1,5-COD desorption state), results in a significant loss of intensity for this peak, and an overall de-
crease in intensity for all peaks with binding energies greater than 6 eV. Annealing the surface to 540 K results in a significant decrease in intensity for all spectral features. Similar annealing experiments using XPS (not shown) follow the same trends as the UPS data. AES spectra data after the TPD experiments show that the surface is carbon-free.

It is clear that warming the COD-covered surface to 400 K results in the desorption of some molecular 1,5-COD as observed in the TPD experiments. However, a portion of the adsorbed molecules remained on the surface and decomposed. The decomposition products are observed in the UPS spectra and the spectra are characteristic of hydrocarbon fragments. In the TPD experiments, molecular hydrogen is observed at higher temperatures and a weak desorption state near 480 K for \( \frac{m}{z} = 39 \) is observed; again consistent with a surface reaction leading to decomposition.

4. Conclusions

Adsorption of 1,5-cyclooctadiene (1,5-COD) on the Ge(100)-2 \( \times 1 \) surface has been investigated using ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy. These results show that 1,5-cyclooctadiene chemisorbs on the surface at room temperature. The adsorption of 1,5-cyclooctadiene on the Ge(100)-2 \( \times 1 \) surface occurs via the interaction of one \( \pi \)-bonds within the organic molecule with one or more Ge=Ge dimers on the surface. Ab initio calculations predicted that the reaction products are stable with respect to the reactants. UPS spectra are not able to distinguish between these possible adsorption geometries. A portion of the organic layer desorbs upon heating to 400 K. The remaining fraction dissociates at higher temperatures and removes any carbon-containing species from the Ge(100)-2 \( \times 1 \) surface which AES spectra show to be clean after annealing.

References