

Surface Science Letters

Reaction of 1,3-cyclohexadiene with the Ge(100) surface

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Abstract

The adsorption and reaction of 1,3-cyclohexadiene with the Ge(100)-(2 × 1) surface are investigated. The possibility of a surface Diels–Alder reaction ([4 + 2] cycloaddition), as well as a [2 + 2] cycloaddition reaction are explored. The surface reactions are followed by ultraviolet photoelectron and high-resolution electron energy loss spectroscopies. The vibrational spectroscopy results are compared with theoretically predicted frequencies for each of the possible surface reactions. © 1998 Published by Elsevier Science B.V. All rights reserved.

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Fifty years have now passed since the invention of the point contact transistor by Bardeen and Brattain [1]. The invention of the transistor was a significant event in itself, but it also served to inspire a much larger revolution in the realm of electronics, which continues today. The use of these semiconductor-based electronic devices has directed a large number of investigations with the goal of trying to understand the chemical and physical properties of semiconductor interfaces.

On semiconductor surfaces, the majority of the reactions with hydrocarbons occur at or near the dangling bonds of the reconstructed surface. The dangling bonds on a Si(100)-(2 × 1) or Ge(100)-(2 × 1) surface are arranged in surface dimers, and these dimers are also arranged in an ordered

manner. This means that it is possible to form a molecularly ordered thin film that is covalently bound to the surface, provided that one can direct the reaction to occur at dangling bond sites.

Konecny and Doren [2] have recently extended this theme and proposed a reaction in which the surface silicon dimers are directly involved in the bonding of hydrocarbons. In their reaction scheme, two covalent bonds are formed between the silicon surface and each unsaturated hydrocarbon molecule. Their calculations show that the [4 + 2] addition (Diels–Alder) product is thermodynamically more stable than the [2 + 2] addition (direct addition) product when using 1,3-cyclohexadiene as the adsorbate. This prediction offers a method in which functionality can be introduced at the surface and allow for the synthesis of ordered thin films. The prediction of a [4 + 2] addition reaction at a silicon surface was verified recently by Bent

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and co-workers [3,4] when 1,3-butadiene and 2,3-dimethyl-1,3-butadiene were reacted with a silicon surface, and the products of the reaction were consistent with Diels–Alder addition.

The adsorbed structure of cyclic unsaturated hydrocarbons with silicon surfaces has been reported by Hamers et al. [5–7]. A combination of infra-red spectroscopy and scanning tunneling microscopy was used to investigate the reaction products and the surface order of the adsorbed organic monolayer. In each of these unsaturated hydrocarbon studies, the π -bond in the hydrocarbon reacted with the silicon surface dimer bonds to form a [2+2] cycloaddition adduct.

The Ge(100) surface is structurally similar to the Si(100) surface, and the motivation for these studies is to examine whether similar cycloaddition reaction chemistry can be extended to the Ge(100) surface. Here, we report the adsorption and reaction of 1,3-cyclohexadiene with the Ge(100)-(2 × 1) surface to form a cycloaddition adduct. The vibrational spectroscopy results, obtained by high-resolution electron energy loss spectroscopy (HREELS), are directly compared with the theoretically predicted frequencies of R. Konecny and D.J. Doren (pers. commun.). The results are consistent with the formation of a surface cycloaddition adduct.

The UPS experiments are performed in a stainless steel ultra-high vacuum (UHV) chamber that is described in detail elsewhere [8]. 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 HREELS experiments are performed in a separate UHV system at the University of Texas at Austin. It is described in detail elsewhere [9]. Briefly, it comprises an LK 2000 HREEL spectrometer and a 10-mm pinhole doser. HREEL spectra were taken with a primary electron beam energy of 3 eV and a resolution of 100–120 cm^{-1} full width at half-maximum (FWHM).

1,3-Cyclohexadiene (Aldrich Chemical Co., Milwaukee, WI; 97% purity) is further purified by several freeze–pump–thaw degassing cycles, and the purity of the gas is checked in-situ by mass spectrometry. The gas is admitted to the chamber through an effusive doser directed on to the front face of the crystal for various periods of time.

Sample preparation and cleaning procedures have been described previously [10]. All the reported UPS binding energies are referenced to the Ge valence band edge, which is assigned a binding energy of 0 eV.

A series of He II UPS experiments examining the adsorption of 1,3-cyclohexadiene on Ge(100) are summarized in Fig. 1. The spectrum shown above Fig. 1a is the gas phase photoelectron spectrum of 1,3-cyclohexadiene [11]. Fig. 1c is the UPS spectrum obtained for the clean Ge(100) surface and is included for reference. The lowest energy peak in the gas phase spectrum is aligned with the lowest binding energy feature in Fig. 1a. Spectrum 1a is obtained from a physisorbed multilayer of 1,3-cyclohexadiene that is generated by exposing the Ge(100) surface held at a surface temperature of 90 K to 1,3-cyclohexadiene. The presence of the multilayer is observed in separate thermal desorption experiments, where a low-temperature molecular desorption state is observed for these experimental conditions (S.W. Lee, L.N. Nelen, H. Ihm, B. Flint, C.M. Greenlief, unpublished results). Adsorption of 1,3-cyclohexadiene on to Ge(100) at a surface temperature of 90 K results in five distinct features as observed in Fig. 1a. The measured positions of the peaks correspond to binding energies of 2.4, 5.3, 8.1, 10.5, and 13.5 eV. The agreement between the gas-phase and measured (Fig. 1a) photoelectron spectra is interpreted as further evidence for a physisorbed multilayer of 1,3-cyclohexadiene on Ge(100).

Fig. 1b is the result obtained after warming the 1,3-cyclohexadiene-covered surface to 373 K or exposing 1,3-cyclohexadiene to Ge(100) at a surface temperature of 373 K, cooling to 90 K, and obtaining the He II photoelectron spectrum. Five peaks are observed corresponding to binding energies of 1.5, 4.5, 6.9, 9.7, and 12.7 eV. The feature centered at 1.5 eV is due to the valence band of the Ge substrate. The positions of these

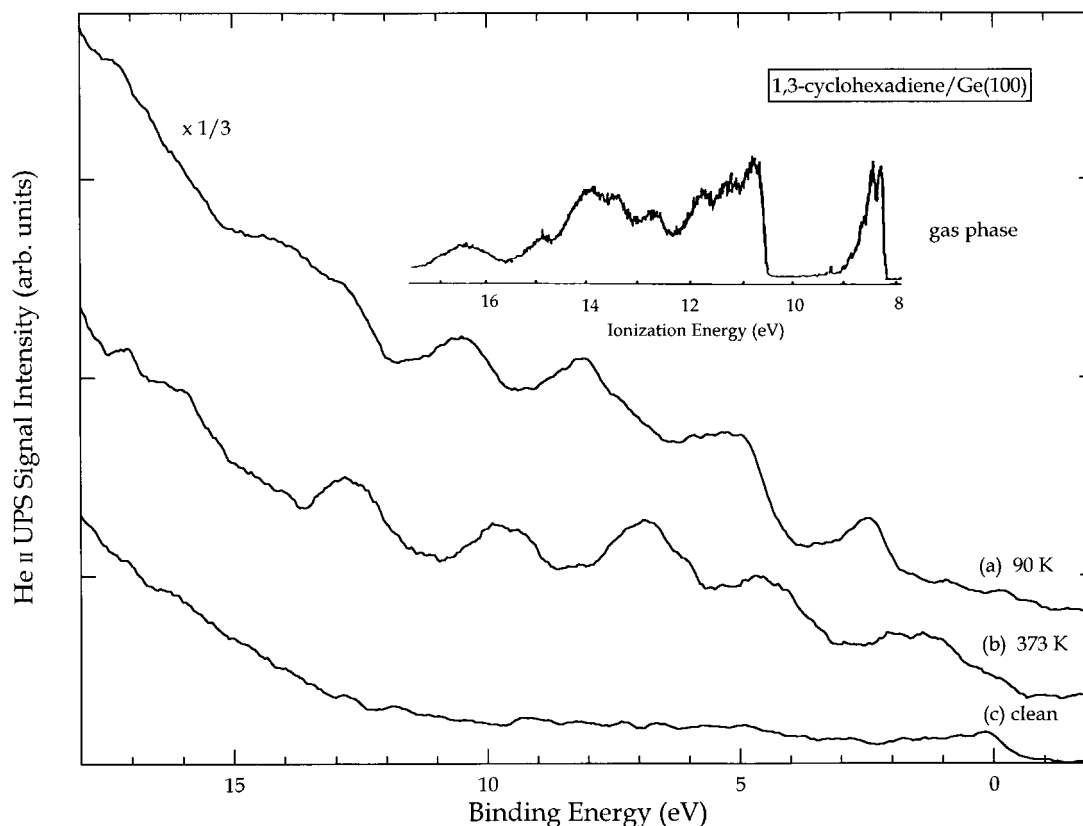


Fig. 1. (a) He II UPS spectrum of a multilayer of 1,3-cyclohexadiene at a surface temperature of 90 K. (b) He II UPS spectrum after annealing the multilayer of 1,3-cyclohexadiene to 373 K. The gas phase spectrum for 1,3-cyclohexadiene [11] is also shown for comparison with spectrum (a). (c) He II UPS spectrum of a clean Ge(100)-(2 × 1) surface.

peaks are indicative of a surface reaction where the reaction products are not molecularly adsorbed 1,3-cyclohexadiene.

The removal of the peak at 2.4 eV in Fig. 1a upon annealing to 373 K gives some insight into the surface reaction. This peak is due to a molecular orbital with $p_{C=C^-}$ character [11]. The front edge of the peak at 5.3 eV binding energy in Fig. 1a is a molecular orbital due to $p_{C=C^+}$ character [11]. The lack of these two peaks upon annealing to 373 K shows that the p-bond(s) within the 1,3-cyclohexadiene molecule are reacting with the Ge(100) surface.

The adsorption and reaction of 1,3-cyclohexadiene with Ge(100) are investigated further with HREELS as shown in Fig. 2. Fig. 2a is a HREEL spectrum of a 1,3-cyclohexadiene multi-

layer prepared at 100 K. The vibrational frequencies and mode assignments are summarized in Table 1. These measured frequencies are compared with liquid 1,3-cyclohexadiene [12]. The results of Fig. 2a can be described as being due to the presence of molecularly adsorbed 1,3-cyclohexadiene at 100 K.

Annealing the 1,3-cyclohexadiene covered surface from 100 to 300 K, cooling to 100 K, and recording the HREEL spectrum yields Fig. 2b. Several changes in the energy loss spectrum compared with Fig. 2a are observed. The major changes include the CH stretching region, which is now asymmetrically shaped to the lower energy side. Five new loss features at 555, 780, 1095, 1195, and 1280 cm^{-1} are now observed. The loss feature originally observed at 1640 cm^{-1} is

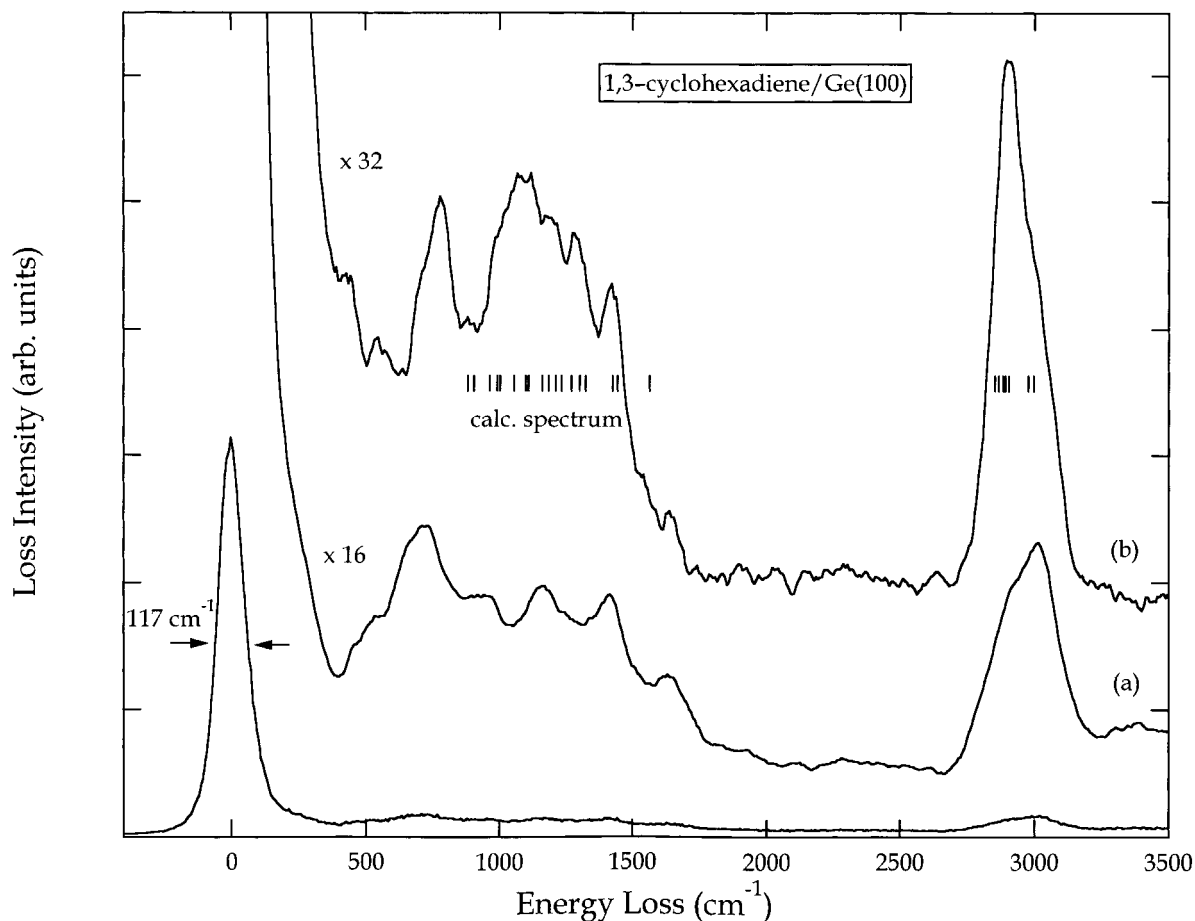
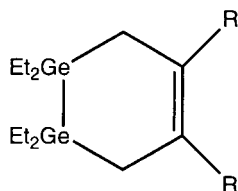


Fig. 2. (a) HREEL spectrum of a multilayer of 1,3-cyclohexadiene at a surface temperature of 100 K. (b) HREEL spectrum after annealing the multilayer of 1,3-cyclohexadiene to 300 K. The bar graph indicates the calculated vibrational frequencies (R. Konecny, D.J. Doren, pers. commun.) for a Diels–Alder cycloaddition reaction. The calculated frequencies are scaled by a factor of 0.94.

now reduced in intensity and is observed at 1635 cm^{-1} in the annealed spectrum. Comparison of the loss features with related germanium containing compounds, as pictured below [13], aid in the assignment of these peaks. The loss at 1635 cm^{-1} is assigned as a ring C=C stretch and



R = H, Me

the low energy loss at 555 cm^{-1} is assigned as a combination Ge–Ge–C stretch. The remaining losses can be attributed to ring modes. The shifts in energy for the ring modes compared with the 100-K spectrum and the changes observed in the CH stretching region are consistent with a cycloaddition reaction.

To help interpret Fig. 2b further, the vibrational frequencies for the Diels–Alder adduct calculated by R. Konecny and D.J. Doren (pers. commun.) on Si(100) are shown in Fig. 2. The calculated frequencies are scaled by a factor of 0.94, which is a typical value for comparison with experimental results. It is also the same factor used to compare

Table 1
Vibrational assignments for 1,3-cyclohexadiene/Ge(100)

Mode	Measured	IR spectrum (liquid) ^a	Raman spectrum (liquid) ^b
Ring deformation	670 740	660 750	n.r.c 754
Ring breathing	900	850	849
Ring stretch	970	930, 940	947,952
CH ₂ wagging; twisting; rocking; CH in-plane, out-of-plane bending	1170	1060, 1160, 1240, 1370	1057, 1145, 1177, 1241, 1325
CH ₂ scissors, ring C–C stretch	1415	1430	1408, 1426, 1437
Ring C=C stretch	1640	1720	1563, 1579
CH ₂ stretch	n.r.	2860	2822, 2854, 2873
=CH stretch	2930, 3010	2940, 3030	2938, 3042

^aCoblentz Society Spectral Collection 2682.

^bRef. [12].

n.r., not resolved.

The mode assignments are based on Ref. [12].

the calculated results with Bent and co-workers' IR results on Si(100) [3]. The agreement between the calculated frequencies in the CH stretching region and the experimental spectrum is quite good. However, the agreement with between the measured and calculated frequencies below 1700 cm⁻¹ is poorer. This difference can be attributed to reduced mass effects when comparing the experimental results on Ge(100) with the calculated results on silicon. Taken together, the UPS and HREELS data clearly show that 1,3-cyclohexadiene reacts readily with the Ge(100) surface via a cycloaddition reaction. Comparison of these experimental results with calculated frequencies on a Ge surface would enable us to determine better whether the surface reaction proceeds via a [2 + 2] or [4 + 2] cycloaddition reaction.

The thermal desorption behavior of 1,3-cyclohexadiene on Ge(100)-(2 × 1) was also examined. The TPD results and the adsorption of 1,3-cyclohexadiene and 1,4-cyclohexadiene will be reported elsewhere (S.W. Lee, L.N. Nelen, H. Ihm, B. Flint, C.M. Greenlief, unpublished results).

In conclusion, the adsorption and reaction of 1,3-cyclohexadiene on the Ge(100)-(2 × 1) surface has been investigated. Adsorption of this molecule at 300 K results in the formation of a cycloaddition surface adduct.

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