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Evidence for a Retro-Diels−Alder Reaction on a Single Crystalline Surface: Butadienes on Ge(100)

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The analogue of one of the most important reactions in organic chemistry, the Diels−Alder reaction, has recently been reported for conjugated dienes on a Si(100)-2×1 surface.[1−3] This reaction leads to the formation of a six-membered cycle, containing the two silicon atoms of a dimer at the (100)-(2×1) surface of silicon and the four carbon atoms of the reactant diene. Although newly identified, Diels−Alder chemistry at semiconductor surfaces already has exciting potential as a method for controlled synthesis of organic/semiconductor interfaces. Furthermore, this reaction may be used as a starting point for lithographic patterning schemes if appropriate methods can be found to remove unmodified Diels−Alder adducts from the surface. One promising possibility is the so-called retro-Diels−Alder reaction.

Unfortunately, the retro-Diels−Alder process is not observed on the Si(100)-2×1 surface. Instead, the principal pathway for the thermal transformation of the Diels−Alder adduct on silicon is found to be decomposition.[3]

Here we report what is to our knowledge the first observation of retro-Diels−Alder reactions between conjugated butadienes and the Ge(100)-2×1 surface. It will be shown that Diels−Alder chemistry occurs on Ge(100)-2×1 at room temperature as readily as on Si(100)-2×1; however, in contrast to Si(100)-2×1, butadienes are reformed and released into the gas phase upon thermal annealing.

The experimental results presented here were obtained in two ultrahigh vacuum chambers. The first chamber is designed for temperature-programmed reaction/desorption (TPR/D) studies and Fourier transform infrared spectroscopy using multiple internal reflection (MIR−FTIR). The second chamber is equipped with a mass spectrometer, an ion gun for surface cleaning, and a Retarding Field Analyzer (RFA), which can be used both for Low Energy Electron Diffraction (LEED) studies and for Auger Electron Spectroscopy (AES) analysis. Both chambers have been described in detail previously.[3,4] The Ge(100) samples were mounted on manipulators with capabilities for heating the sample to 950 K and cooling it to 100 K. For the MIR-FTIR studies, a 50 × 20 × 1 mm^3 sample of Ge(100) with 45° beveled edges (Harrick) was used. The samples were cleaned by sputtering with Ar$^+$ ions at room temperature followed by annealing at 875 K for 5 min,[5−7] until a sharp (2×1) LEED pattern was observed and no carbon was detected by AES. TPR/D studies were performed with use of a DC power supply with a temperature controller (Eurotherm) to maintain the temperature ramp of 1 K/s.

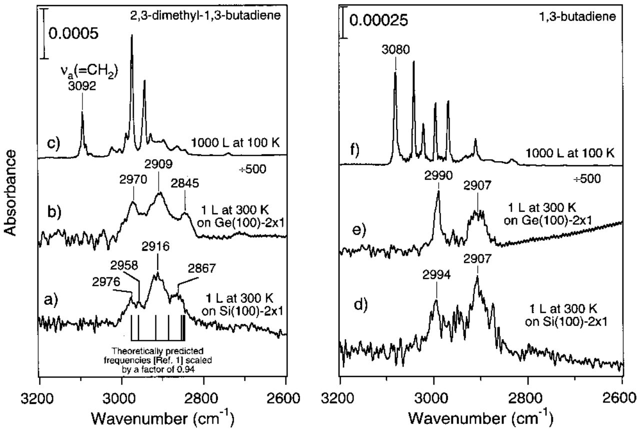

Figure 1. Infrared spectra of 2,3-dimethyl-1,3-butadiene (a) chemisorbed on Si(100)-2×1 at 300 K, (b) chemisorbed on Ge(100)-2×1 at 300 K, and (c) physisorbed in multilayers at 100 K and 1,3-butadiene (d) chemisorbed on Si(100)-2×1 at 300 K, (e) chemisorbed on Ge(100)-2×1 at 300 K, and (f) physisorbed in multilayers at 100 K. The theoretically predicted frequencies (in cm^{-1}) occur at 2846, 2850, 2854, 2885, 2916, 2958, and 2976 [ref 1].

The results of MIR-FTIR studies of 1,3-butadiene and of 2,3-dimethyl-1,3-butadiene are presented in Figure 1. In Figure 1b, the infrared spectrum of 1 L of 2,3-dimethyl-1,3-butadiene chemisorbed on the Ge(100)-2×1 surface at room temperature is compared to chemisorption on the Si(100)-2×1 surface reported earlier (Figure 1a)[2] and to a spectrum of multilayers of 2,3-dimethyl-1,3-butadiene physisorbed at 100 K (Figure 1c). The MIR-FTIR results for 1,3-butadiene are also shown chemisorbed at room temperature on Si(100)-2×1 (Figure 1d), chemisorbed on Ge(100)-2×1 (Figure 1e), and physisorbed at 100 K (Figure 1f).

For both butadienes, the spectra of chemisorbed species are consistent with Diels−Alder-type addition of butadiene to the dimers of the Ge(100)-2×1 surface. It is evident from Figure 1 that the chemisorbed spectra on Ge(100)-2×1 are very similar to those on Si(100)-2×1, and that the bonding structure of the diene must be the same on the two surfaces. As for Si(100)-2×1,[3] the spectra of butadienes on Ge(100)-2×1 can be assigned to the Diels−Alder adduct largely due to the absence of the terminal vinylic CH$_2$ stretch, since upon formation of the Diels−Alder ring, this functional group in the molecule is lost. These modes, which are the higher wavenumber peaks seen in the physisorbed hydrocarbon spectra (near 3090 cm^{-1}), completely disappear upon chemisorption. It can also be seen that the spectrum of 2,3-dimethyl-1,3-butadiene chemisorbed at room temperature on Si(100)-2×1[2] agrees well with the theoretical prediction by Konecny and Doren[1] for the Diels−Alder product. Therefore, we conclude that as on Si(100)-2×1, Diels−Alder adducts with both butadienes are formed on the Ge(100)-2×1 surface. Minor differences in the spectra for butadiene chemisorbed on Si(100) versus Ge(100) exist, particularly in the CH$_2$ modes, suggesting that the small difference in size between the dimers of the Si(100)-2×1 and Ge(100)-2×1 surfaces[8] affects these vibrational frequencies. These small frequency differences observed for the butadienes are consistent with studies of other hydrocarbons obtained in our group, which also show shifts of less than 15 cm^{-1} between the two surfaces.

Importantly, the thermal chemistry is notably different on Ge compared to Si. Whereas on Si(100)-2×1, decomposition is the major reaction pathway for chemisorbed 1,3-butadiene,[3] the only

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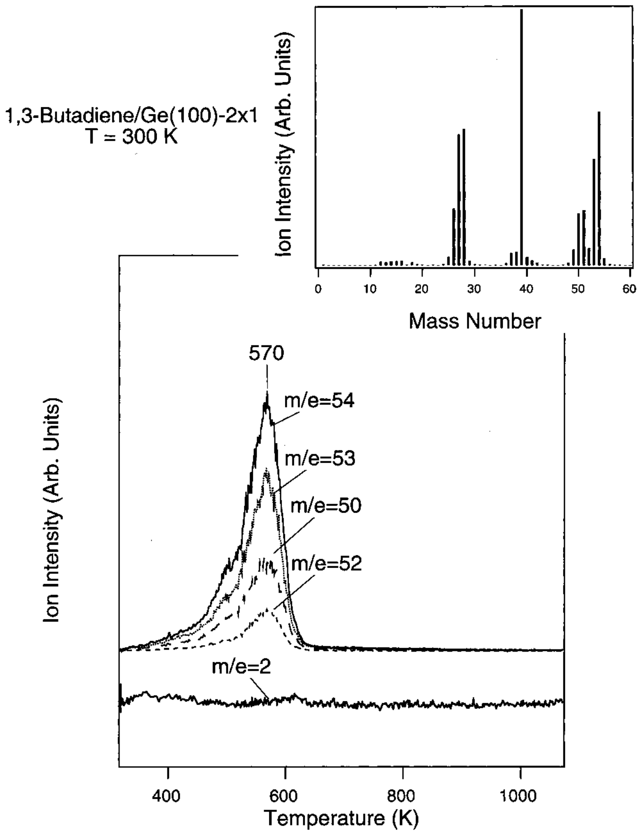

Figure 2. Temperature-programmed reaction/desorption mass spectra for 1,3-butadiene chemisorbed on Ge(100)-2×1. The inset shows the mass spectrum for 1,3-butadiene.

thermal reaction pathway observed for 1,3-butadiene on the Ge(100)-2×1 surface is a retro-Diels−Alder transformation. This retro-reaction leads to the evolution of the original 1,3-butadiene near 570 K, as shown in Figure 2. The cracking pattern of the hydrocarbon desorbing from Ge(100)-2×1 at 570 K is nearly identical to that recorded for 1,3-butadiene gas (see inset). No evidence for evolution of other hydrocarbons or their fragments was obtained from the Ge(100)-2×1 surface within the sensitivity of our experimental methods. Hydrogen, which is reported to desorb from germanium between 570 and 600 K,[9,10] does not appear to be a significant product. The small increases in hydrogen ($m/e = 2$) signal in Figure 2 are within the level of noise, indicating that 1,3-butadiene does not dehydrogenate to a significant extent.

While the thermal chemistry is not as clean nor as simple for 2,3-dimethyl-1,3-butadiene, the principal pathway is nevertheless found to be retro-Diels−Alder. Although some decomposition is observed upon thermal treatment, as evidenced by an H_2 peak at 600 K, the majority of butadiene molecules desorb over a wide temperature range from 350 to 650 K. No other hydrocarbon fragments have been found to evolve from the surface in this temperature range.

These TPR/D results are consistent with the AES results obtained in a separate ultrahigh vacuum chamber. No carbon was detected to remain on the Ge(100)-2×1 surface after retro-Diels−Alder reaction of chemisorbed 1,3-butadiene. Only small coverages of carbon were found to remain on the surface after annealing Ge(100)-2×1 predosed with 2,3-dimethyl-1,3-butadiene at room temperature. For both dienes, the LEED studies before adsorption showed a sharp (2×1) pattern; following adsorption, the LEED pattern, although less sharp, remained (2×1).

These results demonstrate the generality of the Diels−Alder reaction for single-crystalline covalent (Group IV) surfaces. It is shown that Diels−Alder chemistry occurs on Ge(100)-2×1 as it does on Si(100)-2×1. It is probable that the reaction will also proceed on the C(100)-2×1 diamond surface. There are clear differences, however, in the detailed thermal chemistry on the different surfaces. While the forward Diels−Alder reaction is the principal chemisorption pathway on both Si(100)-2×1 and Ge(100)-2×1, the reverse Diels−Alder reaction competes with an alternative pathway of dehydrogenation of the hydrocarbon. On silicon, this dehydrogenation reaction prevails over the retro-Diels−Alder reaction, whereas on germanium, retro-Diels−Alder chemistry dominates. These results clearly demonstrate the exciting opportunities for further studies to understand and exploit the differences in reactivity of hydrocarbons on silicon versus germanium surfaces.

The use of Diels−Alder reactions for surface modification may allow for the formation of controllable and highly reactive substrates for further surface functionalization, and may become an important synthetic tool for electronics and nonlinear optical materials. At the same time, the possibility of a retro-Diels−Alder process on semiconductor surfaces covered with chemisorbed hydrocarbons presents new opportunities for lithographic methods of surface modification. On Ge(100)-2×1, chemisorbed butadienes can potentially be modified in a spatial fashion by photoinduced or electron-induced chemistry, while unreacted butadienes can be easily removed from the surface by the retro-reaction to generate clean Ge.

In conclusion, we have shown that 1,3-butadiene and 2,3-dimethyl-1,3-butadiene react with the dimers of the Ge(100)-2×1 surface to form a Diels−Alder adduct, in a reaction similar to that which occurs on Si(100)-2×1. A retro-Diels−Alder reaction, leading to the evolution of the original butadiene molecules, was observed on Ge(100)-2×1, in contrast to Si(100)-2×1.

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Supporting Information Available: Temperature programmed desorption spectrum for 2,3-dimethyl-1,3-butadiene (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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