



Reaction of *tert*-butyl isocyanate and *tert*-butyl isothiocyanate at the Ge(100) – 2 × 1 Surface

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ABSTRACT

The adsorption of *tert*-butyl isothiocyanate and *tert*-butyl isocyanate at the Ge(100) – 2 × 1 surface was probed using multiple internal reflection Fourier transform infrared (FTIR) spectroscopy X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) modeling. Results indicate that there are multiple surface products for each molecule. FTIR studies of *tert*-butyl isothiocyanate reveal adsorption through an S-dative bonded state, while XPS studies further suggest a reactive desorption product which leaves excess sulfur atoms at the surface. Studies of *tert*-butyl isocyanate indicate that the molecule dissociatively adsorbs at the surface, resulting in *tert*-butyl and germyl isocyanate groups, as the major pathway, in addition to forming several minor products, including a [2 + 2] cycloaddition product across the C=N bond. DFT was used to simulate vibrational spectra and map the reaction pathways, and confirms that the assigned products are energetically favorable.

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1. Introduction

With the continued pursuit of smaller feature sizes, the microelectronics industry is facing a need for atomic scale control of device dimensions. This level of control increases the importance of interfaces, where well-defined, sharp transitions between materials are necessary to generate the desired architectures. A promising technique for controlling interfaces is organic functionalization, in which organic molecules are reacted with an inorganic surface. By building these organic/inorganic structures, functionality can be added to the device, and an extensive library of organic moieties becomes available for device integration, with specific applications including biological interfacing [1,2], inorganic electronics [3–5], and molecular electronics [6,7]. Since the relevant dimensions in these applications are those of the organic molecules, a tight control over the interface properties is required.

Organic functionalization of group IV semiconductors, particularly the (100) – 2 × 1 reconstructed surfaces of silicon and germanium, has received increased attention in the last 10 years [8–13]. Although silicon was the primary surface of interest initially, germanium has gained considerable attention in the past several years, due to its high charge mobility, which is up to four times that of silicon [14]. Additionally, the Ge(100) – 2 × 1 surface has been shown to be more selective towards organic reaction products than the Si(100) – 2 × 1 surface, owing to the generally weaker bonding of the organics to Ge

[15,16], which allows for a thermodynamic product distribution, rather than the kinetic distribution often observed for the Si surface.

The bonding of organic molecules at the Ge(100) – 2 × 1 surface occurs primarily at the Ge dimer. The reconstructed surface is comprised of rows of dimers, with the dimer bond consisting of a strong σ interaction and a weak π interaction. At room temperature, these dimers are statically tilted, with a corresponding electron charge redistribution, resulting in an electron-rich atom tilted outward from the surface and an electron-poor atom tilted inward. With this interesting bond character, the dimer bond has been shown to react with organic molecules in a manner analogous to organic moieties, most commonly behaving akin to an olefin or carbonyl. This reactivity of the dimer bond leads to a diverse library of potential reactions, including cycloaddition reactions, dative bond formation, proton abstraction, and nucleophilic addition [9,11,12,17].

The isocyanate and isothiocyanate functional groups are highly reactive and each contain two heteroatoms in a cumulated double bond. This leads to the possibility for many products upon reaction with the Ge(100) – 2 × 1 surface. In the reaction of phenyl isocyanate with the Ge(100) – 2 × 1 surface, a [2 + 2] cycloaddition product is formed across the C=N bond creating a thermodynamically favorable carbonyl [18]. The reactivity of phenyl isothiocyanate shows a marked difference from that of phenyl isocyanate. Two products are formed: a [2 + 2] cycloaddition adduct across the C=S bond as a major product and a [2 + 2] cycloaddition adduct across the C=N bond as a minor product [18]. Additionally, evidence suggests a desorption product, which results in excess sulfur at the surface.

The interesting reactivity of phenyl isocyanate and phenyl isothiocyanate at the Ge(100) – 2 × 1 surface leads to questions

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about the reactivity of other molecules containing isocyanate and isothiocyanate moieties. In phenyl isocyanate and phenyl isothiocyanate, the isocyanate and isothiocyanate group are conjugated with the phenyl ring, and the electronic effects of the ring affect the reactivity at the surface. Molecules without such conjugation may provide new information into the reactivity of these functional groups, and to identify reaction pathways, we have studied the reaction of *tert*-butyl isocyanate and *tert*-butyl isothiocyanate at the Ge(100)– 2×1 surface. The *tert*-butyl group lacks the electron donation of the phenyl ring, or contribution from any other unsaturated chemical moiety.

Potential reactions for *tert*-butyl isocyanate and isothiocyanate with the Ge(100)– 2×1 surface dimer are summarized in Fig. 1. The products include dative-bonded states through either of the heteroatoms and cycloaddition products through a [2+2] reaction across the C=N or C=X bonds or through a 1,3-dipolar cycloaddition reaction. With a *tert*-butyl substituent, α -H elimination is not possible, hence this pathway was not considered. Despite all of these potential products, we will show that *tert*-butyl isothiocyanate forms an S dative-bonded product, whereas *tert*-butyl isocyanate forms several products, including a dissociation of the isocyanate to *tert*-butyl bond across the Ge dimer, forming a germyl isocyanate product, and a CN [2+2] product.

2. Experimental

Experiments were carried out on the Ge(100)– 2×1 reconstructed surface in two separate ultra-high vacuum chambers. In each of the chambers the base pressure was less than 2×10^{-10} torr, and the surface reconstruction was achieved by argon sputtering followed by high temperature annealing, with specifics given below. Fourier transform infrared (FTIR) spectroscopy studies were performed in a chamber that has been described previously [19]. The Ge crystal substrate was a trapezoid with dimensions of 19 mm \times 14 mm \times 1 mm and 45° beveled edges (Harrick Scientific). Argon ion sputtering (20 mA emission current at 0.5 keV accelerating voltage with 7–8 μ A sample current) for 20 min at room temperature, followed by a 900 K anneal for 5 min resulted in the reconstructed surface, with undetectable levels of carbon, oxygen and nitrogen by Auger electron spectroscopy, and verified by a 2×1 low-energy electron diffraction (LEED) pattern. IR spectra were collected in a multiple internal reflection (MIR) geometry using a BioRad FTS-60A spectrometer with a narrow band mercury–cadmium–telluride (MCT) detector. Baseline

corrections to the spectra were performed using linear fitting functions between spectral features.

X-ray photoelectron spectroscopy (XPS) studies were also performed on a chamber which has been described previously [15]. Samples were approximately 8 mm \times 8 mm \times 0.5 mm (MTI Corp.) in size. Room temperature argon ion sputtering (20 mA emission current at 1 keV accelerating voltage for 12 μ A sample current, with an incident ion beam at 12° from the surface normal) for 30 min., followed by annealing to 900 K for 15 min yielded the 2×1 surface reconstruction, verified by LEED. The difference in sputtering parameters between the XPS and IR chambers was due to the difference in chamber geometries and beam focus on the sputter controllers. XPS after cleaning did not reveal detectable levels of carbon, nitrogen or oxygen. Spectra were collected with a pass energy of 25 eV, with energy scale and peak intensity calibrated using the Ge(3d) photoelectron peak. Spectra were fit to pure Gaussians with a Shirley baseline and a realistic number of components, each held to the same fwhm within a spectrum.

Tert-butyl isocyanate ($\geq 99\%$ Sigma-Aldrich) and *tert*-butyl isothiocyanate ($\geq 99\%$ Sigma-Aldrich), both clear liquids at room temperature and atmospheric pressure, were transferred to sample vials under dry air. Compounds were purified by several freeze-pump-thaw cycles and then introduced to the chambers after sample cleaning through variable leak valves. Exposures are reported in Langmuirs (1 L = 10^{-6} torr-s) and pressures were not corrected for ionization gauge sensitivity. *In situ* mass spectrometry confirmed the molecular identity of each compound within the chamber.

All quantum chemical calculations were carried out using Becke3 Lee-Yang-Parr (B3LYP) three-parameter density functional theory (DFT) with the Gaussian 03 software suite [20]. Previous studies on similar systems indicate that B3LYP provides results that agree well with experimental results when available [15,19,21,22]. The surface was modeled by a single-dimer Ge₉H₁₂ cluster in most cases, with the use of a Ge₂₃H₂₄ 2-dimer trench cluster or a Ge₁₅H₁₆ 2-dimer row cluster to capture interdimer reactions when necessary. The systems were calculated with a split basis set, using a triple- ζ 6-311++G(d,p) basis set for the Ge dimer atoms and adsorbate atoms, and using the LANL2DZ pseudopotential for subsurface Ge atoms. This kept calculations computationally practical and provided sufficient accuracy in the results. Subsurface Ge-cluster atoms were terminated with hydrogen atoms modeled using the 6-31G(d) basis set to approximate neighboring Ge atoms. In all frequency calculations, these terminating

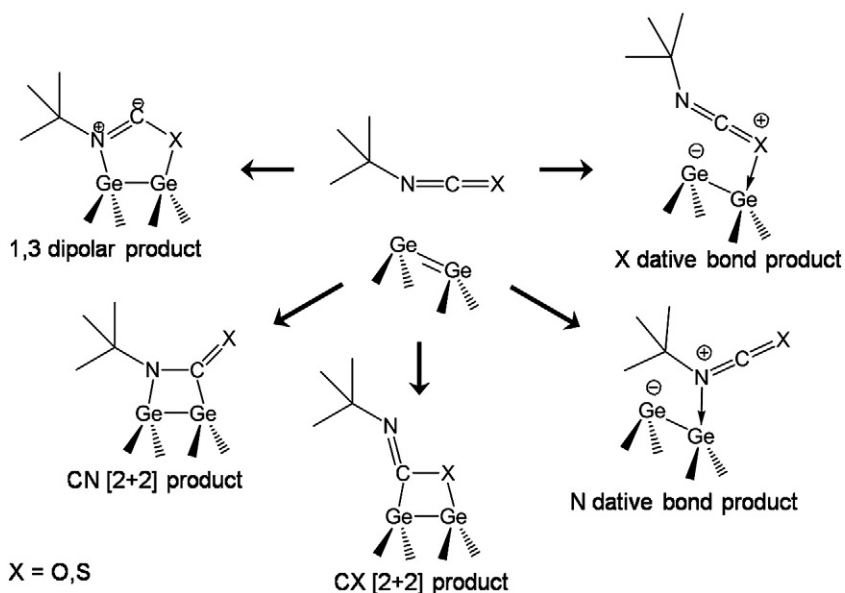


Fig. 1. Potential surface products for *tert*-butyl isocyanate and isothiocyanate groups reacting with the Ge(100)– 2×1 surface dimer.

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