Surface Science 615 (2013) 72–79

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Competing geometric and electronic effects in adsorption of phenylenediamine structural isomers on the Ge(100)-2 × 1 surface

Jessica S. Kachian, Kristin H. Squires, Stacey F. Bent *

Department of Chemical Engineering, Stanford University, 381 North South Mall, Stanford, CA 94305-5025, USA

ARTICLE INFO

Article history:
Received 8 February 2013
Accepted 30 March 2013
Available online 6 April 2013

Keywords:
Germanium
Aniline
Phenylenediamine
X-ray photoelectron spectroscopy
Infrared spectroscopy
Density functional theory

ABSTRACT

The adsorption behavior of ortho-, meta-, and para-phenylenediamine (PD) structural isomers (o-, m- and p-PD) at the Ge(100)-2 × 1 surface has been studied and compared with aniline. Our results indicate that at room temperature, aniline and all PD isomers adsorb on Ge(100)-2 × 1 via N–H dissociation, with no dative-bonded adducts observed. For each PD isomer on Ge(100)-2 × 1, a fraction of the adducts are adsorbed through both amino groups. This fraction is greatest for m-PD, somewhat lower for o-PD, and significantly lower for p-PD. The observed trend in reactivity is ascribed to a combination of geometric and electronic effects. Our results indicate that geometrically, the ortho isomer is best suited to surface attachment through both amino groups, while electronically, the aromatic nature of the benzene spacer between isomer amino groups renders dual N–H dissociation most favorable for the meta isomer. The results elucidate the competing role of electronic and geometric effects in this adsorption system.

1. Introduction

Over the past two decades, considerable attention has been directed toward organic functionalization of Group IV semiconductor surfaces due to its potential applications in the development of molecular-scale devices [1–3]. Combining the tailorability of organic materials with the precise interface control provided by atomically clean surfaces can impart novel functionalities to nanoscale devices. Realizing this vision requires a detailed understanding of the chemistry taking place at the semiconductor surface. In particular, interest in the attachment of bifunctional molecules at the semiconductor surface is driven by the potential to create versatile multilayer structures and films. As a starting point in development of a sequential "molecular layer deposition" process for growth of ultrathin organic films [4–7], molecular design rules must first be determined to select a bifunctional molecule in which one moiety reacts with the surface while the other functional group remains available for attachment to a subsequent layer.

Recent studies have shown that analogies between the organic functionalization of (100)-2 × 1 Group IV semiconductor surfaces and classic solution-phase organic chemistry constitute a means for characterizing and understanding these surface reactions [8–11]. Upon proper preparation, Ge(100) and Si(100) surfaces undergo a 2 × 1 reconstruction, which entails the formation of surface dimers possessing a strong σ bond and a weak π bond. The tilting of these dimers creates an uneven distribution of charge within the dimer, resulting in an electron-rich, nucleophilic "up" atom and an electron-deficient, electrophilic "down" atom [12]. Consequently, the up and down atom of a dimer can function as a Lewis base and Lewis acid, respectively [8,13,14].

This chemical description is invoked in our present study of the adsorption of structural isomers of phenylenediamine (PD) and of aniline on the clean Ge(100)-2 × 1 surface. These molecules (shown in Fig. 1) contain one or two amine groups, each of which can form a dative bond to the germanium surface by donating the nitrogen lone pair of electrons to the electron-deficient down atom of the germanium dimer. At room temperature, these dative-bonded adducts may remain stable or alternatively may undergo a subsequent N–H dissociation event in which a nucleophilic up atom of the germanium surface abstracts a hydrogen from the nitrogen atom of a dative-bonded amino group. At room temperature, both aniline [15–19] and p-phenylenediamine [15] undergo N–H dissociation on the analogous Si(100)-2 × 1 surface, with the latter reacting through only one amino group [15]. However, the same products may not form on Ge(100)-2 × 1, since the literature has shown significant differences in amine reactivity between these two surfaces [14,20,21]. For monofunctional molecules, this is due mostly to the difference in proton affinity between the two surfaces [14]. All the monofunctional alkyl and aromatic amines investigated thus far on Si(100)-2 × 1 have been shown to adsorb via N–H dissociation at room temperature [14,15,17–19,22–26]. On the other hand, whereas some amines such as pyrrolidine [24] and pyrrole [24] undergo N–H dissociative adsorption on Ge(100)-2 × 1 at room temperature, others such as methylamine [14] remain trapped in the dative bonded state under the same conditions. However, because the amino group of an aromatic amine is considerably more acidic than that of an alkylamine,

* Corresponding author. Tel.: +1 650 723 0385; fax: +1 650 723 9780.
E-mail address: sbent@stanford.edu (S.F. Bent).

0039-6028/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.susc.2013.03.024

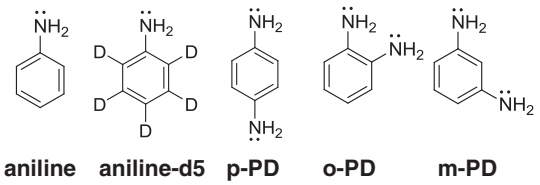

Fig. 1. Aniline, aniline-d5, para-phenylenediamine (p-PD), ortho-phenylenediamine (o-PD) and meta-phenylenediamine (m-PD).

aniline and the PD isomers may be expected to undergo some N–H dissociation on Ge(100)-2 × 1.

The interest in studying phenylenediamine adsorption on Ge is also motivated by the potential altered reactivity of a functional group at Ge or Si when present within a polyfunctional molecule. This has been illustrated by the results for glycine both on Ge(100)-2 × 1 [21] and on Si(100)-2 × 1 [20]. Whereas methylamine adsorbs only through N dative bonding on Ge(100)-2 × 1 [14], at the same surface the primary amine group in glycine forms a combination of N dative-bonded and N–H dissociated adducts [21]. Moreover, on Si(100)-2 × 1 [14], methylamine undergoes N–H dissociation at room temperature whereas the primary amine group of glycine does not react at this surface. These examples also illustrate the difference in reactivity of polyfunctional molecules on Ge(100)-2 × 1 versus Si(100)-2 × 1.

In the present work, we use a combination of experimental and theoretical methods to investigate the adsorption products of aniline and the PD isomers on the Ge(100)-2 × 1 surface. Our results will show that at room temperature, as described in a recent paper [27], aniline adsorbs on Ge(100)-2 × 1 via N–H dissociation, with no dative-bonded adduct observed. Phenylenediamine provides an interesting system for study because it allows examination of the role of a second amine group on the same aromatic molecule. Specifically, by examining adsorption of the phenylenediamine structural isomers, we aim to determine the effects of adsorbate geometry and electronic structure on reactivity with the Ge(100)-2 × 1 surface. We will show that reaction of each PD isomer with the Ge(100)-2 × 1 surface at room temperature leads to a fraction of adducts in which only *one* amino group has undergone N–H dissociation, with *no* dative bonding observed. Moreover, the isomers differ in the fraction of dually N–H dissociated adducts, and the factors driving this difference are examined in this paper.

The study of the PD structural isomers allows us to elucidate whether the factors influencing the reaction pathways for adsorption are primarily geometric or electronic in nature. If the electronic structure of the adsorbate is the dominant influence on reactivity, aromatic chemistry predicts that the fraction of dually N–H dissociated adducts will be similar for o-PD and p-PD while it will be larger for m-PD, which should experience a greater degree of resonance stabilization upon N–H dissociation on Ge(100)-2 × 1. On the other hand, the benzene ring may effectively act as a rigid, planar spacer, thus rendering adsorbate geometry the key determinant of reactivity. In this case, having spacing between amino groups on the benzene ring that is similar to surface interdimer distances will favor dual dissociation, because it minimizes ring strain. Our DFT results indicate that the ortho adducts are the least strained and are, therefore, slightly favored geometrically over the meta adducts, and significantly favored geometrically over the para adducts.

In this paper, we will show that the observed trend in reactivity of the PD isomers with the Ge(100)-2 × 1 surface is as follows: the extent of dual N–H dissociation is greatest for the meta isomer, slightly less for the ortho isomer, and least for the para isomer. Hence, our results will show that *both* geometric and electronic effects play a significant role in controlling the product distribution at the surface.

2. Experimental and Computational Details

Infrared experiments were completed under ultrahigh vacuum conditions (UHV) in a previously described reaction chamber [14] with a base pressure of less than 1×10^{-10} Torr. Briefly, the UHV chamber was paired with a BioRad FTS-60A Fourier transform infrared (FTIR) spectrometer equipped with a liquid nitrogen-cooled narrow-band mercury–cadmium–telluride (MCT) detector. A trapezoidally shaped Ge(100) crystal (19 × 14 × 1 mm, 45° beveled edges) designed for multiple internal reflection (MIR) experiments was conductively heated by a resistive tungsten heater and cooled by heat exchange with a copper braid connected to a liquid nitrogen reservoir. The temperature of the sample was monitored using a thermocouple directly attached to the crystal. Ge(100) surface cleaning via two cycles consisting of sputtering (0.5 keV Ar^+ ions, 20 min, room temperature) followed by annealing (900 K, 5 min) resulted in the reconstructed surface, as confirmed by a 2 × 1 low-energy electron diffraction (LEED) pattern. Levels of carbon, oxygen, and nitrogen were below the detection limit of our Auger electron spectrometer following this cleaning procedure. The unpolarized beam from the FTIR spectrometer entered the chamber through a CaF_2 viewport, was focused onto the beveled edge of a germanium MIR crystal (Umicore), and then exited through another CaF_2 viewport at a right angle to the first viewport. The beam path was purged by nitrogen gas to eliminate gas phase H_2O and CO_2 spectral features. The spectral range of the collected infrared data is limited by absorption by the CaF_2 windows, resulting in a low-frequency cutoff of ~1050 cm^{-1}. To record infrared spectra of unreacted molecules, several multilayers were condensed on the surface of the sample at low temperature (<140 K). All spectra were corrected for baseline sloping via placement of linear functions between points enclosing regions with no spectral features.

X-ray photoelectron spectroscopy (XPS) studies were performed using a separate UHV chamber, which has also been described previously [28]. The base pressure of this chamber is $<2 \times 10^{-10}$ torr. For XPS experiments, the Ge (100) crystal (MTI Corp.), which is approximately 8 mm × 8 mm × 1 mm in size, was cleaned by room-temperature Ar + sputtering (20 mA emission current, 1.0 keV accelerating voltage, ~18 μA sample current) for 30 min followed by annealing to 900 K for 20 min. Following the sample preparation procedure, carbon, oxygen, and nitrogen levels were below the detection limit of our X-ray photoelectron spectrometer, and the LEED pattern confirmed that the 2 × 1 surface reconstruction was achieved with this cleaning procedure. Due to interference by the Ge Auger series, it was necessary to record the C(1s) photoelectron spectra with the Al anode and the O(1s) and N(1s) photoelectron spectra with the Mg anode, where anode power is 250 W (12.5 kV anode voltage, 20 mA emission current.) Spectra were collected with a pass energy of 25 eV, and the Ge(3d) photoelectron peak was used as an internal standard for calibration of the energy scale and peak intensity. Shirley baseline subtractions were applied to the photoelectron spectra, which were fit with a chemically realistic number of Voigt components constrained to the same full width at half maximum (FWHM) value for a given spectrum.

Aniline (99.5%, Sigma-Aldrich) and aniline-d5 (98 atom % D, Sigma-Aldrich) are clear, colorless to light yellow liquids at room temperature. Each liquid compound was purified by several freeze-pump-thaw cycles before exposure to the clean crystal surface. Exposure of a compound was accomplished by backfilling via a variable leak valve. p-phenylenediamine (99%, Fluka); o-phenylenediamine (99.5%, Sigma-Aldrich); and m-phenylenediamine (99%, Sigma-Aldrich) are solids at room temperature. The phenylenediamine samples were purified by repeated pumping cycles. The vapor in equilibrium with the solid sample was then leaked into the vacuum chamber by means of a gate valve separating the solid doser from the chamber. Surface exposures are reported in Langmuir (1 L) (1 L = 10^6 Torr*s), and pressures were not corrected for ionization gauge sensitivity. An in