Thermally Activated Reactions of Phenol at the Ge(100)-2 × 1 Surface

Bonggeun Shong,[1,2,+] Abu Saad Ansari,[2,+] and Stacey F. Bent [1,*]

1 Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States

2 Department of Chemical Engineering, Hongik University, Seoul 04066, Republic of Korea

+ These authors contributed equally.

Abstract

Organic functionalization of semiconductor surfaces may be utilized to couple the properties of semiconductor materials with organic molecules. In this work, the adsorption and thermal reaction of phenol on the Ge(100)-2 × 1 surface were studied. A combination of multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy under ultrahigh vacuum (UHV) conditions and density functional theory (DFT) calculations was used to elucidate the surface chemical reactions of phenol. While phenol initially chemisorbs on Ge(100)-2×1 via O−H dissociation to form phenoxy (C_6H_5O*), annealing to 573 K transforms the adsorbate into phenyl (C_6H_5*). A sequential reaction pathway for the migration of oxygen into substrate and formation of phenyl is suggested, which requires significant thermal activation and yields slight exothermicity.

Introduction

With shrinking critical dimensions of electronic devices to the nanometer scale, there has been continuing research interest on utilization of germanium (Ge) as a next-generation semiconductor material, inspired by its advantageous material properties such as higher carrier mobility and lower dopant activation temperature than those of Si [1–3]. Still, challenges remain toward integration of Ge into microelectronics fabrication, such as engineering of the dielectric-semiconductor interface with sufficient reliability. On the other hand, organic functionalization of semiconductor surfaces is a scheme to combine established knowledge of inorganic semiconductor processing techniques with the tailorability of organic molecules [4,5], with potential applications such as nanoscale patterning, molecular electronics, and chemical and biological sensors. Functionalization of semiconductors has been studied on a variety of surfaces, with specific focus on the (2×1) reconstructed (100) surfaces of Ge and Si that exhibit "dimer" moieties with chemical properties of both zwitterion and double bond [6].

Various aromatic molecules' adsorption chemistry has been studied on the Ge(100) surface [7–11]. Unlike on reactive surfaces of catalytic metals such as Ni or Pt at which molecular decomposition readily occurs [12,13], the aromaticity of the molecules on Ge is often well preserved upon adsorption due to the moderate reactivity of the surface [14]. Even in some examples such as adsorption of nitrobenzene (C_6H_5-NO_2) and phenyl isocyanate (C_6H_5-NCO) on Ge(100), by which post-adsorption transformation of the molecular structure was observed, an intact phenyl (C_6H_5-) moiety was observed as part of the final reaction product [15,16]. The adsorption product of phenol (C_6H_5-OH) on Ge(100) at room temperature also has been reported as a surface phenoxy moiety (C_6H_5O*), formed by a proton transfer reaction to the Ge surface dimer [17].

In this work, the thermal transformation reactions of phenol adsorbed on the Ge(100)-2 × 1 surface are studied using Fourier transform infrared (FTIR) spectroscopy under ultrahigh vacuum (UHV) conditions and density functional theory (DFT) calculations. While phenol initially chemisorbs on the surface at 300 K to form adsorbed phenoxy, annealing the phenol-exposed surface to 573 K yields phenyl directly bonded to the surface (C_6H_5*). Sequential migration of O into the substrate is suggested as a possible reaction mechanism, as summarized in Figure 1.

Experimental and Computational Methods

FTIR spectroscopy experiments were conducted in a previously described UHV chamber [18] with a base pressure in the 10^{-10} Torr regime. A trapezoidal Ge(100) crystal (Harrick Scientific, 19 × 14 × 1 mm^3, 45° beveled edges) was used as substrate after alternative cycles of Ar^+ sputtering and annealing. The 2 × 1 reconstruction of the surface was confirmed using low-energy electron diffraction (LEED).[19] The sample was radiatively heated by a resistive tungsten heater, whose temperature was monitored by a type K thermocouple directly attached to the crystal. Phenol (>99%, Acros Organics) was purified by repeated freeze-pump-thaw cycles. The Ge crystal was exposed to phenol vapor at 300 K. IR spectra were collected in a multiple internal reflection (MIR) geometry by a Nicolet 6700 FTIR spectrometer using an external HgCdTe detector. The CaF_2 viewports of the UHV chamber resulted in a low-frequency cutoff of ca. 1050 cm^{-1}. The FTIR spectra were corrected for baseline sloping by subtracting spline functions fit to points devoid of spectral features. To observe the effect of annealing, the temperature of the Ge crystal exposed

to the precursor vapor was raised to and held at 573 K for 5 min and then cooled back to 300 K, after which the IR spectra were collected.

DFT calculations were performed using Orca 3.0 software package [20]. PBE0 hybrid functional with D3BJ dispersion correction was used with def2-TZVP basis set for H, C, and O atoms, and def2-SVP basis set for Ge. A $Ge_{15}H_{16}$ "two-dimer row" cluster was used to model the Ge(100)-2 × 1 surface, whose top two Ge layers were allowed to relax from the ideal Ge crystal positions. The transition state geometries were initially obtained from relaxed scan of the potential energy surface between the reactant and product, and then confirmed after optimization to have a single imaginary vibrational frequency along the reaction coordinate. In the simulated FTIR spectra, the frequencies were scaled by a factor of 0.9682, which is obtained by averaging the scale factors for the experimental [21] and calculated frequencies for the 4 strong νCC/βCH (CC stretching / CH in-plane bending) modes of the gaseous phenol molecule (Table S1, Supporting Information). The bond dissociation energies (BDEs) of Ge-Ge, Ge-O, Ge-C, and C-O are obtained by calculating energy change accompanying homolytic cleavage of the respective bonds between $Ge(GeH_3)_3$, $-C(CH_3)_3$, and $-O(C_2H_5)$.

Results and Discussion

Figure 2a shows the FTIR spectra of 40 L phenol (1 L = 10^{-6} Torr·s) adsorbed on Ge(100)-2 × 1 at 300 K. The positions and assignments of the peaks are summarized in Table 1. The current data well reproduce previously reported FTIR spectra of 40 L phenol exposed to Ge(100) at 310 K [17]. Given this exposure, a quasi-saturation of surface phenoxy (C_6H_5O*) is formed upon

dissociative chemisorption of the O-H moiety with “lying down” configuration, whose coverage can be assumed to be ca. one adsorbate per two Ge dimers [17]. Also, DFT-calculated spectra for the phenoxy on Ge(100) (Figure 2d) match well with the initial experimental FTIR spectra after chemisorption at 300 K. Unlike phenyl isocyanate adsorbed on Ge(100)-2 × 1, which showed spectral changes over timescale of minutes [16], no noticeable change in the IR spectra is observed within several hours after phenol adsorption at 300 K.

Then, annealing the Ge(100) surface exposed to phenol to 573 K significantly changes the spectra (Figure 2b). While the CO stretching mode of surface phenoxy at 1226 cm^{-1} becomes absent, the peaks related to characteristic symmetric vibration of the aromatic ring show distinct red-shifts, which can be due to the phenyl group becoming bonded to a heavier substituent [22]. Especially, the positions of the remaining peaks resemble those of phenyl adsorbates directly bonded on various surfaces, such as those on Ni(100) [23], Au(111) [24], and Mo_2C/Mo(100) [25]. Therefore, DFT calculations were carried out assuming formation of C_6H_5* on the Ge(100) surface. The DFT-calculated FTIR spectra of phenyl adsorbate as shown on Figure 2d match well with the experimental FTIR spectra of phenol upon annealing. The three distinct FTIR peaks were assigned to stretching modes of the C_6H_5 ring directly bonded to the Ge surface by evaluating the DFT-calculated displacements in each vibrational mode (Table 1).

Upon thermal activation, the oxygen atom that link phenoxy of initial chemisorption structure may migrate into the surface. Similar reactions were observed for organic molecules that bond to Si and Ge surfaces through a nitro (-NO_2) functionality, by which interfacial oxynitride-like structures are formed [15,26–28]. Detailed mechanistic investigation for the nitro

groups' surface chemistry suggested that O atoms detached from the organic adsorbate sequentially were inserted into Si-Si or Ge-Ge bonds of the substrate.

Figure 3 shows energies of critical points along a possible thermal reaction pathway of chemisorbed phenol on Ge(100). In the present study, we suggest that stepwise transformation of phenoxy to phenyl occurs via the following mechanism. First, a metastable intermediate state (III, +26.8 kcal/mol) can form by insertion of the phenoxy O into the Ge dimer bond. Through the transition state II, the dimer Ge bond becomes broken (Ge-Ge: 2.463, 3.182, and 3.761 Å in I, II, and III, respectively), and O becomes bonded to the dimer Ge with the H adatom (Ge-O: 3.563, 2.246, and 1.889 Å in I, II, and III, respectively). This step involves a significant activation energy of 53.1 kcal/mol (transition state II) from the phenoxy state, and thus would not readily occur during initial adsorption at 300 K. Then, the phenyl moiety becomes directly bonded to the Ge surface, and the oxygen atom of phenoxy would become inserted into the dimer Ge-Ge bond (V, -7.2 kcal/mol). Via the transition state IV, the C_6H_5 moiety forms bond with the Ge atom on which phenoxy was originally bonded (C-Ge: 2.944, 2.169, and 1.939 Å in III, IV, and V, respectively), losing the bond with O (C-O: 1.387, 1.708, and 2.952 Å in III, IV, and V, respectively). This second step of phenyl migration (transition state IV) also requires thermal activation: the energy barrier height is estimated as 35.0 kcal/mol from the intermediate III, and 61.8 kcal/mol from the initial phenoxy (I). It is noted that other reaction pathways, such as emergence of gaseous byproducts, similarly to those observed for propanol on Si(100) [29] and nitrobenzene on Ge(100) [15], or reactions involving multiple Ge surface dimers [30], may be also available, but are not considered in this work for clarity of the discussion.

Overall, formation of phenyl from phenoxy is exothermic, so that once V is formed by thermal activation, the probability for the reverse reaction to III or I would be small. However, the magnitude of the estimated release of energy is smaller for the thermal reaction of phenol (-7.2 kcal/mol, current work) compared to that of nitrobenzene/Ge(100) (ca. -25 kcal/mol per O atom, ref. [15]). Such a difference can be described by the nature of the chemical bonds present in each adsorbates [14]. First, many nitro-aromatic compounds are often utilized as highly energetic materials that contain large chemical potential energy in their bonds [31]. Therefore, structural decomposition of nitrobenzene adsorbates is expected to involve large release of energy, which is confirmed by our previous analysis on the DFT calculations along the reaction of the nitro group, where weaker N-O bonds are replaced by stronger Ge-O bonds [15]. Meanwhile, for the thermal transformation reaction of surface phenoxy, i.e., formation of Ge-O and Ge-C bonds at the expense of C-O and Ge-Ge bonds' breakage, the BDEs of the involved bonds are rather similar. The calculated BDE values are similar for (Ge-O, 78.3 kcal/mol; C-O, 82.2 kcal/mol) and (Ge-C, 66.0 kcal/mol; Ge-Ge, 69.8 kcal/mol) pairs, respectively. Therefore, it can be understood that new bonds are formed along with breakage of similarly stable bonds, and therefore the magnitude of overall energy change accompanying thermal reaction of phenoxy/Ge(100) is small. Also, although structures with further subsurface migration of O were also attempted by DFT calculations, no structure with additional stability compared to the state V could be located, possibly due to low reactivity of the Ge substrate toward oxidation [32,33].

Conclusions

The structural transformation of phenol chemisorbed on the Ge(100)-2 × 1 surface upon thermal annealing is studied via UHV FTIR experiments and DFT calculations. Phenol initially forms phenoxy adsorbates at 300 K upon adsorption on Ge(100). After annealing to 573 K, phenyl directly bonded to surface Ge is observed, preserving the aromaticity of the adsorbate. A sequential O-migration pathway is suggested as the mechanism for the thermal transformation, which involves a significant activation energy, but is overall exothermic. The resulting product structure has the O atom inserted into substrate Ge-Ge bond. Our study provides new fundamental knowledge on the organic functionalization of semiconductor surfaces and the thermal reactions of the adsorbates on the Ge surface.

ASSOCIATED CONTENT

Supporting information. Experimental and DFT-calculated IR frequencies of gaseous phenol molecule; IR spectra of the adsorbates in 1000-3800 cm^{-1} range; coordinates of the DFT-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* E-mail: sbent@stanford.edu

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Table 1. Summary of the vibrational peak positions (cm^{-1}) and assignments for phenol on Ge(100)-2 × 1 and related C_6H_5 adsorbates. β: bending, ν: stretching, ν_{as}: asymmetric stretching of C_6H_5, ν_s: symmetric stretching of C_6H_5.

Mode	Exp. 300 K (Fig 2a)	Exp. 573 K (Fig 2b)	Phenoxy DFT (Fig 2c)	Phenyl DFT (Fig 2d)	Phenyl /Ni(100) [23]	Phenyl /Au(111) [24]	Phenyl /Mo_2C/Mo [25]
β(CH)	1157		1150	1171	1188		1150
ν(CO)	1226		1256				
ν_{as}(ring)1	1283		1325	1322			
ν_{as}(ring)2		1429		1427			
ν_s(ring)1	1473	1467	1485	1475	1469	1459	
ν_s(ring)2	1574	1564	1611	1598		1557	1550

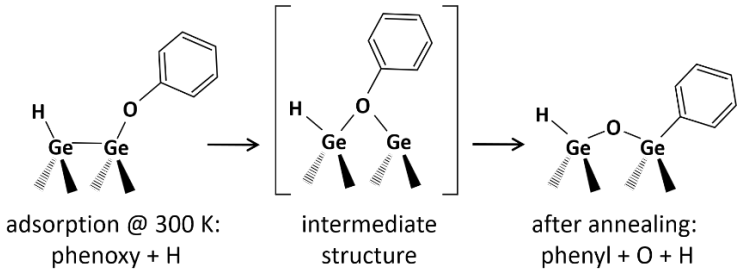


Figure 1. Suggested thermal reaction mechanism of phenol adsorbates on the Ge(100)-2 × 1 surface.

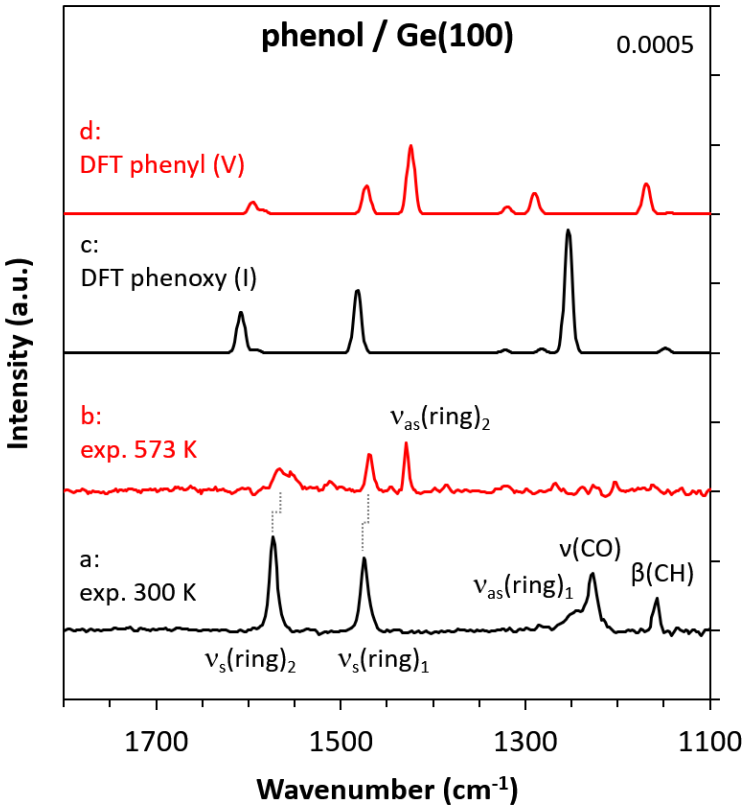


Figure 2. Experimental (a,b) and DFT-calculated (c,d) FTIR spectra of phenol adsorbed on the Ge(100)-2 × 1 surface. a, after 40 L adsorption at 300 K; b, after 573 K annealing of the sample probed in a; c, surface phenoxy (structure I in Figure 3b); and d, surface phenyl (structure V in Figure 3b).

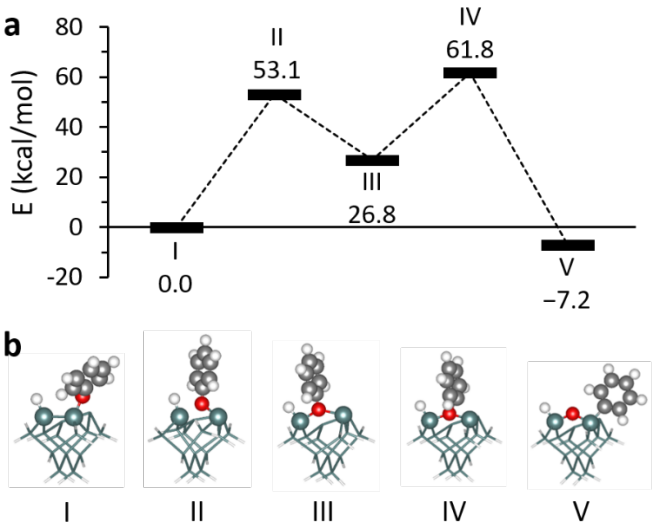
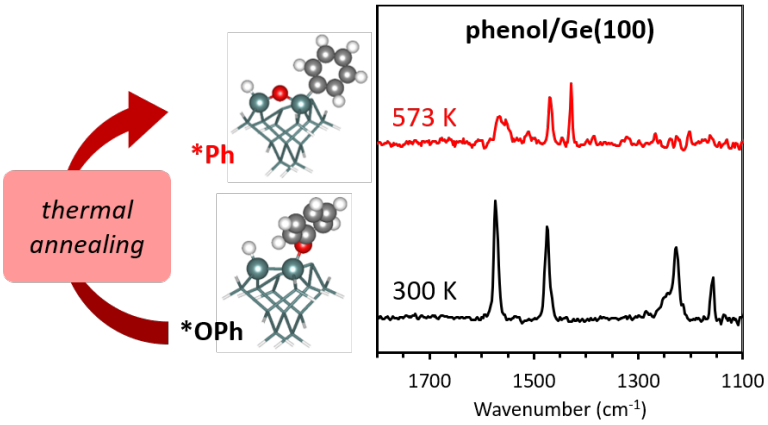


Figure 3. a, DFT-calculated reaction coordinate diagram for thermal reaction of phenol adsorbed on Ge(100); b, optimized geometries of the critical points: I) surface phenoxy formed by adsorption of phenol, II) O-insertion transition state, III) phenoxy-inserted metastable state, IV) phenyl migration transition state, and V) surface phenyl. In b, the subsurface atoms are hidden for clarity; Ge=green, O=red, C=gray, and H=white.

TOC image



Keywords

adsorption; adsorbate; germanium; surface functionalization; thermal reaction;