

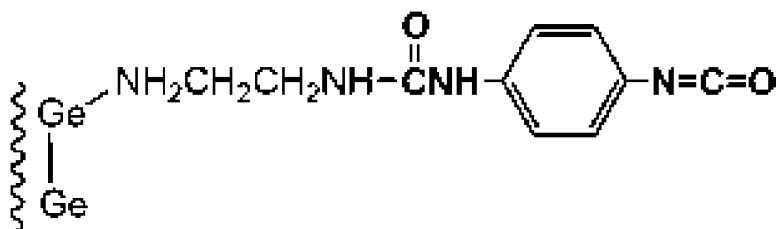
Article

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## Layer-by-Layer Growth on Ge(100) via Spontaneous Urea Coupling Reactions

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**Abstract:** We have demonstrated the layer-by-layer growth, via a urea coupling reaction between two bifunctional molecules, ethylenediamine and 1,4-phenylene diisocyanate, to form an ultrathin film on Ge(100)- $2 \times 1$  at room temperature under vacuum conditions. The initial adsorption and subsequent growth of each layer was studied with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy. Ethylenediamine reacts with Ge(100)- $2 \times 1$  to produce a surface-bound amine group which is available for additional reaction. Subsequent exposure of 1,4-phenylene diisocyanate leads to a spontaneous urea coupling reaction between the surface-bound amine and the highly reactive isocyanate functional group. Three bands at 1665, 1512, and 1306  $\text{cm}^{-1}$  are characteristic of a urea linkage and provide evidence of the coupling reaction. The coupling procedure can be repeated in a binary fashion to create covalently bound ultrathin films at room temperature, and in the present work, we demonstrate the successful growth of four layers. In addition, we have found that an initial exposure of 1,4-phenylene diisocyanate to Ge(100)- $2 \times 1$  produces an isocyanate-functionalized surface which, upon exposure to ethylenediamine, also forms urea linkages. This layer-by-layer deposition method provides a strategy with which to design and produce precisely tailored organic materials at semiconductor interfaces.

### I. Introduction

The organic functionalization of semiconductor surfaces is a burgeoning area of surface science which is poised to play a major role in the creation and development of revolutionary molecule-based semiconductor devices. The incorporation of organic molecules with specific properties at the semiconductor interface has the potential to add novel functionalities to chemical, biological, and electronic devices. In an attempt to understand the reactivity, structure, and interfacial properties of such hybrid organic-semiconductor systems, numerous investigations of the covalent attachment of model organic molecules to vacuum-prepared C(100),<sup>1-3</sup> Si(100),<sup>4-11</sup> and Ge(100)<sup>12-15</sup> surfaces have been completed. Interestingly, many

of the reported surface products are analogous to those from the organic chemistry literature, and similarities are attributed to the electronic nature of group IV semiconductor surface dimers.<sup>16</sup>

More recent studies have begun to focus on the competition and selectivity of bi- or multifunctional molecules on semiconductor surfaces.<sup>16-21</sup> These investigations have explored the possibility that one functional group of a bifunctional molecule will selectively react with the surface, leaving the other group available to undergo a subsequent chemical reaction. The ultimate goal is the controlled deposition of multiple organic layers so that precisely tailored surfaces may be prepared with a variety of useful functionalities. Such molecular-level control is currently achievable in solution with well-known chemistries, including Langmuir-Blodgett film deposition<sup>22,23</sup> and the creation of self-assembled monolayers (SAMs).<sup>22,24</sup> In contrast,

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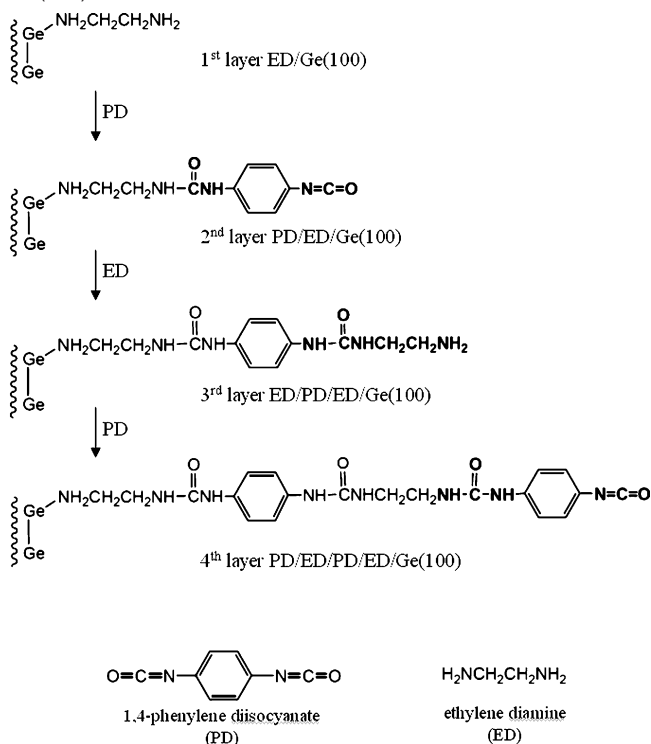
vacuum-based growth methods are in their infancy. A viable vacuum-based growth method would provide important advances, such as extremely precise interface control and seamless integration into cluster tools. It is also expected that the ability to carry out in situ diagnostics as molecules are deposited from the vapor will make it possible to elucidate the underlying chemistry and structure of the growing organic film.

In one of the only examples of multilayer functionalization under vacuum conditions, Richardson and co-workers have demonstrated the growth of an ultrathin organic film on Si(100)-2 × 1 via sequential imide coupling reactions.<sup>25,26</sup> To create the polyimide film, 1,4-phenylene diamine and pyromellitic dianhydride were sequentially deposited on Si(100)-2 × 1, forming an amic acid intermediate; subsequent imidization was initiated by thermal curing of the amic acid film at 200 °C.<sup>25</sup> They also explored the use of maleic anhydride, 1,4-phenylene diamine, and pyromellitic dianhydride sequentially deposited at room temperature and thermally cured to 430 °C as an alternative method with which to prepare ultrathin polyimide films.<sup>26</sup>

In general, developing a dry method for multiple layer organic functionalization faces several challenges compared to solution-based methods. Most solution-based synthetic approaches used to promote reactions are difficult or impossible to implement under vacuum. For example, in vacuum-based reactions, it is difficult to apply a catalyst, to control the chemical environment (e.g., acidic or basic conditions), or to utilize solvent effects, such as polarity. Also, traditional protecting groups that might prevent reaction at one end of a bifunctional molecule (to allow for selectivity) render most reactants too involatile for vapor delivery. The vacuum-based constraints of reaction without catalyst or solvent further require that gas-phase reactants undergo spontaneous reaction with the terminal functional groups at the surface. Only certain reactions will meet this severe requirement.

In the present work, we show how spontaneous, layer-by-layer surface reactions between diamines and diisocyanates under vacuum conditions enable the creation of a polyurea ultrathin film on Ge(100)-2 × 1 at room temperature. Polyurea, a tough, high melting elastomer, which is suitable for fiber applications,<sup>27,28</sup> is synthesized industrially via a simple step-growth addition polymerization between diamines and diisocyanates with no byproducts.<sup>28</sup> This well-known reaction chemistry, which is characterized by nucleophilic attack by the amine nitrogen lone pair at the isocyanate carbon,<sup>29</sup> is highly exothermic and is the basis for the layer-by-layer growth method

**Scheme 1.** Schematic Illustration of the Idealized Synthetic Route for the Layer-by-Layer Growth of Polyurea Films on the Ge(100)-2 × 1 Surface



described here. A similar reaction scheme has been employed in the solution phase to create polyurea films attached to oxide surfaces.<sup>30</sup>

Scheme 1 illustrates the first few cycles of the layer-by-layer growth of a polyurea ultrathin film on Ge(100)-2 × 1. We have employed ethylenediamine (ED), a bifunctional molecule with an amine group (-NH<sub>2</sub>) at either terminus, as the first layer on the Ge(100)-2 × 1 surface. Upon adsorption on clean Ge(100)-2 × 1, an amine group remains and is available for another reaction. Subsequently, 1,4-phenylene diisocyanate (PD), another bifunctional molecule, is exposed to and reacts with the remaining amine group of the previously created ED/Ge(100) surface to form a urea linkage. Due to the bifunctional nature of each precursor, an amine or isocyanate group remains intact after each deposition cycle and is thus available to initiate additional film growth at each subsequent layer.

The initial attachment of ethylenediamine to the clean Ge(100)-2 × 1 surface and the formation of urea linkages in each deposition cycle thereafter were monitored in situ with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy. The infrared spectra of urea linkages exhibit several infrared bands, which represent different vibrational modes of the urea bond and are shown in Table 1.<sup>30-33</sup> The amide I band results from the  $\nu(\text{C}=\text{O})$  stretching vibration of

**Table 1.** Characteristic Vibrational Bands of Urea Linkages<sup>30-33</sup>

band	vibration	wavenumber range (cm <sup>-1</sup> )
amide I	$\nu_s(\text{C}=\text{O})$	1635-1705
amide II	$\delta(\text{NH})^a$	1515-1560
	$\nu_s(\text{N}-\text{C}-\text{N})$	1300-1360
	$\nu_s(\text{N}-\text{C}-\text{N})$	1140-1190

<sup>a</sup> The amide II band is attributed mainly to a  $\delta(\text{N}-\text{H})$  bending mode with a smaller contribution from the  $\nu(\text{C}-\text{N})$  stretch.<sup>34</sup>

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the carbonyl group, and the amide II band is associated mainly with  $\delta(\text{N-H})$  bond deformation. In addition, the strong asymmetric and weaker symmetric  $\nu(\text{N-C-N})$  stretching modes spectroscopically distinguish urea linkages from amide bonds. With our experimental setup, the three high-energy bands are observable in the surface reaction products, and the assignment of these modes and others is used to show that reactions occur by spontaneous urea coupling chemistry to form organic multilayers at the Ge(100) surface.

## II. Experimental and Computational Details

All experiments were carried out in an ultrahigh vacuum (UHV) chamber, which has been described in detail previously.<sup>35</sup> The base pressure is less than  $1 \times 10^{-10}$  Torr, and the chamber is equipped with a quadrupole mass spectrometer (QMS), an Auger electron spectrometer (AES), low-energy electron diffraction (LEED) optics, and an ion sputter gun. Infrared spectra are collected by employing a Fourier transform infrared (FTIR) spectrometer equipped with a narrow-band HgCdTe detector, with the crystal in a multiple internal reflection (MIR) geometry. The unpolarized IR beam from the FTIR spectrometer enters and exits the chamber by means of two  $\text{CaF}_2$  infrared windows at right angles to each other. The optical path outside the vacuum chamber is purged by dry,  $\text{CO}_2$ -free air. For each spectrum, at least 1000 scans are averaged at  $4 \text{ cm}^{-1}$  resolution.

A trapezoidally shaped Ge(100) crystal ( $19 \times 14 \times 1 \text{ mm}$ ,  $45^\circ$  beveled edges) is conductively heated by a resistive tungsten heater and cooled by heat exchange with a copper braid connected to a liquid nitrogen reservoir. The crystal is cleaned using  $\text{Ar}^+$  ion sputtering ( $8\text{--}9 \mu\text{A}$  sample current,  $0.5 \text{ keV}$  beam energy) at room temperature, followed by annealing to  $900 \text{ K}$  for  $5 \text{ min}$ . After several sputtering/annealing cycles, the LEED pattern of the  $2 \times 1$  surface reconstruction is clearly visible. A thin tantalum plate covers the back face of the crystal to minimize unwanted adsorption/reaction on the uncleaned side.

Ethylenediamine (Aldrich, 99+%) and 1,4-phenylene diisocyanate (Aldrich) are transferred to a sample vial in a nitrogen-purged glovebox. Ethylenediamine is purified by several freeze-pump-thaw cycles before being introduced into the system. 1,4-Phenylene diisocyanate is solid under ambient conditions. Introduction into the chamber is accomplished by placing the sample vial in a boiling water bath and heating the gas manifold lines to  $150 \text{ }^\circ\text{C}$ . The two chemicals are introduced into the chamber through a variable leak valve and a directed doser. The molecular identity and purity of both compounds are verified after exposure to the crystal with a quadrupole mass spectrometer. Surface exposures are measured in Langmuirs ( $1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$ ), and dosing is performed by filling the chamber to a particular pressure for a specified period of time. Pressures are not corrected for ion gauge sensitivity.

A background IR emission spectrum for the clean crystal is recorded, and subsequent scans after adsorption of ethylenediamine and 1,4-phenylene diisocyanate on Ge(100)- $2 \times 1$  are ratioed to this background and transformed to absorbance spectra. For subsequently formed layers, via exposure of either ethylenediamine or 1,4-phenylene diisocyanate, each spectrum is ratioed to the saturation spectrum for the previous layer. In these incremental spectra, vibrational modes of newly produced and reactively eliminated functional groups appear as positive and negative peaks, respectively, thus allowing the changes upon formation of the second layer to be more clearly visualized. Several multilayers are condensed on the surface near  $130 \text{ K}$  to obtain infrared spectra (not shown) of the unreacted precursors. The multilayer spectra are used to help assign modes in the chemisorbed vibrational spectra as well as to confirm the purity of each molecule once inside the reaction chamber. All spectra are corrected for baseline sloping.

Vibrational frequency and intensity calculations are completed with the Jaguar 5.5 software package using the Becke3 Lee-Yang-Parr (B3LYP) three-parameter density functional theory.<sup>36</sup> A single  $\text{Ge}_9\text{H}_{12}$  dimer cluster is used to model the Ge(100)- $2 \times 1$  surface. The geometries of important local minima on the potential energy surface are determined at the B3LYP/LACVP\*\* level of theory.<sup>37</sup> The LACVP\*\* is a mixed basis set, using the LACVP basis set to describe the Ge atoms and the 6-31G basis set for the remaining atoms. The LACVP basis set uses the Los Alamos effective core potential developed by Hay and Wadt<sup>37</sup> to describe atoms heavier than Ar in the periodic table. Structures are fully optimized without geometrical constraints, followed by vibrational frequency calculations at the same level of theory. A scaling factor of 0.9558 for the B3P86/6-31G\* level of theory<sup>38</sup> is used to scale the calculated frequencies.

## III. Results and Discussion

**(A) Sequential Reaction on the ED/Ge(100) Surface: First and Second Layers.** To form an amine-terminated Ge(100) surface, ethylenediamine (ED) was exposed to the clean Ge(100)- $2 \times 1$  surface. ED was selected such that one amine group would react with surface dimer while the other would remain unreacted and available for further layer attachment. Mui et al. have reported that simple methylamines undergo molecular chemisorption on Ge(100)- $2 \times 1$  via a Ge-N dative bond between the N lone pair and the electrophilic Ge dimer atom.<sup>35</sup> In the case of ED on Ge(100), possible reaction products include the formation of a Ge-N dative bond, similar to that of the case for methylamines, as well as an N-H dissociation product. While N-H dissociation was not observed for methylamines,<sup>35</sup> we cannot rule it out a priori for ED since the presence of the second amine group may affect its reactivity.

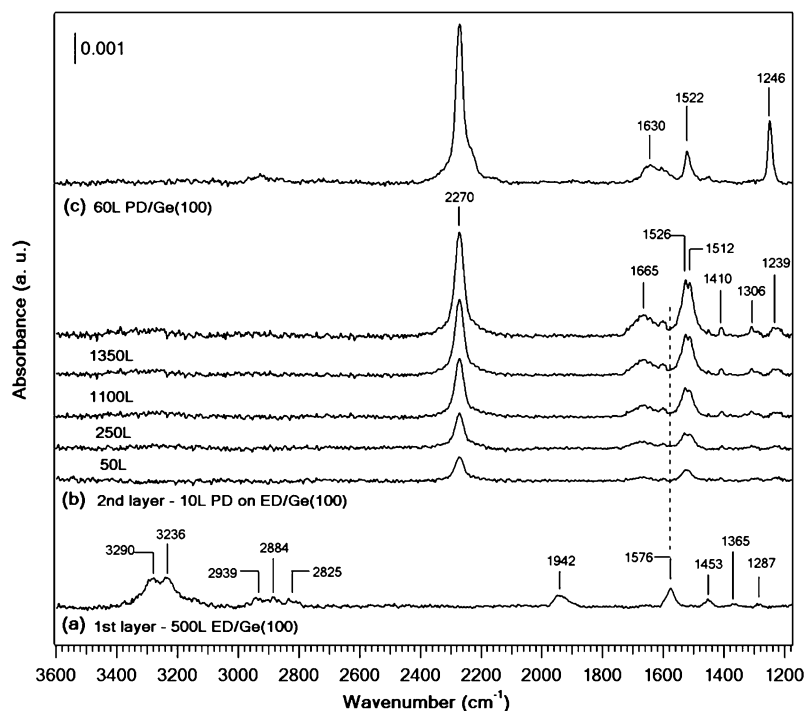
Figure 1a shows the infrared spectrum obtained at room temperature after a 500 L saturation dose of ED on clean Ge(100)- $2 \times 1$ . The vibrational mode assignments are summarized in Table 2. Chemisorbed ED exhibits absorption peaks at  $3290$ ,  $3236$ , and  $1576 \text{ cm}^{-1}$ , which we assign to the asymmetric  $\nu_{\text{as}}(\text{NH}_2)$  stretch, symmetric  $\nu_{\text{s}}(\text{NH}_2)$  stretch, and  $\delta(\text{NH}_2)$  scissoring deformation modes, respectively. The observation of infrared peaks associated with the  $\text{NH}_2$  functional group provides evidence of their presence on the ED-saturated Ge(100)- $2 \times 1$  surface. Retention of at least some amine functionality following chemisorption, as demonstrated by the IR spectrum, opens the door to further reaction with additional precursors, as will be discussed below.

A  $\nu(\text{Ge-H})$  stretching mode is clearly visible at  $1942 \text{ cm}^{-1}$ , indicating the dissociation of at least some N-H bonds. This is markedly different from the observed dative bond formation for methylamines on Ge(100)- $2 \times 1$ , where  $\nu(\text{Ge-H})$  was not observed.<sup>35</sup> On the basis of a coverage-dependent and isotopic-labeling study of ED on Ge(100)- $2 \times 1$ , to be published elsewhere,<sup>39</sup> it appears that dual N-H dissociation (where both amine groups undergo N-H dissociation on neighboring surface dimers) occurs at low coverage, while a product containing a single Ge-N dative bond is formed as coverage increases.

Although we observe that multiple surface products are present for ED on Ge(100)- $2 \times 1$ , these do not greatly affect our ability to demonstrate layer-by-layer growth. In principle, either product could participate in subsequent layer reaction.

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**Figure 1.** Infrared spectra (a) of ethylenediamine (ED) on clean Ge(100)- $2 \times 1$ , (b) subsequent coverage dependence of 1,4-phenylene diisocyanate on the ED/Ge(100) surface, and (c) of 1,4-phenylene diisocyanate on clean Ge(100)- $2 \times 1$ ; (a and c) are overall spectra, ratioed to the clean surface, and (b) are incremental spectra, ratioed to the previous layer (ED/Ge(100)).

**Table 2.** Infrared Spectral Assignment of PD/Ge(100), ED/Ge(100), PD/ED/Ge(100) Surfaces (for the Spectra in Figure 1)

1,4-phenylene diisocyanate on Ge(100)	frequency (cm <sup>-1</sup> )
asymmetric N=C=O stretch	2270
asymmetric C=O stretch	1630
aromatic ring modes	1522, 1450
C <sub>ar</sub> -N stretch	1246
1st layer; ED/Ge(100)	frequency (cm <sup>-1</sup> )
NH <sub>2</sub> and NH stretch	3290, 3236, 3227
CH <sub>2</sub> stretch	2939, 2884, 2825
Ge-H stretch	1942
NH <sub>2</sub> scissor	1576
CH <sub>2</sub> bend	1453, 1365
NH <sub>2</sub> bend	1287
2nd layer; PD/ED/Ge(100)	frequency (cm <sup>-1</sup> )
asymmetric N=C=O stretch	2270
amide I, asymmetric C=O stretch	1665
aromatic ring modes	1526 <sup>a</sup> , 1410
amide II, N-H bend	1512
asymmetric N-C-N stretch	1306
C <sub>ar</sub> -N stretch	1239

<sup>a</sup> Although it is difficult to make a definitive assignment, the peak located at 1526 cm<sup>-1</sup> is most likely due to the  $\nu$ (aromatic ring) because it falls closer to the  $\nu$ (aromatic ring) mode observed on the PD/Ge(100) surface.

One product of ED saturation adsorption on Ge(100)- $2 \times 1$  is the dative-bonded species with two undissociated NH<sub>2</sub> groups, of which one is likely directed away from the surface and, thus, is more accessible for second layer reaction. Previous work has shown that nitrogen dative bonds, formed via exposure of methylamines to Ge(100)- $2 \times 1$ , have binding energies near 25 kcal/mol.<sup>35</sup> In addition, a study of pyridine on Ge(100)- $2 \times 1$  reveals that 90% of the dative-bonded surface adducts remain after a day at room temperature under ultrahigh vacuum

conditions.<sup>14</sup> The N-H dissociated product could also undergo subsequent layer reaction. However, attack by the isocyanate group at secondary amines is less favorable than at primary amines, and we also expect the reaction to be sterically inhibited by the proximity of the amine to the surface.

To form the second layer, 1,4-phenylene diisocyanate (PD), was exposed to the amine-terminated Ge(100) surface at room temperature. We desire that only one isocyanate group of each PD molecule will react with a free amine group on the ED/Ge(100) surface. Thus, the other isocyanate group would potentially be directed away from the surface and available for further reaction to form the third (or further) layer in a layer-by-layer deposition scheme. Due to the rigidity and  $\pi$ - $\pi$  interaction of phenyl rings, as well as the steric interaction with the initial ED monolayer, we suggest that only one isocyanate group reacts at the surface-bound amine functionality, and integrated intensities discussed in section C support this hypothesis.

Figure 1b shows coverage-dependent IR spectra of the PD/ED/Ge(100) surface ratioed to the ED/Ge(100) spectrum (Figure 1a). The IR spectra of the second layer (PD/ED/Ge(100)) show not only the peaks associated with PD but also three characteristic urea bands (see Table 1). The intense absorption features observed at 2270, 1526 and 1410, as well as at 1239 cm<sup>-1</sup>, are attributed to  $\nu_a$ (N=C=O) stretching,  $\nu$ (aromatic ring) breathing, and  $\nu$ (C<sub>ar</sub>-N) stretching modes, respectively. Assignment of these peaks is possible by comparison of the spectrum in Figure 1b with that of a saturation exposure of PD on a clean Ge(100)- $2 \times 1$  surface (Figure 1c). The  $\nu$ (aromatic ring) breathing and  $\nu$ (C<sub>ar</sub>-N) stretching modes indicate that PD reacted with the ED/Ge(100) surface without disruption of the aromatic ring, while the  $\nu_a$ (N=C=O) mode provides substantial evidence that at least some isocyanate functionality remains for subsequent layer attachment. Additional peaks are also observed at 1665, 1512, and 1306 cm<sup>-1</sup>. We assign these features to

$\nu(\text{C}=\text{O})$  stretching,  $\delta(\text{N}-\text{H})$  bending, and  $\nu_{\text{a}}(\text{N}-\text{C}-\text{N})$  stretching modes, respectively. The two higher-energy absorbance features are often termed “amide I and II” bands, while the low-energy band is unique to urea bonds and strongly suggests the formation of a urea linkage at the second layer. The location of these infrared bands is consistent with the infrared literature for polyurea,<sup>30,33</sup> providing additional evidence of the urea coupling reaction proposed in Scheme 1. The carbonyl stretching mode at  $1665\text{ cm}^{-1}$  is red shifted compared to that of common ketones and esters due to the delocalization of electrons from the N lone pair into the carbonyl  $\pi^*$  orbital. In addition, the in-plane  $\delta(\text{N}-\text{H})$  bending mode at  $1512\text{ cm}^{-1}$  is intense, as is commonly observed in solution.<sup>30,32</sup>

The lack of negative absorption features in the second layer spectra suggests that displacement of previously adsorbed ED does not occur during PD exposure. For example, Figure 1b shows no negative peaks in the  $\nu(\text{C}-\text{H})$  region between  $2800$  and  $2850\text{ cm}^{-1}$ . However, since the terminal amine groups of the ED/Ge(100) monolayer react with the isocyanate groups of PD, as shown in Scheme 1, one would expect to observe a negative  $\delta(\text{NH}_2)$  scissoring mode in the second layer spectra. Although negative peaks are not experimentally visible, the vertical dashed line between the first and second layer spectra (Figure 1) reveals that significant spectral overlap with peaks associated with the urea linkage likely obscures their observation. Data from the third and fourth layers, discussed in section B, provide support that this assignment is correct.

Examination of PD adsorbed on a clean Ge(100)- $2 \times 1$  surface is necessary to rule out reaction of PD directly at the surface following exposure to an ED/Ge(100) surface. Detailed analysis of the adsorption chemistry of this molecule will be discussed further in section D. However, comparison with the PD spectrum on clean Ge(100)- $2 \times 1$  (Figure 1c) suggests that the second layer PD likely does not react with surface dimers but only with tethered amine groups from the first layer. The carbonyl frequency for PD/Ge(100) is red shifted  $35\text{ cm}^{-1}$  relative to its position in the urea linkage at the second layer (Figure 1b). We found that the calculated carbonyl frequency of PD adsorbed on Ge(100)- $2 \times 1$  in a  $[2 + 2]$  C=N cycloaddition product is predicted to be red shifted nearly  $30\text{ cm}^{-1}$  due to the proximity of inorganic germanium surface atoms.<sup>13</sup> Furthermore, calculations predict that the  $\nu(\text{C}_{\text{ar}}-\text{N})$  stretch of the  $[2 + 2]$  C=N cycloaddition product should be approximately 4 times as intense as that of the urea linkage in the second layer. Together, these results lead us to conclude that the PD reacts primarily with the terminal amine groups on the ED/Ge(100) surface and not with dangling bonds of the Ge surface.

As shown in Figure 1b, the second layer absorption peaks appear to grow in at similar rates and saturate around  $1350\text{ L}$ . The saturation exposure of PD on the amine-terminated ED/Ge(100) surface is higher than the  $60\text{ L}$  necessary to saturate a clean Ge(100)- $2 \times 1$  surface. Furthermore, assuming only one isocyanate group reacts with the clean and the ED/Ge(100) surface, the integrated intensities of the isocyanate stretching mode indicate a second layer saturation coverage of approximately 80% of that on the clean surface. We primarily attribute the decrease in sticking probability to the reduced reactivity of an amine group when compared to that of the Ge

surface dimer, while we attribute the decrease in saturation coverage to steric interactions at the second layer.

Finally, no evidence of side reactions is experimentally observed at the second layer. Although aromatic isocyanates are known to undergo an intermolecular reaction in the condensed phase to form dimers (uretidinones) or trimers (isocyanurates),<sup>40–42</sup> we do not observe their characteristic  $\nu(\text{C}=\text{O})$  vibrational signature near  $1750\text{ cm}^{-1}$ .<sup>42</sup> Additionally, trimerization requires the use of an amine catalyst for significant reaction to be observed.<sup>42,43</sup>

**(B) Sequential Reaction on the ED/Ge(100) Surface: Third and Fourth Layers.** Following second layer attachment, the remaining isocyanate group provides the possibility for additional reaction with ED to form a third layer via another urea linkage (Scheme 1). To create the third layer, ED was exposed to the isocyanate-terminated PD/ED/Ge(100) surface at room temperature. Figure 2c shows coverage-dependent IR spectra of the third layer, ratioed to the saturation spectrum of the second layer (Figure 2b). For reference purposes, Figure 2a,b shows the ED/Ge(100) and PD/ED/Ge(100) spectra, respectively. The spectral assignment of each absorption feature is compiled in Table 3. Figure 2c shows that all infrared peaks grow in at similar rates as ED exposure is increased and saturate around  $7560\text{ L}$ . An intense negative peak associated with the isocyanate group is observed at  $2270\text{ cm}^{-1}$  and provides clear evidence for the loss of the terminal isocyanate groups of the PD/ED/Ge(100) surface. Integrated intensities of the  $\nu(\text{N}=\text{C}=\text{O})$  stretching peaks are  $0.158$  and  $-0.155$  at the second and third layer, respectively, indicating the near complete reaction of the terminal isocyanate groups at the second layer. Absence of negative peaks for other key modes of PD at the third layer indicates that desorption of the second layer does not occur. Three characteristic urea bands are observed at  $1674$  (amide I),  $1511$  (amide II), and  $1296\text{ cm}^{-1}$  (asymmetric N-C-N stretch) providing support that reaction of the terminal isocyanate groups with ED leads to the formation of a urea bond, similar to that at the second layer.

Vibrational frequencies associated with ED are observed at  $3274$ ,  $3214$ , and  $1583/1557\text{ cm}^{-1}$  and are attributed to  $\nu_{\text{as}}(\text{NH}_2)$ ,  $\nu_{\text{s}}(\text{NH}_2)$ , and  $\delta(\text{NH}_2)$  modes, respectively (Table 3). Appearance of these modes as well as the broad alkane  $\nu(\text{C}-\text{H})$  stretching modes centered at  $2937$  and  $2873\text{ cm}^{-1}$  indicates the successful attachment of ED to the PD/ED/Ge(100) surface and suggests that at least some amine functionality remains following third layer reaction. Just as with the ED/Ge(100) surface, the free amine at the third layer enables the sequential growth of yet another molecular layer. We believe the two  $\delta(\text{NH}_2)$  scissoring peaks observed at  $1583$  and  $1557\text{ cm}^{-1}$  are likely due to different chemical environments of the terminal  $\text{NH}_2$  groups.

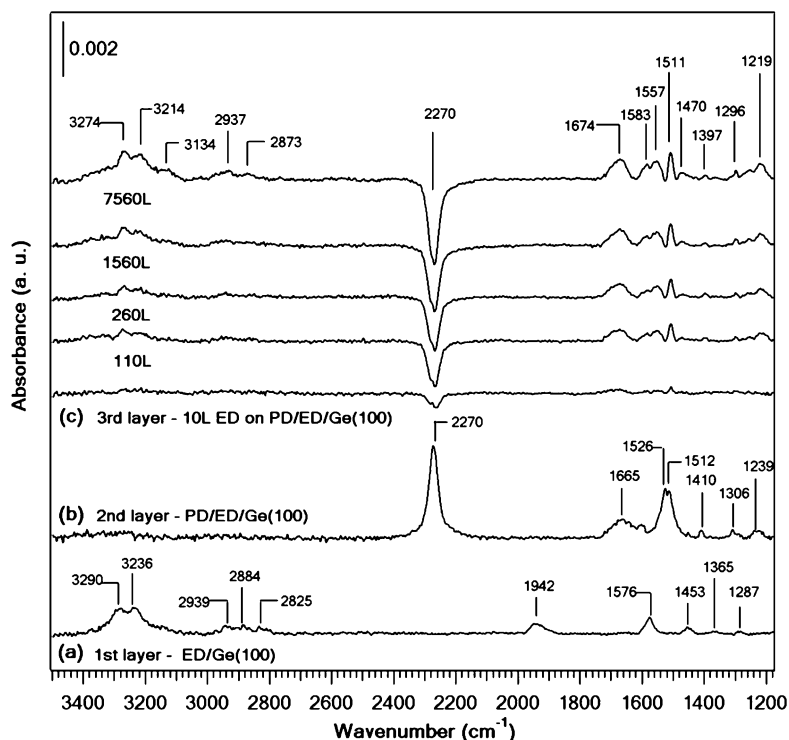
The terminal amine groups produced after reaction of ED at the third layer can react with PD to form the fourth molecular layer. Figure 3a–c shows the first, second, and third layer spectra, respectively, while Figure 3d shows the coverage-dependent infrared spectra for the exposure of PD to the ED/PD/ED/Ge(100) surface at room temperature. The fourth layer

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**Figure 2.** Saturation infrared spectra of (a) the ED/Ge(100) and (b) the PD/ED/Ge(100) surfaces; (c) coverage-dependent infrared spectra of the ED/PD/ED/Ge(100) surface; (a) is overall, (b and c) are incremental.

**Table 3.** Infrared Spectral Assignment of ED/PD/ED/Ge(100) and PD/ED/PD/ED/Ge(100) Surfaces (for the Spectra in Figures 2 and 3)

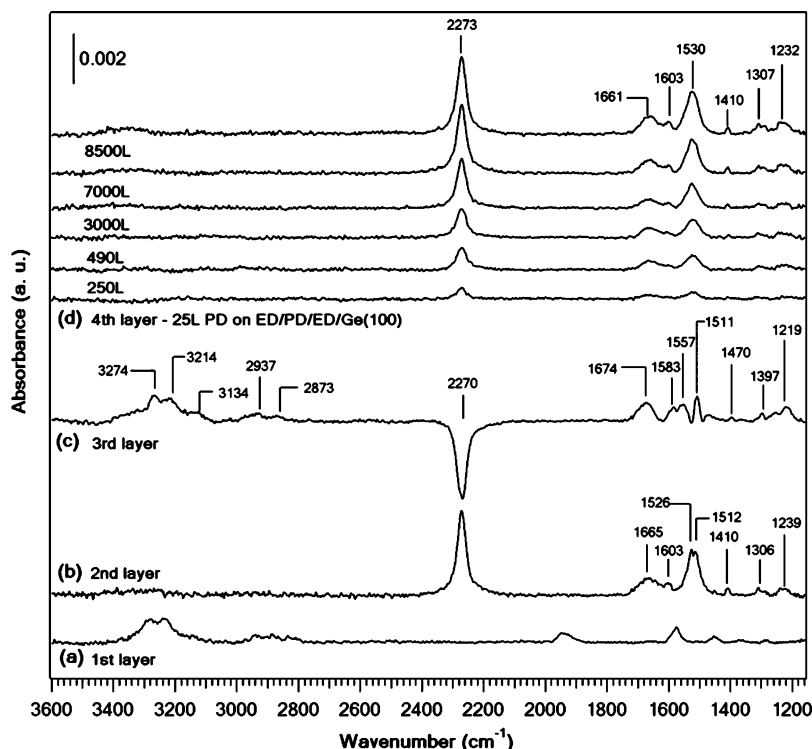
		frequency (cm <sup>-1</sup> )	
3rd layer; ED/PD/ED/Ge(100)	NH <sub>2</sub> and NH stretch	3274, 3240, 3214	
	CH <sub>2</sub> stretch	3134, 2937, 2873	
	asymmetric N=C=O stretch	2270 (negative)	
	amide I, asymmetric C=O stretch	1674	
	NH <sub>2</sub> scissor	1583, 1557	
	amide II, N-H bend	1511	
	CH <sub>2</sub> bend	1470, 1397	
	asymmetric N-C-N stretch	1296	
	4th layer; PD/ED/PD/ED/Ge(100)	asymmetric N=C=O stretch	2273
		amide I, asymmetric C=O stretch	1661
		amide II, N-H bend	1530
aromatic ring modes		1530, 1410	
asymmetric N-C-N stretch		1307	
C <sub>ar</sub> -N stretch		1232	

spectra are ratioed to the saturation spectrum of the third layer (Figure 3c), and vibrational assignments are compiled in Table 3. Since the urea coupling reaction at the fourth layer is the same as that of the second layer (Scheme 1), one would expect that the incremental spectra of these two layers would be similar. Figure 3b,d clearly shows that this is the case. The appearance of an intense asymmetric  $\nu_{as}(\text{N}=\text{C}=\text{O})$  stretch, now at 2273 cm<sup>-1</sup> in Figure 3d, again suggests that at least some of the PD isocyanate groups remain available for fifth layer growth. Similar to those of the previously deposited layers, the characteristic urea bands are also observed for the fourth layer, indicating the formation of a urea linkage. The infrared peaks centered at 1661 and 1307 cm<sup>-1</sup> are assigned to the  $\nu(\text{C}=\text{O})$  stretching (amide I) and  $\nu_a(\text{N}-\text{C}-\text{N})$  stretching vibrations, respectively. The doublet observed in Figure 3b near 1520 cm<sup>-1</sup>, associated with the  $\nu(\text{aromatic ring})$  stretching and  $\delta(\text{N}-\text{H})$  bending (amide II) modes of the second layer, cannot be fully resolved in the fourth layer spectra. However, the fourth layer peak near 1530 cm<sup>-1</sup> is as broad as its second layer counterpart,

and we believe that this peak likely encompasses both modes. As one would expect, the carbonyl stretching frequency (1661 cm<sup>-1</sup>) is nearly identical to that of its second layer frequency (1665 cm<sup>-1</sup>).

Similar to the spectra of other layers, all peaks increase as a function of PD exposure, and the growth saturates at 8500 L of PD. The absolute value of the integrated area of the isocyanate peak at 2273 cm<sup>-1</sup> is similar to that of the second and third layers, suggesting the near complete coverage of PD on the ED/PD/ED/Ge(100) surface. The larger exposure necessary to reach saturation at the fourth layer when compared to the second layer is potentially due to the use of ethylenediamine as one of the precursor species. Its flexible methylene chain could lead to increasing disorder in the growing film, making it more difficult for reaction to occur at the layers farthest away from the surface.

In the second and fourth layer spectra, we observe a small peak at 1603 cm<sup>-1</sup>, which is too red shifted to be assigned to a  $\nu(\text{C}=\text{O})$  stretch of a urea linkage.<sup>33,44</sup> Since the second and fourth layers are formed following exposure to PD, it follows



**Figure 3.** Saturation infrared spectra of (a) the ED/Ge(100), (b) PD/ED/Ge(100), and (c) ED/PD/ED/Ge(100) surfaces; (d) coverage-dependent infrared spectra of the PD/ED/PD/ED/Ge(100) surface; (a) is overall, and (b, c, and d) are incremental spectra.

that the PD may cause a side product leading to the presence of the peak at  $1603\text{ cm}^{-1}$ . It has been reported that the isocyanate functional group can react rapidly with water to form thermally unstable carbamic acids, which undergo decarboxylation to create an amine and carbon dioxide.<sup>30,45</sup> We suspect that either prior to surface exposure (in the manifold) or after forming the second and fourth layer (in the reaction chamber), the isocyanate groups of PD may react with residual water, resulting in isocyanate hydrolysis and production of an aromatic amine group. In the gas-phase spectrum of aniline,  $\delta(\text{NH}_2)$  scissoring and  $\nu(\text{aromatic ring})$  breathing modes appear at  $1622$  and  $1603\text{ cm}^{-1}$ , respectively.<sup>34</sup> Therefore, the peak at  $1603\text{ cm}^{-1}$  in the second and fourth layer spectra may result from the aromatic ring breathing vibration of an aromatic amine group. Furthermore, the higher energy  $\delta(\text{NH}_2)$  scissoring mode of the aromatic amine (near  $1622\text{ cm}^{-1}$  for aniline) may be overlapping with the amide I  $\nu(\text{C}=\text{O})$  stretching mode of the urea linkage, leading to the broad  $\nu(\text{C}=\text{O})$  peak observed in Figure 3b,d.

### (C) Molecular Layer Coverages and Extent of Reaction.

The integrated infrared peak intensities from Figures 1–3 can be used to provide information on relative coverages and saturation behavior of the consecutively deposited molecular layers. Figure 4 shows two characteristic infrared peak areas plotted as a function of PD or ED exposure for the second through the fourth layers (Figure 4a–c, respectively). For the third layer (Figure 4b), the area of the negative-going  $\nu_a(\text{N}=\text{C}=\text{O})$  stretching peak from Figure 2 is plotted as an absolute value. Because the  $\nu_a(\text{N}=\text{C}=\text{O})$  stretching peak is intense and not overlapping with any other vibrational modes, it can easily be

employed to monitor the progress of the urea coupling reaction in each layer. It should be noted that the following analysis is only first order in its accuracy and assumes that absorption cross-sections for each mode are not strongly influenced by effects such as proximity to the semiconductor surface.

As shown in Figure 4, the integrated  $\nu_a(\text{N}=\text{C}=\text{O})$  peak areas at saturation coverage are  $0.158$  (2nd layer),  $0.155$  (3rd layer), and  $0.144$  (4th layer). If all terminal functional groups react completely with sequentially deposited molecules, the value of the  $\nu_a(\text{N}=\text{C}=\text{O})$  peak area at saturation coverage in the fourth layer should be the same as that of the second layer. Furthermore, the absolute value of the negative  $\nu_a(\text{N}=\text{C}=\text{O})$  peak area for the third layer should also be of comparable magnitude. The nearly identical peak areas in the second and third layers suggest that the terminal isocyanate groups of the PD/ED/Ge(100) surface almost completely react with exposed ED to create the third layer.

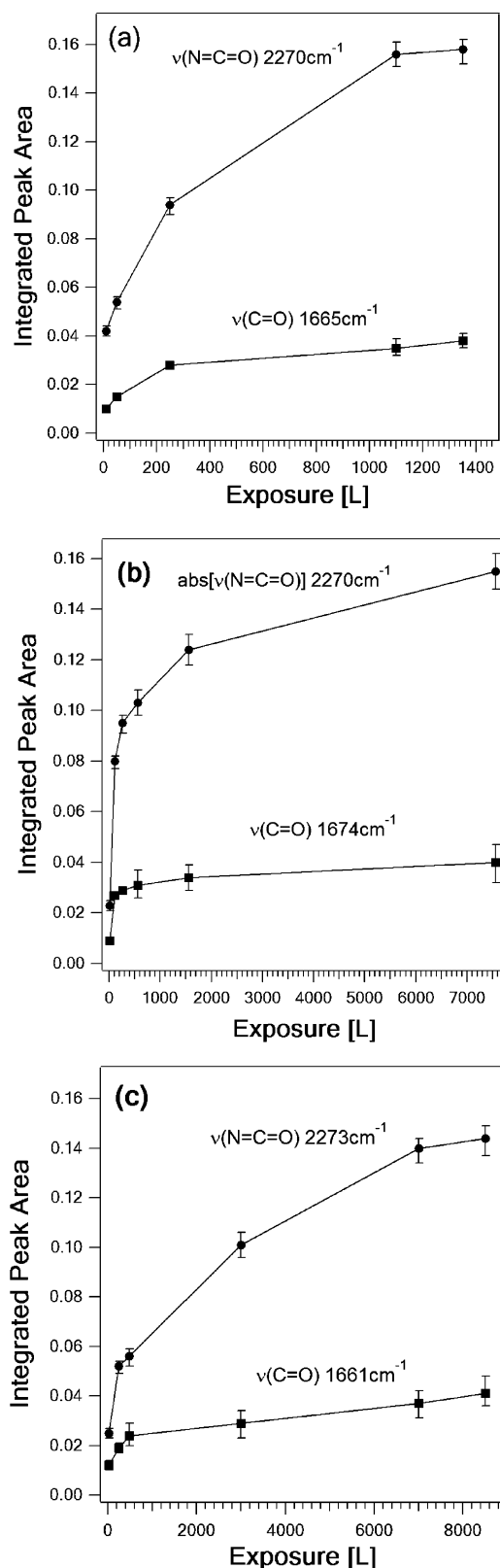
The integrated intensity of the urea  $\nu(\text{C}=\text{O})$  stretching mode (amide I band) as a function of ED or PD exposure at each layer is also plotted in Figure 4. Since one carbonyl group is created per molecule of ED or PD adsorbed beyond the first layer, we expect the peak areas of each layer to be approximately equal. The C=O peak areas at saturation coverage are observed at  $0.038$  (2nd layer),  $0.040$  (3rd layer), and  $0.041$  (4th layer), suggesting that nearly the same number of urea bonds are formed by each sequential reaction.

If biterminal reactions were occurring upon either ED or PD adsorption, the loss of reactive sites is expected to lead to a reduction in the integrated intensities of both the isocyanate and C=O peaks with each subsequent layer. Interestingly, the integrated intensity of the fourth layer  $\nu_a(\text{N}=\text{C}=\text{O})$  peak is slightly less than that of the previous two layers, suggesting that such a biterminal reaction might be possible. Although the

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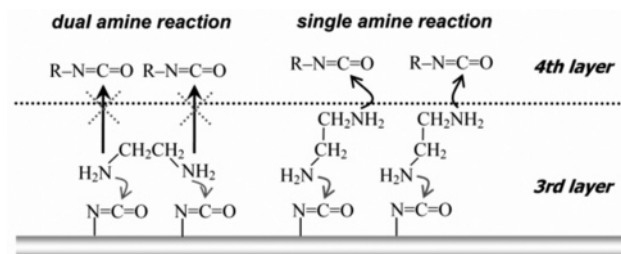




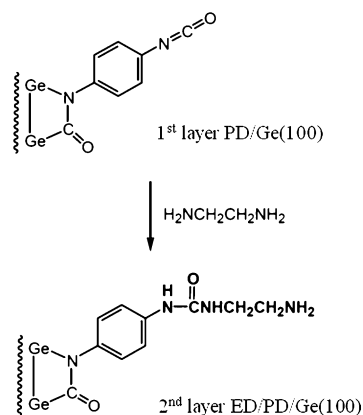
**Figure 4.** Characteristic infrared peak areas plotted as a function of exposure for the (a) second, (b) third, and (c) fourth molecular layers. Areas are plotted for both the  $\nu(\text{N}=\text{C}=\text{O})$  isocyanate stretch near  $2270\text{cm}^{-1}$  and the  $\nu(\text{C}=\text{O})$  amide I stretching mode near  $1660\text{cm}^{-1}$ . In (b), the absolute value of the  $\nu(\text{N}=\text{C}=\text{O})$  peak area, which is negative in the difference spectra, is shown.

rigid phenyl ring of PD would likely hinder biterminal reaction at both isocyanate groups, the short alkane chain of ED is more

**Scheme 2.** Schematic Illustration of a Biterminal Reaction of ED at the Third Layer and the Potential Hindrance of Subsequent PD Attachment



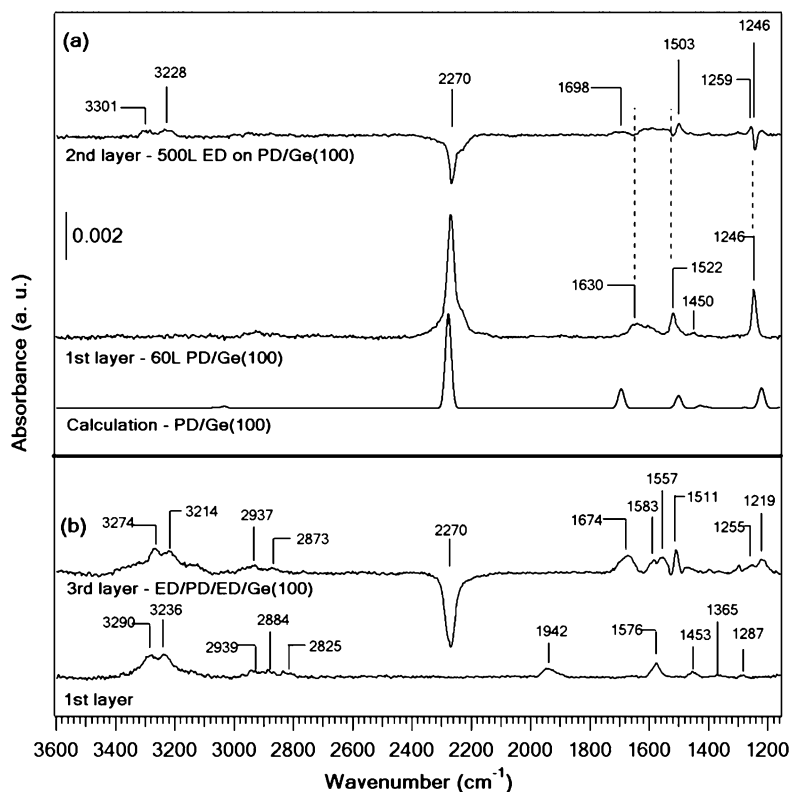
**Scheme 3.** Schematic Illustration of PD Adsorbed on  $\text{Ge}(100)-2 \times 1$  and Second Layer Reaction with Subsequent Exposure to ED



flexible and may allow for an experimentally significant number of dual-amine reactions at the third layer, as illustrated in Scheme 2. However, removal of reaction sites by termination of the growing film with a biterminal reaction should also lead to a reduction in the integrated intensity of the  $\nu(\text{C}=\text{O})$  stretch of the urea linkage, and this is not observed. While the idea of biterminal reaction “defects” is interesting, our results give mixed indications as to their presence.

**(D) Sequential Reaction on the PD/Ge(100) Surface.** In the layer-by-layer growth studies discussed in sections A–C, the first layer was formed by ED exposure to the clean  $\text{Ge}(100)-2 \times 1$  surface at room temperature. However, PD can also be employed to form the initial layer. Scheme 3 illustrates the proposed adsorption product of PD on  $\text{Ge}(100)-2 \times 1$  and the subsequent urea coupling reaction between ED and the isocyanate-terminated PD/Ge(100) surface. According to previous studies of related molecules, PD is not expected to react through the phenyl ring on  $\text{Ge}(100)-2 \times 1$ . For example, in the case of benzene on  $\text{Ge}(100)-2 \times 1$ , Fink et al. have reported that benzene does not chemisorb on  $\text{Ge}(100)-2 \times 1$  at room temperature.<sup>46</sup> In addition, Hamers and co-workers have investigated the adsorption of phenyl isothiocyanate, which has a molecular structure similar to that of PD, on  $\text{Si}(100)-2 \times 1$ .<sup>47</sup> They report that adsorption occurs through the isothiocyanate group ( $-\text{N}=\text{C}=\text{S}$ ) with high selectivity, and not through the aromatic ring. On the basis of these previous studies, we expect PD to adsorb on  $\text{Ge}(100)-2 \times 1$  through at least one of its two isocyanate groups ( $-\text{N}=\text{C}=\text{O}$ ).

Figure 5a shows the IR spectrum after exposing a clean  $\text{Ge}(100)-2 \times 1$  surface to 60 L of PD. Spectral assignments are summarized in Table 2. The dominant absorption feature is an intense and narrow peak at  $2270\text{cm}^{-1}$  associated with the



**Figure 5.** Infrared spectra of layer-by-layer growth using (a) PD and (b) ED as the initial layer on the Ge(100)- $2 \times 1$  surface. Incremental spectra are shown. The uppermost spectrum in (a) is not at saturation, and overall intensities cannot be directly compared to those in the spectra of (b).

asymmetric  $\nu_a(\text{N}=\text{C}=\text{O})$  stretch, suggesting that at least some of the isocyanate groups remain unreacted following adsorption on Ge(100)- $2 \times 1$ . The vibrational modes at 1522 and 1450  $\text{cm}^{-1}$  are assigned to the aromatic breathing modes of the surface-bound phenyl group of PD. We assign the absorption features at 1630 and 1246  $\text{cm}^{-1}$  to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}_{\text{ar}}-\text{N})$  stretching modes, respectively. These observed vibrational modes likely correspond to the formation of a [2 + 2] C=N cycloaddition product on Ge(100)- $2 \times 1$ . Weak alkane  $\nu(\text{C}-\text{H})$  modes centered near 2925  $\text{cm}^{-1}$  suggest the creation of a minor side product, which is currently under investigation. Figure 5a shows the theoretically calculated vibrational spectra for the [2 + 2] C=N cycloaddition product of PD, and the agreement with the experimentally obtained spectra is good. We propose that the nucleophilic Ge dimer atom can attack the electrophilic carbon atom of the isocyanate group concomitantly with attack of the electrophilic dimer atom by the nitrogen atom of the isocyanate group, creating the [2 + 2] C=N cycloaddition adduct shown in Scheme 3.

After forming the initial PD/Ge(100) surface, at least some isocyanate groups remain intact and available for additional reaction. To study this possibility, 500 L of ED was exposed to the PD/Ge(100) surface at room temperature. The uppermost spectrum in Figure 5a shows the infrared spectrum of the ED/PD/Ge(100) surface, which is ratioed to the PD/Ge(100) saturation spectrum below it. For comparison, Figure 5b shows spectra of the first and third layers starting with the ED/Ge(100) surface. Because the newly formed second layer urea linkage (Scheme 3) is identical to that of the third layer when ED was initially deposited (ED/PD/ED/Ge(100)), their infrared spectra

are expected to be similar. However, it is important to note that the spectrum of the ED/PD/Ge(100) surface is not a saturation spectrum, and intensities cannot be directly compared to those of the ED/PD/ED/Ge(100) layer.

The infrared spectrum of ED/PD/Ge(100) exhibits an intense negative peak at 2270  $\text{cm}^{-1}$  (Figure 5a), indicating the disappearance of isocyanate functionality upon ED exposure. Three medium to weak urea bands are also observed at 1698, 1503, and 1302  $\text{cm}^{-1}$ , providing evidence of urea bond formation. In the behavior of these modes, the spectrum of ED/PD/Ge(100) resembles that of ED/PD/ED/Ge(100), as expected. However, unlike the infrared results of the layer-by-layer growth initiated with ED on Ge(100)- $2 \times 1$ , a clear negative absorption feature is present at 1246  $\text{cm}^{-1}$  and the possibility of additional negative peaks at 1630 and 1522  $\text{cm}^{-1}$  cannot be ruled out. The two peaks at 1522 and 1246  $\text{cm}^{-1}$  were previously assigned to the aromatic breathing and  $\nu(\text{C}_{\text{ar}}-\text{N})$  stretching vibrations of the [2 + 2] C=N cycloaddition product, respectively, and their reduction indicates that some of the PD likely desorbs upon ED exposure. The observation of surface adduct displacement suggests that the binding energy of the [2 + 2] C=N cycloaddition product is low, in agreement with the expected ring strain of the surface-bound four-membered ring. It is interesting to note that the dative-bonded structure formed by ED adsorption on Ge(100)- $2 \times 1$  is more stable than the [2 + 2] C=N cycloaddition product of PD and, hence, appears to form a superior first layer.

Further analysis of the dominant infrared peaks at 2270 and 1246  $\text{cm}^{-1}$ , associated with the  $\nu(\text{N}=\text{C}=\text{O})$  and  $\nu(\text{C}_{\text{ar}}-\text{N})$  stretches of the [2 + 2] C=N cycloaddition product, respectively, yields additional information regarding the percentage of PD displacement. Figure 5a clearly shows a negative peak

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at  $2270\text{ cm}^{-1}$  following a 500 L exposure of ED to the PD/Ge(100) surface, which is attributed to the creation of urea linkages as well as displacement of PD from the surface. IR peak areas of  $\nu(\text{N}=\text{C}=\text{O})$  in the spectrum of PD/Ge(100) and ED/PD/Ge(100) are 0.194 and  $-0.07$ , respectively, a reduction of 36%. On the other hand, the negative peak of the  $\nu(\text{C}_{\text{ar}}-\text{N})$  stretching mode at  $1246\text{ cm}^{-1}$  can be attributed only to PD displacement since that surface bond should not be affected by reaction with ED. Integrated intensities of the  $\nu(\text{C}_{\text{ar}}-\text{N})$  stretching mode in the PD/Ge(100) and ED/PD/Ge(100) spectra are 0.04 and  $-0.007$ , respectively, a reduction of 17%. This implies that nearly 50% of the negative  $\nu(\text{N}=\text{C}=\text{O})$  stretching peak area can be attributed to PD displacement (assuming attachment of only one isocyanate group per molecule), and we can therefore conclude that PD is not as strong of a candidate as ED for the initial layer of our sequential deposition scheme.

#### IV. Conclusions

By using MIR-FTIR spectroscopy, we have demonstrated that the binary exposure of two bifunctional precursors, ED and PD, on Ge(100) leads to the formation of a polyurea ultrathin film under vacuum conditions. We have carried out the reaction up to four molecular layers at room temperature. The relative surface coverage of the higher-order layers approaches that of the first layers, indicating that the number of reactive sites is largely preserved for each layer. A small percentage of "defects" were also observed at each layer. These may result from the

hydrolysis of isocyanate groups by residual water in the vacuum chamber or gas delivery lines in addition to dual amine and isocyanate reaction at each layer. We expect that film growth via urea coupling reactions may be improved by employing phenylene diamine instead of ED because its rigid phenylene ring may hinder the possibility of a dual coupling reaction. We have also explored formation of an isocyanate-functionalized Ge(100)- $2 \times 1$  surface and spontaneous urea coupling reactions upon subsequent exposure to ED. In addition to the reaction, displacement of surface-bound PD was observed as a consequence of the weakly bound four-membered ring of the [2 + 2] C=N cycloadduct. Demonstration of these layer-by-layer deposition methods now opens the door to a strategy with which to design and produce precisely tailored organic materials.

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