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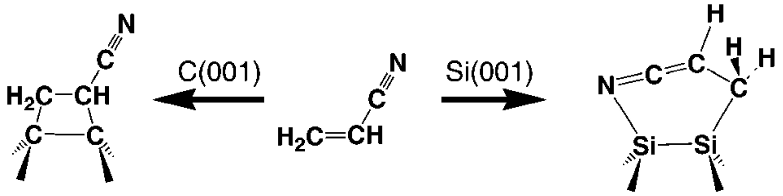

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Adsorption of Acrylonitrile on Diamond and Silicon (001)−(2 × 1) Surfaces: Effects of Dimer Structure on Reaction Pathways and Product Distributions

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Abstract: Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) are used to compare the reaction of acrylonitrile with Si(001) and C(001) (diamond) surfaces. Our results show that reaction with Si(001) and C(001) yield very different product distributions that result from fundamental differences in the ionic character of these surfaces. While acrylonitrile reacts with the C(001) surface via a [2 + 2] cycloaddition reaction in a manner similar to nonpolar molecules such as alkenes and disilenes, reaction with the Si(001) surface occurs largely through the nitrile group. This work represents the first experimental example of how differences in dimer structure lead to very different chemistry for C(001) compared to that for Si(001). The fact that Si(001) reacts with the strongly polar nitrile group of acrylonitrile indicates that the zwitterionic character of this surface controls its reactivity. C(001) dimers, on the other hand, behave more like a true molecular double bond, albeit a highly strained one. Consequently, while alternative strategies will be necessary for chemical modification of Si(001), traditional schemes from organic chemistry for functionalization of alkenes and disilenes may be available for building molecular layers on C(001).

Introduction

Interest in integrating semiconductor technology with organic and biological materials has fueled great interest in understanding how organic molecules react with the surfaces of diamond,[1−5] silicon,[6−9] and germanium.[8−16] While much activity has been directed toward understanding how the structurally similar Si(001) and Ge(001) surfaces differ in their overall chemistry,[8,12−15,17] less work has focused on comparing the different rates and reaction pathways of molecular interactions with the Si(001) and C(001) surfaces.[1,2,18]

In general, the group IV (001) surfaces of diamond, silicon, and germanium are composed of pairs of atoms, referred to as surface dimers. The dimer atoms are bonded to each other through a highly strained double bond, which is forced into a nonplanar geometry by virtue of being bonded to the underlying substrate atoms. Analogies can be made between the group IV (001) surface dimers and molecular double bonds. For carbon, the smallest group IV atom, molecular C═C species prefer to be planar. In the case of C(001) dimers, the constraint of bonding to the bulk significantly distorts the dimer double bond, which has been described as a biradical,[19] but it remains symmetric.[20−23]

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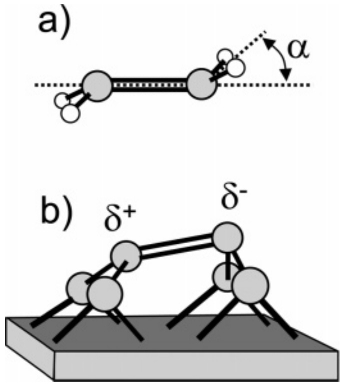

Figure 1. Illustration of the structures for (a) disilene and (b) a tilted Si(001) surface dimer. The angle α represents the pyramidalization angle, which is the degree to which the two H atoms are bent out of the planar position relative to the two Si atoms.

In contrast, distortion away from planarity can occur for molecular disilenes and digermenes,[24,25] as depicted in Figure 1a for $H_2Si{=}SiH_2$.[24] For example, disilenes can adopt planar or trans-bent configurations, with the folding angle α depending on the substituent.[24−31] Similarly, Si(001) surface dimers can adopt a buckled configuration, especially near defects, as shown in Figure 1b.[21,32,33] Only trans-bent molecular digermene species have been isolated,[34−36] and analogously, Ge(001) surface dimers are buckled, with an energy barrier between opposite tilted geometries larger than that for silicon dimers.[21] These similarities in the structure of molecular double bonded species compared to the structure of surface dimers suggest that there may also be a correlation in their reactivity.

Despite the above-anticipated similarities, there is an important difference between diamond and silicon (or germanium) surface dimers and molecular species. While analogous to bent disilenes and digermenes, tilting of the Si and Ge surface species leads to charge transfer within the dimer as the down atom adopts a similar geometry to the planar SiH_3^+ ion[37] and the up atom resembles the strained SiH_3^- ion.[38] Because of charge transfer within a Si(001) surface dimer, electron-rich and electron-deficient molecules can react through nucleophilic or electrophilic addition, respectively.[6,39−43] Charge transfer has also been found to influence the chemistry of Ge(001) surface dimers.[15−17,44]

In contrast to Si(001) and Ge(001), the surface dimers of the C(001) surface are symmetric, with little or no charge transfer between the two carbon atoms of the dimer, making them similar to alkene C=C bonds.[19,21−23,45] Previous studies have shown that C(001) is much less reactive than Si(001) or Ge(001) toward simple C=C containing molecules and have attributed this lower reactivity primarily to the inability of C=C dimers to tilt.[1,2] However, these previous studies on C(001) involved non-polar alkene species, which made it difficult to distinguish whether differences in surface chemistry were due to π-bond strength (and $\pi-\pi^*$ splitting) or the ionic character of the surface dimers.

In this article, we report experiments using acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$), a model polar alkene containing both a polar nitrile group and a nonpolar vinyl group, to probe differences in the reaction pathways on C(001) and Si(001) surfaces. While previous studies showed acrylonitrile readily reacts with Si(001)[42] and Ge(001)[17,44] via the polar nitrile functional group, we find that the reaction of acrylonitrile with the diamond(001) surface occurs primarily through its nonpolar C=C group. Our results suggest that differences in ability of the surface dimers to tilt control their propensity to react with polar versus nonpolar molecular groups. This work helps to further our understanding of the general reactivity trend for group IV double bonded species, and the results suggest that C(001) may provide a unique system for studying strained group IV double bonds.

Experimental Methods

Experiments were performed in separate ultrahigh vacuum (UHV) chambers (base pressures $<10^{-10}$ Torr). X-ray photoelectron spectroscopy (XPS) was used to characterize elemental composition and chemical oxidation states. Fourier transform infrared spectroscopy (FTIR) was used to measure vibrational spectra of chemisorbed monolayers and physisorbed molecular multilayers on silicon and diamond (001) surfaces.

Silicon and Diamond Samples. Silicon wafers (purchased from Wacker) used in the XPS and FTIR experiments were oriented to ±0.5° of the (001) plane. Scanning tunneling microscopy measurements show that these samples have large, flat terraces separated by steps that are one atomic layer in height and have equal amounts of the equivalent (1×2) and (2×1) domains of dimer orientations.[32] We used highly Sb-doped (<0.1 ohm cm) silicon wafers that were polished on one side for XPS experiments and lightly B-doped (>5 ohm cm) silicon wafers that were polished on both sides for FTIR experiments. The ∼0.5-mm-thick silicon samples were cut into ∼1 cm × 2 cm rectangles. For the FTIR experiments, the two narrow edges (∼0.5 mm × 1 cm) were then polished at a 45° angle to form a trapezoid-shaped prism that served as an internal reflection element (IRE). For all silicon experiments, a clean (2×1) reconstructed surface was produced by degassing the samples overnight at 840 K and then flash annealing to 1400 K until the pressure stabilized at $<3 \times 10^{-10}$ Torr.[46]

Two natural type IIa diamond samples were used (the IRE sample was provided by General Electric, and the XPS sample was purchased from Harris International). The major surfaces of each sample were

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oriented to within 2° of the (001) crystal surface. The first sample was cut and polished as a square flat (3 × 3 × 0.5 mm^3) for use in the XPS experiments. The second sample was cut and polished into a trapezoidal prism (15 × 3 × 0.25 mm^3 with 45° bevels on the narrow edges) for use as an IRE in the FTIR experiments. The prism was held in the UHV system on a molybdenum block, the heating and cooling of which are described elsewhere.[47] For both XPS and FTIR experiments, the diamond surfaces were cleaned in a series of acid baths and subsequently treated with an H-plasma to produce a clean, well-ordered C(001)−(2 × 1) reconstructed, H-terminated surface.[48] The diamonds were then transferred into the UHV systems where they were heated to ∼1375 K in UHV to remove the surface hydrogen and produce a clean C(001)−(2 × 1) reconstructed surface.[49]

Reagents and Dosing. Each vacuum chamber used a stainless steel gas handling system. Acrylonitrile (Aldrich, 99+% purity) was transferred under nitrogen into a glass bulb that was attached to a stainless steel valve, and was degassed using three freeze−pump−thaw cycles. Lecture bottles of propene (Aldrich Chemical Co., 99+%) and propene-3,3,3-d_3 ($CH_2{=}CH{-}CD_3$, C/D/N Isotopes, 99.9 atom % D) were connected to the gas handling system, and the compounds were used without further purification. The purity of the reagents was verified using mass spectrometry and infrared spectroscopy. The compounds were admitted to the UHV chamber from the gas handling system via a leak valve while the chamber pressure was measured with a nude ionization gauge. Configurational variations between each vacuum system, especially the location of the leak valves with respect to the samples and ionization gauges, lead to slight differences in the measured and effective dosing pressures of the reactive gases over the substrates. The pressures used in this work were not corrected for these configurational differences and for the ionization gauge sensitivity for each compound. All doses are expressed in Langmuirs (L), where 1 L = 1 × 10^{-6} Torr s.

X-ray Photoelectron Spectroscopy. The silicon and diamond XPS measurements were performed in the same UHV system with a Physical Electronics monochromatized Al Kα source and hemispherical analyzer with a 16-channel detector array. The Si(2p) and N(1s) regions were probed using a pass energy of 11.75 eV (0.18 eV analyzer resolution), and the O(1s) and C(1s) regions were probed using a pass energy of 5.85 eV (0.09 eV resolution) The XPS data was processed using a Shirley background correction[50] followed by fitting to Voight (Gaussian−Lorentzian convolution) peak shapes. The quality of fit was determined by using a reduced χ^2 statistical analysis. The XPS binding energies were corrected for slight band bending effects by rigidly shifting all C(1s), O(1s) and N(1s), and Si(2p) peaks so that the Si(2p)$_{3/2}$ and Si(2p)$_{1/2}$ peaks occurred at binding energies 99.4 and 100.0 eV, respectively. On diamond, all peaks were similarly adjusted using the bulk C(1s) line at 285.0 eV.

Fourier Transform Infrared Spectroscopy. Multiple internal reflection infrared absorption spectra of adsorbates on Si(001) were obtained using a Mattson RS-1 FTIR spectrometer coupled to a UHV system through two BaF$_2$ windows. The infrared light was focused into the narrow edge of the trapezoidal samples. After being propagated through multiple internal reflection down the ∼2-cm length of the sample, the light emerged from the narrow edge at the opposite end, exited the chamber, and was focused onto a liquid nitrogen-cooled InSb detector. Spectra were acquired with 4 cm^{-1} resolution. Transmission spectra of liquid acrylonitrile were obtained using a Nicolet 740 FTIR with a triglycine sulfate (TGS) detector at 1 cm^{-1} resolution.

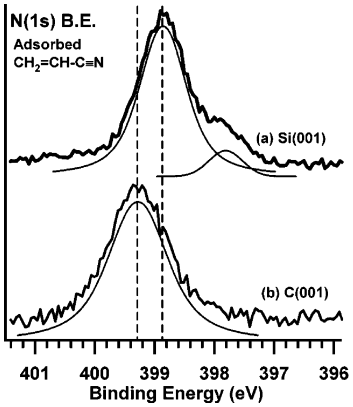

Figure 2. N(1s) XPS spectra for saturation exposure of acrylonitrile adsorbed on (a) a Si(001) surface and (b) a C(001) surface, each at 300 K.

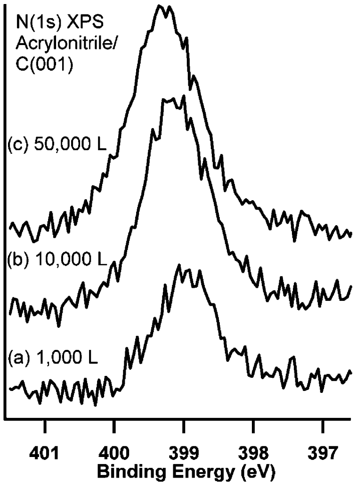

Figure 3. N(1s) XPS spectra for a C(001) surface that has been exposed to (a) 1000, (b) 10 000, and (c) 50 000 L exposure of acrylonitrile at 300 K.

Multiple internal reflection infrared spectra of adsorbates on diamond(001) were collected by signal averaging 5000 scans with 8 cm^{-1} resolution using a Nicolet 800 FTIR spectrometer. Similar to the Si(001) FTIR experiments, infrared light from the spectrometer was focused through a KBr window into the UHV chamber and onto one of the beveled edges of the diamond. The light propagated the 15-mm length of the sample via multiple internal reflection, exited the opposite end of the IRE, passed through a slit, and was transmitted through a second KBr window before being focused on a liquid nitrogen-cooled InSb detector.

Results

XPS Data. Figure 2 shows the N(1s) XPS spectra of (a) a Si(001) surface that was exposed to 10 L acrylonitrile at 300 K and (b) a C(001) surface that has been exposed to 50 000 L acrylonitrile at 300 K. The N(1s) XPS spectrum of a Si(001) surface exposed to acrylonitrile (Figure 2a) was fit to two peaks: a dominant peak at 398.9 eV (91% total N(1s) area) and a minority peak at 397.8 eV (9%). In contrast, the N(1s) XPS spectrum of a C(001) surface exposed to acrylonitrile at 300 K (Figure 2b) can be fit to a single peak at 399.3 eV. The peak at 398.9 eV for acrylonitrile/Si(001) was reported previously and attributed to a ketenimine ($C{=}C{=}N$) species.[42] The peak at 397.8 eV for acrylonitrile/Si(001) was not previously assigned, but its binding energy is almost identical to the 397.9 eV energy observed for acetonitrile/Si(001), which was attributed to a four-member $Si_2C{=}N$ ring.[43]

Figure 3 shows N(1s) XPS spectra of a C(001) surface after exposure to (a) 1000, (b) 20 000, and (c) 50 000 L acrylonitrile,

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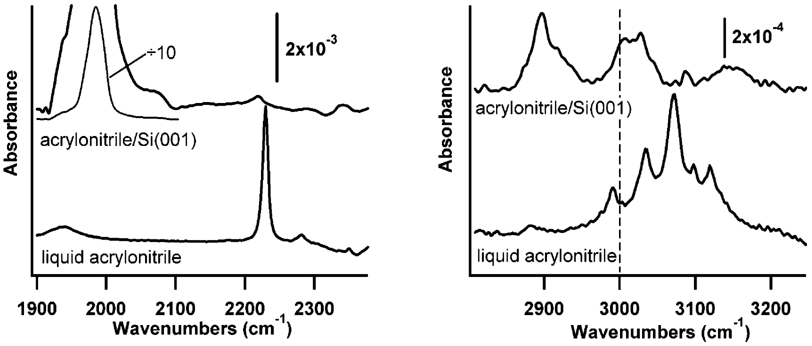

Figure 4. Comparison of the FTIR spectra of liquid acrylonitrile and spectrum of a Si(001) surface after saturation exposure to acrylonitrile in different spectral regions. Adsorption-induced changes include the appearance of new peaks at 1985 and 2898 cm^{-1}, and the disappearance of the C≡N stretching peak at 2230 cm^{-1}.

each at 300 K. These spectra can be fit to one peak (χ^2 value < 1) for all exposures up to 50 000 L. As the exposure is increased from 1000 to 50 000 L, the peak shifts from 399.0 to 399.3 eV and broadens from 0.82 (close to the effective limit of the XPS system) to 1.2 eV fwhm. The presence of one peak in the N(1s) XPS spectra indicates that only one distinguishable species is present on the C(001) surface after exposures of acrylonitrile up to 50 000 L.

Acrylonitrile/Si(001) FTIR. Figure 4 compares FTIR spectra of a Si(001) surface that has been exposed to 3 L acrylonitrile at 300 K and liquid acrylonitrile in the 1900−2400 cm^{-1} (left panel) and 2800−3200 cm^{-1} (right panel) regions. The FTIR spectra of acrylonitrile/Si(001) in Figure 4 are characterized by a very strong absorbance at 1985 cm^{-1}, a weak peak at 2218 cm^{-1}, and several intermediate intensity peaks at 2556, 2617, 2898, 3008, 3028, 3087, 3145, and 3347 cm^{-1}. Figure 4 also shows that the FTIR spectrum of liquid acrylonitrile is characterized by a strong C≡N stretching peak at 2230 cm^{-1} and several alkene C−H stretching peaks at 3034, 3073, and 3119 cm^{-1}, as assigned previously.[51]

Comparison of the FTIR spectrum of intact acrylonitrile with the acrylonitrile-saturated Si(001) surface shows that there are very distinct changes in the infrared spectrum upon adsorption. When acrylonitrile adsorbs on Si(001), the C≡N stretching mode at 2230 cm^{-1} that is seen for liquid acrylonitrile is not observed. The disappearance of this peak correlates with the appearance of a very strong absorption mode at 1985 cm^{-1}. These observations indicate that the nitrile group is involved in bonding acrylonitrile to the Si(001) surface. Also, examination of the C−H stretching region shows that while liquid acrylonitrile shows FTIR peaks almost exclusively above 3000 cm^{-1} (in the region associated with unsaturated C═C−H species),[51] after chemisorption on Si(001), a new peak appears at 2898 cm^{-1} (well within the alkane C−H stretching region). The presence of alkane absorbance indicates that some molecules react via the vinyl group. The fact that FTIR peaks above 3000 cm^{-1} remain indicates that some C═C−H species persist. The FTIR spectrum for acrylonitrile chemisorbed on Si(001), with the combination of an alkane absorbance, an alkene absorbance, and, especially, the very strong mode at 1985 cm^{-1}, is consistent with there being a ketenimine (C═C═N) species present, as previously observed. [42] Clearly, the nitrile group is strongly involved in the reaction with the Si(001) surface.

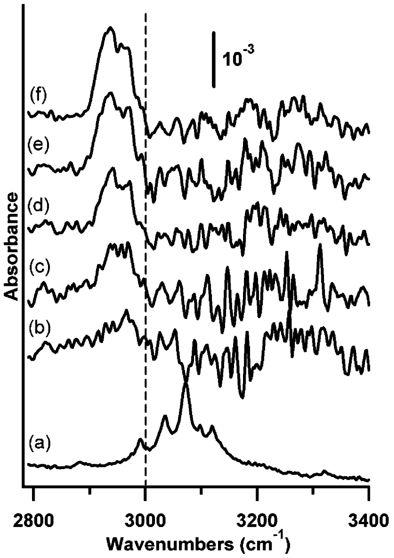

Figure 5. FTIR spectrum of (a) liquid acrylonitrile and multiple internal reflection FTIR spectra for a 300 K C(001) surface that was exposed to a total of (b) 1000, (c) 5000, (d) 10 000, (e) 30 000, and (f) 50 000 L acrylonitrile. Peaks for the adsorbed species occur only below 3000 cm^{-1}.

Acrylonitrile/C(001) FTIR. Figure 5 shows FTIR spectra arising from acrylonitrile and its interaction with the C(001) surface. Figure 5a shows a spectrum of liquid acrylonitrile, while Figure 5b−g shows multiple internal reflection FTIR spectra after a room temperature C(001) surface was exposed to increasing doses of acrylonitrile. While liquid acrylonitrile primarily is characterized by peaks above 3000 cm^{-1}, indicative of C−H stretching of sp^2-bonded C atoms,[51] the acrylonitrile/C(001) spectra are characterized by peaks at ~2937 and 2964 cm^{-1}, which are indicative of sp^3-bonded C atoms. There is no evidence for any peaks above 3000 cm^{-1} within the signal-to-noise of our experiment; the absence of high-frequency vibrations indicates that upon reaction with the C(001) surface, C atoms of the vinyl group of acrylonitrile have changed from having sp^2 to sp^3 character. Unfortunately, the diamond prism is opaque from ~1500−2700 cm^{-1} due to strong absorption by the bulk 2-phonon mode. Consequently, we were not able to investigate C═N, C═C═N, or C≡N vibrations on the diamond surface.

FTIR of Propene/C(001) and *d*$_3$-Propene/C(001). Our data indicate that acrylonitrile bonds with the C(001) surface almost entirely through the C═C group. The infrared spectrum of *d*$_3$-propene (CH_2═CH−CD_3) provides an interesting point of comparison. Previous studies have shown that simple alkenes

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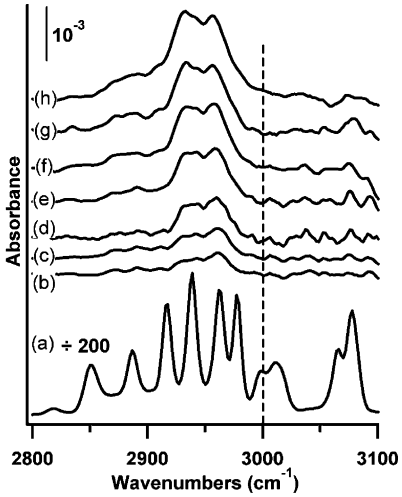

Figure 6. FTIR spectra of (a) a multilayer of propene at 100 K and a C(001) surface at 300 K after exposure to (b) 1000, (c) 2000, (d) 5000, (e) 10 000, (f) 30 000 (g) 60 000, and (h) 100 000 L propene.

react with C(001) via a [2 + 2] cycloaddition reaction between the C=C bond of the alkene and the C=C bond of the diamond surface.[1,18] Thus, d_3-propene and acrylonitrile can react with the C(001) surface via their C=C groups; in both cases the result would be a four-member C_4H_3 ring at the surface, with a pendant CD_3 group (propene) or C≡N group (acrylonitrile). Thus, if acrylonitrile interacts through its C=C group, the infrared spectrum is expected to be very similar to that produced by $CH_2{=}CH{-}CD_3$. To test this idea, we first conducted experiments using nonlabeled propene ($CH_2{=}CH{-}CH_3$) to verify its bonding via [2 + 2] reaction through the C=C group, and then we conducted experiments comparing the spectra of d_3-propene/C(001) and acrylonitrile/C(001).

Figure 6 shows FTIR spectra of (a) a multilayer of propene ($CH_2{=}CH{-}CH_3$) adsorbed at 100 K and a room-temperature C(001) surface after exposure to increasing amounts of propene. The spectrum of a multilayer of propene is characterized by several absorbance features above and below 3000 cm^{-1}, indicative of sp^2 (alkene) and sp^3 (alkane) hybridized carbon atoms. However, propene chemisorbed on the C(001) surface is characterized by FTIR peaks at 2873, 2889, 2933, and 2956 and shoulders at 2910 and 2943 cm^{-1}, each of which is below 3000 cm^{-1}. The spectrum is indicative of only sp^3-bonded carbon atoms within the chemisorbed species and is similar to what has previously been observed for methylcyclobutane.[52,53] The strong attenuation of the high-frequency C=C−H modes upon adsorption demonstrates that propene reacts with diamond via the C=C group, forming a [2 + 2] cycloaddition product similar to those previously reported for alkene (cyclopentene) adsorption on C(001).[1]

With the [2 + 2] reaction pathway for normal propene established by the data in Figure 6, we now compare the spectra of the *labeled* compound d_3-propene ($CH_2{=}CH{-}CD_3$) with that of acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$) to isolate the contribution of the vinyl group of each molecule to the C−H spectrum. Figure 7 shows a comparison of the C−H stretching region for a room-temperature C(001) surface exposed to (a) 20 000 L d_3-propene and (b) 20 000 L acrylonitrile. The spectrum of d_3-propene/C(001) is virtually identical to that of acrylonitrile/C(001). This similarity indicates that each molecule bonds to the C(001) surface via the vinyl group in a similar manner.

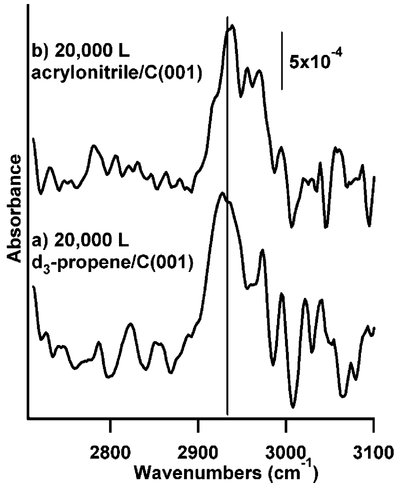

Figure 7. Comparison of the C−H stretching region for a C(001) surface after exposure to (a) 20 000 L d_3-propene and (b) 20 000 L acrylonitrile.

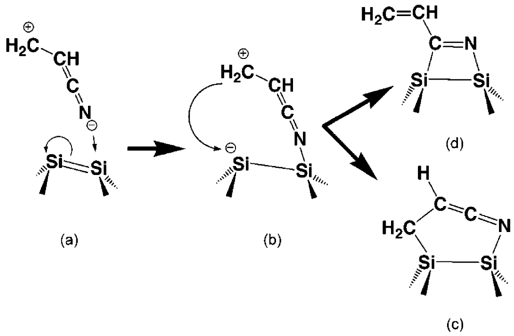

Figure 8. Reaction mechanisms that could lead to formation of the observed surface products for a Si(001) surface that has been exposed to saturation coverage acrylonitrile (a) initially attacks a silicon dimer to form (b) a dative-bonded intermediate state. The dative-bonded intermediate then continues along two reaction pathways to form (c) a ketenimine (C=C=N) species and (d) a [2 + 2] product through the nitrile group.

Discussion

Bonding Configurations for Acrylonitrile/Si(001). The presence of two N(1s) XPS peaks (Figure 2a) indicates that there are at least two bonding configurations present for saturation coverage of acrylonitrile on Si(001). It has previously been experimentally established that acrylonitrile predominantly forms a ketenimine (C=C=N) species upon reaction with Si(001).[42] Theoretical work has predicted that acrylonitrile reacts with Si(001) to form C=N and C=C=N surface species via the mechanisms illustrated in Figure 8.[54] For these reaction pathways, acrylonitrile initially forms a dative bond (Figure 8b) with a silicon dimer and then links through the terminal C atom to form a C=C=N species (Figure 8c) or through the nitrile C atom to form a four-member $Si_2C{=}N$ ring species (Figure 8d). We similarly assign the majority bonding configuration for acrylonitrile on Si(001) to a ketenimine species based on the presence of an XPS peak at 398.9 eV (Figure 2a), which represents ~91% of the surface species, and a characteristic

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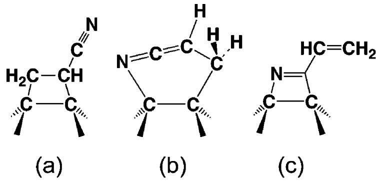

Figure 9. Three possible bonding configurations for acrylonitrile/C(001): (a) a [2 + 2] product through the vinyl group, (b) a ketenimine species, and (c) a [2 + 2] product through the nitrile group.

very intense FTIR peak at 1985 cm^{-1} (Figure 4).[17,42,43] While the minority N(1s) species was not previously identified for acrylonitrile on Si(001),[42] theoretical predictions, combined with the observation of an XPS peak at 397.9 eV (Figure 2a) that is almost identical to a peak that was assigned to a $Si_2C{=}N$ ring species for acetonitrile/Si(001),[43] lead us to conclude that the minority species is a $Si_2C{=}N$ ring species. Therefore, acrylonitrile reacts almost exclusively through the nitrile moiety on Si(001), likely through an initial dative bond formed by electron donation from the N atom of the nitrile group to the silicon dimer.[42,54]

Bonding Configurations for Acrylonitrile/C(001). Three possible bonding configurations for acrylonitrile adsorbed on C(001) are illustrated in Figure 9. The observation of only one N(1s) XPS peak for all acrylonitrile exposures (Figure 3) indicates the N atoms of the adsorbed species are in a similar environment and strongly suggests there is a single bonding configuration for acrylonitrile on the C(001) surface. FTIR spectra provide evidence for determining the identity of the bonding configuration. In particular, the FTIR spectra in Figure 5 reveal that the chemical structure for acrylonitrile significantly changes after it adsorbs on the C(001) surface. The loss of absorbance modes above 3000 cm^{-1} and presence of lower-frequency C−H stretching modes below 3000 cm^{-1} indicates a transition from sp^2 to sp^3 hybridization.

The fact that only alkane C−H stretches are observed in the FTIR spectrum of acrylonitrile/C(001) indicates that the reaction occurs through both C atoms of the vinyl group, which strongly indicates that the nitrile group remains unperturbed. This conclusion is further supported by the fact that the C−H spectra produced by acrylonitrile/C(001) and by d_3-propene/C(001) are almost identical (Figure 7), suggesting that the bonding configuration for each involves a similar species.[52,53] Since the H atoms of the methyl group are substituted with D atoms in d_3-propene, all the observed C−H vibrations arise from the C=C portion of the molecule, which is analogous to acrylonitrile. The only likely bonding configuration for propene is a four-member ring via a [2 + 2] cycloaddition through the C=C group. The assignment of a [2 + 2] product for propene is supported by the fact that the four-membered ring containing methylcyclobutane has a very similar FTIR spectrum.[52,53] Therefore, we also conclude that acrylonitrile forms a [2 + 2] product (Figure 9a) when reacting with a C(001) surface dimer.

Mechanistic Pathway Differences on Si(001) and C(001): The Role of Dimer Tilting. While previous studies have shown that alkenes and dienes yield similar reaction products on C(001), Si(001), and Ge(001) (albeit with different rates),[1,2] we find that acrylonitrile yields quite different product distributions. In particular, acrylonitrile reacts with C(001) via the vinyl group to form a [2 + 2] cycloaddition product, but reacts predominantly through the nitrile group on Si(001)[42,54] and Ge(001).[17,44]

Although Si(001) and C(001) have similar physical structures (i.e., dimer units at the surface), one very notable difference between them is the ease with which the surface dimers can tilt. The importance of dimer tilting has been recognized in previous studies demonstrating that simple alkenes will react quite easily with Si(001)[6,55] and Ge(001)[10,11] surfaces. This high reactivity has been attributed to the fact that tilting of the dimers can facilitate reactions by acting as amphoteric sites in which charge can be easily shifted between atoms, resulting in low-symmetry pathways toward forming [2 + 2] products with alkenes.[1,56] In those studies, the net results of reaction were largely the same on Si(001), Ge(001), and C(001) surfaces. In the present study, however, we find that acrylonitrile yields very different products on C(001) and Si(001) surfaces, suggesting that the differences in physical and electronic structure can also give rise to major differences in the reaction pathway that were not obvious in the previous studies.

Si(001) and Ge(001) dimers have been described as having molecular, diradical, and most importantly, *zwitterionic* character.[57−61] The zwitterionic nature of Si(001) and Ge(001) dimers can be attributed to the fact that they form similar structures in which the dimer atoms are tilted,[32,62] leading to charge transfer from the down atom to the up atom. The ionic nature of silicon[39−43] and germanium[13−17,44] dimers plays a very important role in the chemistry of Si(001) and Ge(001) surfaces. Silicon and germanium surface dimers are susceptible to attack by an electron-rich atom such as the N atom of amines,[16,39,41] and both react quite readily with a normally unreactive nitrile group.[17,42,44,63−67] Therefore, zwitterionic silicon and germanium surface dimers facilitate reaction through the electron-rich nitrile group of acrylonitrile for the majority of reacting molecules.[17,42,44,54]

C(001) surface dimers, on the other hand, are symmetric and without significant tilt.[19,20,68,69] Since diamond surface dimers are not tilted, there is little or no charge transfer between the dimer atoms.[19,21−23,45] Consequently, the electron-rich nitrile group of acrylonitrile does not interact with C(001) surface dimers. Instead, the diamond surface dimers preferentially react with the vinyl group of acrylonitrile to form a [2 + 2] cycloaddition product. Although the concerted suprafacial−suprafacial process is symmetry-forbidden, a [2 + 2] cycloaddition reaction can avoid Woodward−Hoffmann constraints by proceeding through a low-symmetry intermediate, such as a

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diradical.[70] C(001) surface dimers have been predicted to have biradicaloid character,[19] and theoretical calculations show that [2 + 2] reactions between ethylene or butadiene and C(001) are facilitated by a diradical intermediate.[3,18]

C(001) dimers can facilitate a low-symmetry intermediate state due to distortion introduced by bulk bonding, which leads to π-bonds that are weaker for C(001) dimers (44−82 kJ/mol)[20] than for alkenes (∼250 kJ/mol).[71] In contrast to [2 + 2] reactions between simple alkenes, which require high temperatures and pressures to observe significant product,[72−74] C(001) reacts with acrylonitrile spontaneously at 300 K. Experimentally, the observation of spontaneous reaction at room temperature for acrylonitrile/C(001) is analogous to previous observations for disilenes,[75] which also have π-bonds weaker than those of alkenes[71,76−78] and have been described as having diradical character.[79] The observation that acrylonitrile reacts with C(001) through the vinyl group to spontaneously form a [2 + 2] surface product at 300 K indicates that the barrier for reaction with the surface dimer is smaller than that for reaction with an alkene. We conclude that the [2 + 2] reaction between acrylonitrile and C(001) proceeds through a low-symmetry pathway, in agreement with theoretical predictions.[3,18]

Conclusions

Acrylonitrile, a model polar alkene, was used to probe differences in the reactivity of C(001) and Si(001) surface dimers. On Si(001), acrylonitrile reacts through initial interaction between the electron-rich N atom of the nitrile group and the electron-deficient down end of a zwitterionic silicon dimer, leading to products that predominantly involve the nitrile portion of the molecule. In contrast, acrylonitrile reacts with diamond (001) via the vinyl group to form a [2 + 2] cycloaddition product. These results show that the degree of zwitterionic character of a group IV (001) surface dimer strongly influences the reaction pathway. The reaction product for acrylonitrile on C(001) is analogous to doubly bonded group IV molecular species since there is no significant charge transfer within the dimer, while silicon surface dimers react in a way that has no molecular counterpart due to their zwitterionic structure. Consequently, while alternative strategies will be necessary for chemical modification of Si(001), traditional schemes from organic chemistry for functionalization of alkenes and disilenes may be available for building molecular layers on C(001).

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