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Adsorption Chemistry of Cyanogen Bromine and Cyanogen Chlorine on Silicon(100)

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The adsorption and decomposition of cyanogen halides, XCN (X = Br, Cl), on Si(100) is investigated utilizing X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). For submonolayer exposures, XPS indicates that the CN triple bond of XCN remains intact upon adsorption at 100 K. The UPS spectrum contains two peaks assigned to the π-electrons in the CN triple bond. The splitting indicates that some fraction of the XCN molecules adsorbs molecularly at low temperature. XPS analyses of the C 1s photoelectron peak following submonolayer exposure at low temperature suggest a greater fraction of BrCN (60%) adsorbs molecularly than ClCN (40%). XPS and UPS measurements at room temperature show that the X−CN bond breaks, while the CN bond remains intact during room-temperature adsorption on Si(100). Thus, the UPS spectrum of XCN adsorbed at room temperature on Si(100) contains a peak at 6.0 eV due to the unperturbed π electrons of the CN species. Upon annealing a CN-saturated Si(100) surface to higher temperatures, the UPS spectra indicate that the CN bond remains intact until approximately 700 K. Simultaneous changes in the C 1s and N 1s photoelectron peaks are consistent with the idea that CN bond cleavage is correlated with silicon carbide and nitride formation. These results are compared with a previous study of ICN adsorption on Si(100).

Introduction

Recently, we have investigated the adsorption and decomposition chemistry of cyanogen iodide (ICN) on Si(100) surfaces both experimentally and theoretically.[1,2] In this paper, the ICN study is extended to include the surface chemistry of two additional cyanogen halides, cyanogen bromide (BrCN) and cyanogen chloride (ClCN), on Si(100). Lu and Lin have recently reviewed reaction of C, N, and O containing molecules with the Si(100) surface.[3] In particular, Lin and co-workers[4−7] have studied hydrogen cyanide (HCN) and cyanogen (C_2N_2), on Si(100) and Si(111) surfaces. Bu and Lin have also studied another similar compound, s-triazine ($(HCN)_3$), on the Si(100) surface.[8] For HCN, Lin and co-workers find that at high exposures, HCN dimerizes and possibly polymerizes on the Si(100) surface at low temperatures.[5] Upon warming to 220 K, iminium (HC−NH) and CN species are identified as decomposition products. At 560 K, the CN species undergoes a reorientation from an end-on to a side-on geometry with a concomitant breakage of one bond to yield a doubly bonded surface species. After annealing to temperatures above 600 K, only the CH group, atomic N, and atomic H are left adsorbed to the surface. Finally, at temperatures greater than 1000 K, only a mixture of silicon nitride and carbide remains. In contrast, both $(HCN)_3$ and C_2N_2 molecules are more stable than HCN on the Si(100) surface. At low exposures, C_2N_2 adsorbs in a side-on geometry that is stable until 550 K. $(HCN)_3$ is believed to lie flat on the Si(100) and also is stable until 550 K. Above this temperature, the NC−CN single bond in C_2N_2 breaks and leaves the CN group, atomic C, and atomic N on the surface. $(HCN)_3$ also decomposes above 550 K to a complex mixture of HCN, NH, and atomic H adsorbed on the Si(100) surface. For both systems, silicon carbides and nitrides are formed after annealing the Si(100) surface to temperatures greater than 800 K.

The adsorption and thermal chemistry of cyanogen iodide (ICN) on Si(100) surfaces have been previously investigated by ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD).[1] The surface chemistry has also been modeled by Kadossov et al.,[2] utilizing a single-dimer silicon cluster. For ICN on Si(100), the surface after a 0.2-langmuir ICN exposure at low temperatures (100 K) consists of intact CN triple bond species. XPS analysis of the C 1s photoelectron peak indicates that up to 25% of the adsorbed ICN species have the IC bond unbroken. Upon annealing to room temperature, the CN bond remains intact, but all the IC bonds are completely broken on Si(100). Upon further annealing the Si(100) surface to higher temperatures, the UPS and XPS spectra indicate that the CN triple bond starts to disappear at approximately 470 K. By 800 K, all adsorbed CN species decompose completely into silicon carbide and nitride.

In this paper, we first briefly describe the experimental apparatus along with details of the syntheses and purification of BrCN and ClCN. The results are presented and then followed by a discussion section where the adsorption chemistry of these three cyanogen halides (ICN, BrCN, and ClCN) is compared and contrasted. Finally, the conclusion is presented.

Experimental Apparatus

The experimental setup has been previously described.[1] Briefly, it consists of a surface analysis system with a typical base pressure of 2×10^{-10} Torr using an uncorrected nude ionization gauge. The XPS measurements are performed by using the Mg anode of a PHI 300 W twin anode X-ray source. The resulting photoelectrons are detected by a PHI double-pass

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cylindrical mirror analyzer (CMA) with a pass energy of 50 eV. UPS is implemented by using a differentially pumped He discharge ultraviolet source (UG Microtech) to provide He(I) radiation. The same double-pass cylindrical mirror analyzer with a pass energy of 5 eV is used to detect the resulting photoelectrons. A copper foil provides the fermi level reference for the UPS photoelectron energies. Silicon (100) wafers from Virginia Semiconductor (100 mm diameter, arsenic doped, 0.01 Ω cm) are cleaved into samples approximately 16 mm in length and 6 mm in width. The wafers are 0.5 mm thick. The method for mounting the silicon sample on the ultrahigh vacuum (UHV) manipulator, thermocouple mounting techniques, and sample heating and cooling is found in ref 9. Before each experiment the silicon samples are cleaned by repeated flashing to temperatures greater than 1400 K. This procedure is repeated until no impurities (C, N, O in particular) are detected by XPS. All exposures are reported in langmuirs, where 1 langmuir is equal to 10^{-6} Torr s. Typical background pressures of 10^{-7} Torr are used for the exposures.

To avoid oxygen and nitrogen contamination, the cyanogen halide is placed in a small UHV compatible container attached to a precision leak valve mounted on the load-lock chamber. A dry ice/acetone mixture is used to cool the sample during repeated freeze−pump−thaw cycles. The pump cycle reduces the pressure in the container to 10^{-7} Torr by employing the turbo molecular pump in the load-lock chamber. ICN is synthesized using standard techniques[10] and is further described in ref 1. BrCN is obtained from Aldrich. Contact between BrCN and the stainless steel container is avoided by first placing a small quantity in a quartz tube, which in turn is slipped into the container. Even with these precautions, cyanogen is found to slowly form in the container and is thus a precedent contaminant. Fortunately, the cyanogen can be removed before each experiment by additional repeated freeze−pump−thaw cycles.

ClCN is synthesized by using standard inorganic preparative techniques.[11] Briefly, ClCN is formed by bubbling Cl_2 gas through a tetrachloromethane solution of sodium cyanide with a trace amount of acetic acid at temperatures between −10 and −5 °C. After the solution turns green, the flowing Cl_2 gas is replaced by He, and the solution is slowly heated to 60 °C. The resulting gas-phase reaction products are collected in a dry ice/acetone cooled flask. Excess Cl_2 gas is removed from the final reaction product by repeated freeze−pump−thaw cycles. The trimer, 1,3,5-triclorotriazine, is found to be a major contaminant. This contaminant is eliminated by cooling the flask down to −5 °C in a water/salt bath. The pure gas-phase ClCN is then collected in a dry ice/acetone cooled receiving flask.

Results and Discussions

XPS Low-Temperature Adsorption Results. The C 1s and N 1s XPS photoelectron spectra as a function of BrCN exposure to Si(100) surfaces at 100 K are shown in Figure 1. A 0.3-langmuir molecular BrCN exposure results in an XPS spectrum with the C 1s and N 1s photoelectron peaks centered at approximately 286 and 399 eV, respectively. These binding energies agree favorably with previous XPS studies of intact CN species adsorbed on various surfaces. In CN_x films prepared by low-power inductively coupled plasma-activated transport reactions from a solid carbon source, XPS studies by Popov et al.[12] attribute a C 1s photoelectron peak at 285.9 eV and N 1s peak at 398.4 eV to the presence of nitrile group ($-C\equiv N$) in the carbon nitride film. In another study, Hammer et al.[13] also assign an N 1s photoelectron peak at 398.4 eV to the presence of a nitrile group. In addition to CN species found in CN_x films, adsorbed intact CN species can be prepared on Rh(110) by a 20-langmuir C_2N_2 exposure at 100 K followed by a 373 K annealing treatment.[14] The XPS spectrum of this CN covered Rh(110) surface shows C 1s and N 1s photoelectron peaks corresponding to adsorbed CN groups at 284.3 and 397.4 eV, respectively.[14]

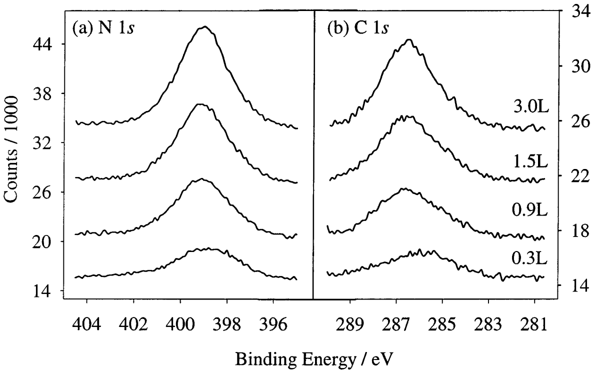

Figure 1. Nitrogen and carbon 1s XPS spectra as a function of BrCN exposure to the Si(100) surface at 100 K. The XPS intensities are relative.

The C 1s photoelectron peak after a 0.3-langmuir BrCN exposure (Figure 1) is slightly broader and skewed toward higher binding energy. Following low ICN exposures to Si(100) at 100 K, a similar high-energy tail is observed for the ICN C 1s photoelectron peak.[1] Based on a combination of UPS and XPS measurements, the high energy tail for the ICN C 1s photoelectron peak is attributed to the presence of molecular ICN, atomic I, and CN species on the Si(100) surface.[1] Assuming a similar adsorption model for BrCN, the BrCN C 1s peak can be fit by using two Gaussians components. One component is assigned to a molecular species at 286.5 eV and the other to a dissociated species at 284.5 eV. The peak position of the dissociated species is justified by the room temperature XPS and UPS results discussed below. The analysis indicates that about 60% is adsorbed molecularly (286.5 eV) following a 0.3-langmuir BrCN exposure with the remaining 40% adsorbed as atomic Br and CN groups (284.5 eV). The 60% adsorbed molecularly is much greater than the 25% found for low ICN exposures to Si(100) at 100 K[1] and can be attributed to the stronger Br−CN bond energy.[15]

As the exposure is further increased to 0.9 langmuir, Figure 1 also shows a simultaneous intensity increase of the C 1s and N 1s photoelectron peaks with increasing BrCN exposures. Both the C 1s and N 1s peaks become more symmetrical and their peak positions shift slightly upward in energy, approaching a constant with the highest exposures. No shift with increasing BrCN exposures is observed for the Si 2p photoelectron peak. With increasing exposures of molecular BrCN to the Si(100) surface at 100 K, an increasingly thick molecular BrCN film with a C 1s binding energy of 286.5 eV is formed. However, a simple adsorption model in which the BrCN first adsorbs as a dissociated species followed by molecular adsorption can be ruled out. The concentration of the dissociated species continually increases until an exposure of approximately 1.2 langmuirs is reached.

Figure 2 shows the C 1s and N 1s XPS spectra as a function of ClCN exposure to the Si(100) surface at 100 K. With increasing ClCN exposures to Si(100), a simultaneous increase in intensity for both the C 1s and N 1s photoelectron peaks is observed. For the C 1s peak, a second peak clearly grows in at 289.2 eV with increasing exposure at 100 K. As in the case of

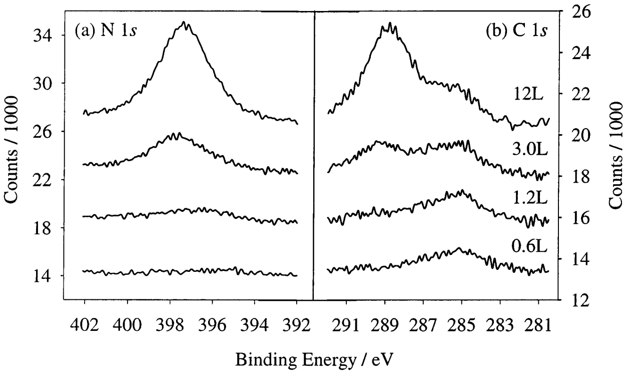

Figure 2. Nitrogen and carbon 1*s* XPS spectra as a function of ClCN exposure to the Si(100) surface at 100 K. The XPS intensities are relative.

TABLE 1: The XPS C 1s Peak Position after a Saturation Exposure of ICN, BrCN, and ClCN on Si(100) Surfaces at Low (100 K) and Room Temperatures (300 K)

	low temperature	room temperature
ICN	285.5 eV[1]	284.5 eV[1]
BrCN	286.5 Ev	284.5 eV
ClCN	289.2 eV	284.5 eV

BrCN and ICN,[1] these results indicate that a molecular film forms with increasing ClCN exposures. The C 1s binding energy for ClCN in the film is 289.2 eV, higher than that for both BrCN and ICN.[1] Table 1 summarizes the measured binding energy for the C 1s photoelectron peak of molecularly adsorbed ICN, BrCN, and ClCN. As expected, the increasing electronegativity of the halogens from I to Cl results in an upward shift in the binding energy of the C 1s the photoelectron peak.

Compared to the analogous experiments for ICN[1] and BrCN, the uptake rate is significantly smaller for ClCN. Visual examination of the 3-langmuir exposures for BrCN (Figure 1) and ClCN (Figure 2) clearly shows the dramatic difference in the uptake. For BrCN, the multilayer film is clearly formed, while for ClCN, the multilayer peak is clearly much smaller in relationship to the peak due to the dissociated species. Unlike ICN and BrCN, ClCN is prepared as a gas at a pressure greater than 760 Torr. In addition, the boiling point of ClCN is 13.8 °C, while for ICN and BrCN they are 146 and 61 °C, respectively.[10,11] Thus, possible undetected contributions to the measured pressure during ClCN dosing, but not ICN or BrCN, are unlikely. In addition, differences in the ionization cross sections between these analogous compounds are unlikely to cause such a dramatic difference in the uptake. The most probable explanation is that the sticking coefficient for ClCN is sufficiently smaller than that for ICN and BrCN.

As in the case of BrCN, the C 1s photoelectron peak for a 0.6-langmuir molecular ClCN exposure to Si(100) is slightly broader than that measured for higher exposures. This low exposure peak possesses a tail toward higher binding energy similar to that found for BrCN and ICN.[1] Using an analysis similar to that utilized for BrCN, nearly 40% of ClCN is found to be adsorbed molecularly (289.2 eV), while the remaining 60% dissociates upon adsorption to form atomic Cl and CN groups (284.5 eV) after a 0.6-langmuir exposure of ClCN to Si(100) at 100 K. As in the case of BrCN, this peak position for the dissociated species is justified by the room-temperature results discussed below. Although the Cl−CN bond strength is stronger than the Br−CN bond,[15] approximately 20% more ClCN adsorbs dissociatively than BrCN after low exposures to Si(100). This contradicts the bond-energy trend inferred from the BrCN and ICN results. One likely explanation is that the low sticking probability of molecular ClCN with respect to ICN and BrCN results in the disproportional buildup of the dissociated species. However, the concentration of the dissociated species continues to increase as the molecular species starts to build in. Thus, ClCN is similar to BrCN in that ClCN does not saturate the dissociated state before molecular adsorption occurs.

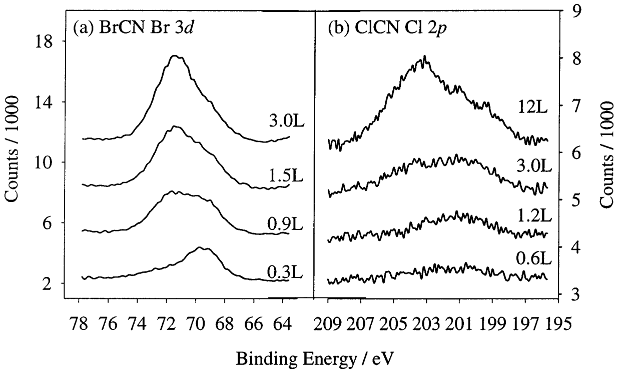

Figure 3. Si(100) XPS spectra for the (a) bromine 3d and (b) chlorine 2p peak as a function of the respective cyanogen halide exposure at 100 K. The XPS intensities are relative.

The Br 3d and Cl 2p XPS spectra provide further support for the BrCN and ClCN adsorption models. For BrCN exposures of 0.3 langmuir to Si(100) at 100 K, the Br 3d photoelectron peak (Figure 3a) is centered at 70 eV with a tail toward higher binding energies. In addition, for exposures sufficient to form a multilayer, the Br 3d peak is found at higher binding energies (72 eV). After a submonolayer exposure of ICN on the Si(100) surface at 100 K, a comparable high energy tail is observed for the I 4d photoelectron peak.[1] Consistent with the ICN C 1s photoelectron studies, the tail toward higher energy is due to a mixture of molecularly adsorbed ICN species and adsorbed atomic I and CN on the Si(100) surface.[1] Therefore, the high-energy tail observed in the Br 3d spectrum for submonolayer BrCN exposures to Si(100) at 100 K supports an analogous adsorption model with both molecular BrCN and dissociated BrCN present on the surface. This conclusion is also consistent with the BrCN C 1s photoelectron results discussed above. The Cl 2p XPS spectrum shown in Figure 3b contains an analogous trend in peak positions and widths. For a 0.6-langmuir exposure of ClCN at 100 K (Figure 3b), the Cl 2p photoelectron peak is observed at 200 eV with a tail toward higher binding energy. For large exposures (33 langmuirs), multilayers of ClCN are formed and the Cl 2p peak is shifted upward to 203 eV. Along with the ClCN C 1s information, these results also support the adsorption model found for ICN and BrCN, with ClCN adsorbed both molecularly and as atomic Cl and CN at low exposures and temperatures on Si(100).

The low-temperature adsorption of BrCN and ClCN is simpler than that found for HCN on Si(100). When high-resolution electron energy loss spectroscopy is performed after low HCN exposures at 100 K, the resulting spectra are complex due to contributions from HCN, HCNH, and CN species along with HCN dimers.[5] At larger exposures and lower temperatures, HCN dimers and possibly polymers become the dominate species on the Si(100) surface.[5] In contrast, the low-temperature cyanogen halide chemistry is similar, with only molecular and one dissociated species adsorbed on the Si(100) surface.

The driving force for the formation of this dissociated species is the replacement of the XC bond with stronger XSi and CSi bonds.[16] The resulting CSi and CN bonds are stronger than an XC or an XN bond. The XC bond in XCN is stronger than the typical XC bond due to overlap between the p orbital on the halide and the π-system on the CN group.[15] However, for possible adsorption geometries where this overlap is not possible, the XSi bond is slightly stronger than the XC bond.[16] Thus, a side-on adsorption geometry for XCN where the CN group adds across the Si dimer bond is not energetically favorable compared to the observed dissociated species. For ICN, computational studies support this conclusion.[2] In contrast for HCN, the formation of a side-on adsorbed HCNH species is possible due to the formation of stronger HC and HN bonds with respect to the HSi bond. Intermediates to this species can react with other adsorbed HCN molecules leading to dimerization or polymerization on the Si(100) surface. Consistent with these ideas, the C_2N_2 molecule adsorbs molecularly on the Si(100) surface at low temperatures due to the stronger CC bond and the lack of surface H.[6] The exclusive molecular adsorption of the aromatic $(HCN)_3$ species can also be rationalized by the strong intramolecular bonds.[8]

UPS Low-Temperature Adsorption. The ground state of the iodide, bromide, and chloride cyanogen halides in the gas phase has been determined to be a $^1\Sigma^+$ state with a $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(2\pi)^4$ electron configuration for the valence electrons.[17−23] An important aspect of the chemical binding between the halogen and the CN group is the overlap between the atomic p orbital centered on the halogen and the π-system of the CN group. This overlap splits the originally degenerate π-system into two energetically distinct molecular orbitals, an in-phase (1π) and an out-of-phase (2π) combinations. For a molecular ICN film on Si(100), the out-of-phase combination results in one broad peak at 4.4 ± 0.4 eV with respect to the fermi energy.[1] The in-phase combination is energetically close to the $^2\Sigma^+$ photoelectron peak from the nitrogen lone pair (the 4σ molecular orbital).[18] Surface broadening merges these transitions into one broad peak at 6.7 ± 0.4 eV with respect to the fermi energy.[1] Finally, the 3σ orbital due to the lone pair on the halogen gives rise to a photoelectron peak at 9.7 ± 0.4 eV.[1]

The UPS spectra as a function of BrCN and ClCN exposure to the Si(100) surface at low temperature are shown in Figure 4, parts a and b, respectively. The small shift between the highest exposures and the 3.0-langmuir exposure is a result of the changing work-function due to the molecular film. At high BrCN exposures, three peaks are visible at 5.3, 7.7 and 11.5 eV. Using ICN as a guide, the peak at 5.3 eV originates from a transition involving the out-of-phase (2π) combinations of molecular orbitals. The 7.7-eV transition is slightly broader and is assigned to a mixture of peaks from the in-phase (1π) combination and to the nitrogen lone pair (4σ). Finally, the 11.5-eV transition is assigned to the 3σ MO of the adsorbed molecular BrCN.

For BrCN exposures between 0.3 and 0.6 langmuir, the BrCN UPS spectra look similar to that at high exposures. Although features from molecular BrCN after a 0.3-langmuir exposure are visible, there is both a shoulder toward lower energy and considerable intensity between the molecular BrCN peaks (5.3 and 7.7 eV). The XPS studies have shown that at low exposure and temperature a fraction of the BrCN is adsorbed as atomic Br and CN. For CN generated from room-temperature adsorption of ICN, a single photoelectron peak at 6.0 eV is visible.[1] Thus, CN generated from BrCN adsorption should appear between the two lowest energy molecular BrCN peaks (5.3 and 7.7 eV). The additional broadening to lower binding energies (5.3 eV) is due to a contribution of atomic Br at 5.0 eV. To confirm this assignment, the Si(100) surface is exposed to molecular Br_2 at room temperature. The UPS spectrum of this system contains a feature at 5.0 eV, which is assigned to the presence of atomic Br on the surface. Similar UPS transition energies are reported for Br on other surfaces. For Br adsorbed on Cu(111), Jones and Kadodwala[24] attribute an UPS peak at 4.7 eV to a state of majority Br character. On the Ag(110) surfaces, Kruger and Benndorf [25] identify a peak at 5.2 eV due to chemisorbed Br.

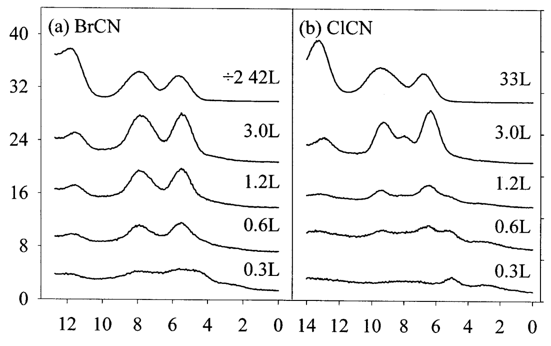

Figure 4. He(I) UPS spectra of Si(100) after various exposures to (a) BrCN and (b) ClCN at 100 K. The UPS intensities are relative.

The UPS spectra as a function of ClCN exposure to the Si(100) surface at low temperature are shown in Figure 4b. An interpretation similar to ICN and BrCN can be applied to the high-exposure ClCN UPS spectra. For a 33-langmuir ClCN exposure, the spectrum of the resulting multilayer film is shifted and broadened with respect to lower exposures. The 3-langmuir ClCN exposure spectrum is better resolved. This spectrum contains four peaks at 6.5, 8, 9.5, and 13 eV. Using the UPS spectra of gaseous ClCN as reference,[19,22] the peak at 6.5 eV can be assigned to the out-of-phase (2π) combination, the 8-eV transition to the nitrogen lone pair (4σ), and the 9.5 eV transition to the in-phase (1π) combination. The 13 eV transition is assigned to the 3σ MO of the adsorbed molecular ClCN.

The UPS spectra following low ClCN exposures to the Si(100) surface at low temperature are more complex than those of BrCN and ICN. For a 0.3-langmuir ClCN exposure, the spectrum (Figure 4b) contains a single peak around 5 eV due to the presence of chlorine from ClCN dissociation. At 0.3 langmuir, no discernible concentration of CN functional groups is detected by XPS. Due to the higher sensitivity of the Cl 2p peak, a very small amount of atomic Cl is detected on the surface. In addition, UPS is found to be very sensitive to atomic Cl. These results indicate that no molecular ClCN is present and that Cl is formed by the dissociation of a trace amount of ClCN. This conclusion is also consistent with the low ClCN sticking probability with respect to BrCN and ICN found by the XPS experiment. After 0.6-langmuir ClCN exposures, the UPS spectrum contains two additional peaks at 6.5 and 9.5 eV. These transitions are assigned to the out-of-phase (2π) and in-phase (1π) combinations, respectively. However, XPS results also indicate the presence of CN groups on the surface, which have a transition at 6.0 eV. Thus, the 6.5-eV peak also contains a decreasing contribution due to the surface CN groups with increasing exposures. This contribution explains the varying intensity of the 6.5-eV transition with respect to the 9.5-eV peak. The 4σ molecular orbital is not clearly seen for exposures less than 3 langmuirs. However, at lower exposures, it contributes to the almost featureless intensity between 6.5 and 9.5 eV.

XPS Room-Temperature Adsorption. Following an exposure of either BrCN or ClCN to the Si(100) surfaces at room temperature, the resulting C 1s and N 1s photoelectron peaks are nearly Gaussian in shape and are centered at approximately

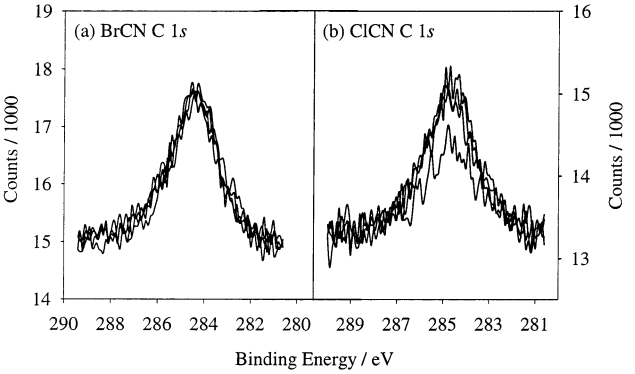

Figure 5. Carbon 1s XPS spectra as a function of (a) 0.3−42-langmuir BrCN and (b) 0.3−33-langmuir ClCN exposures to the Si(100) surface at 300 K. The XPS intensities are relative.

284.5 and 398 eV, respectively. Parts a and b of Figure 5 show the C 1s photoelectron spectrum for BrCN and ClCN, respectively, as a function of exposure to Si(100) at room temperature. The C 1s peak position is consistent with that found for ICN after room-temperature exposure to Si(100).[1] At room temperatures, ICN dissociates into atomic I and CN.[1] This C 1s peak position is also consistent with other XPS studies of intact CN species adsorbed on various surfaces.[12−14] Based on these observations, both BrCN and ClCN dissociatively adsorb on Si(100) at room temperature to form an adsorbed halide and an intact CN functional group. The identification of the 284.5-eV C 1s photoelectron peak in the room-temperature spectra justifies the assignment of the lower binding energy component in low-temperature XPS analysis C 1s of BrCN and ClCN C 1s photoelectron peak to a dissociated species. After approximately a 0.2-langmuir BrCN exposure or a 0.6-langmuir ClCN exposure, Figure 5 shows that the C 1s photoelectron peak position and intensity are unchanging with further exposures of the respective cyanogen halide. Therefore, room-temperature exposure of either BrCN or ClCN to Si(100) results in a saturated layer containing the atomic halide species and intact CN functional groups. For this layer, the ratio of the number of carbon atoms to nitrogen is found to be approximately 1 for BrCN and ClCN. This ratio is computed, taking into account the atomic sensitivity factors,[26] from the integrating area ratio of the C 1s to the N 1s photoelectron peak. Thus, both BrCN and ClCN dissociatively adsorb on Si(100) at room temperature to form an adsorbed halide and a CN functional group.

The Br 3d and Cl 2p photoelectron peaks for BrCN and ClCN, respectively, support the above room-temperature adsorption model. The XPS spectra of the BrCN exposed Si(100) surface at room temperature show a Br 3d photoelectron peak at 69 eV. Consistent with the above adsorption model and in contrast with the low-temperature adsorption results for BrCN, the room-temperature Br 3d peak lacks the high-energy tail previously attributed to molecularly adsorbed BrCN. A similar absence of a high-energy tail is also found for the Cl 2p photoelectron peak at 200 eV for room-temperature ClCN exposed Si(100). Again, this result is consistent with the above adsorption model and in contrast with the low-temperature adsorption results for ClCN. In conclusion, at room temperature the surface chemistry of BrCN and ClCN is analogous to that found for ICN.[1] BrCN is adsorbed as atomic Br and CN groups and ClCN is adsorbed as atomic Cl and CN groups.

UPS Room-Temperature Adsorption. The UPS spectra for the room-temperature adsorption of BrCN and ClCN as a function of exposure are given in Figure 6. In contrast to the low-temperature adsorption (Figure 4), the UPS spectra after room-temperature adsorption contain only one peak due to the CN π-system centered at 6 eV. The XPS results show the surface rapidly saturates at relatively low exposures. Unlike XPS which regulated the power to the anode, the gas flow into the UPS source is not regulated and the photon flux can drift with time. Thus, the small increase in intensity of the larger exposures is attributed to a small drift in the photon flux. Since only one species exists on the surface, possible photochemistry reaction leading to an intensity increase is unlikely. A single peak is also observed after room-temperature adsorption of ICN on Si(100) and is assigned to the degenerate π molecular orbitals on the CN groups.[1] The UPS shows only a single peak from the now degenerate π molecular orbitals. After the dissociation of the I−CN bond, the π molecular orbitals are no longer split by the overlap between the atomic p orbital centered on the halogen with the CN π system. For BrCN and ClCN, the room-temperature UPS results are consistent with the XPS data and support the room-temperature adsorption model found for ICN. In this model, the cyanogen halides (XCN) dissociate to form atomic halogen (X) and intact CN species on the surface. However, in contrast to atomic I, adsorbed Br and Cl have discernible features in the UPS spectra. The UPS photoelectron peak at 5.0 eV resulting from atomic Br originating from the dissociation of BrCN on the surface imparts a shoulder toward the lower binding energy on the measured 6 eV peak due to surface CN groups. The UPS spectrum obtained after a 50-langmuir Br_2 exposure to the Si(100) surface at 300 K contains a broad peak at around 5.5 eV. An examination of the UPS spectra taken after an exposure of ClCN to the Si(100) surface at room temperature reveals that the peak at 6.0 eV is also broader than expected and contains a visible shoulder toward high binding energies. In addition, a small feature is observed at approximately 3.0 eV. These additional fractures are due to the contribution from atomic Cl originating from ClCN dissociation. The UPS spectrum of a Si(100) surface after Cl chemisorbed at room temperature has been studied by a number of authors.[27,28] The resulting spectra are complex and contains many peaks between 3 and 9 eV. Although not as well resolved, similar spectra after a 32-langmuir Cl_2 exposure to the Si(100) surface at 300 K are obtained by our apparatus. Thus, the shoulder at 6.0 eV and the broad feature at approximately 3 eV are due to adsorbed Cl.

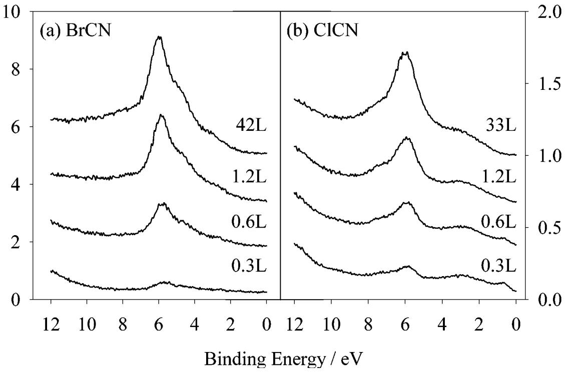

Figure 6. He(I) UPS spectrum for exposure of (a) BrCN and (b) ClCN to the Si(100) surface at 300 K. The UPS intensities are relative.

XPS Temperature-Dependent Studies. Figures 7 and 8 present the XPS spectra of the C 1s and N 1s photoelectron peaks for surfaces prepared by room-temperature saturation exposures of BrCN and ClCN, respectively, and subsequently annealed for 1 min at indicated temperatures. When the saturated surface is annealed to 473 K, the C 1s and N 1s photoelectron peaks start to broaden and shift slightly toward lower binding

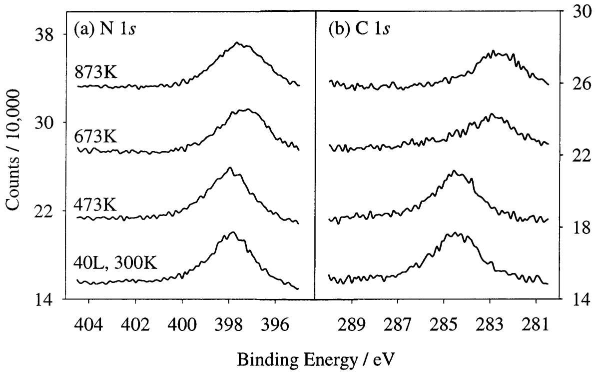

Figure 7. Nitrogen and carbon 1s XPS spectra from a Si(100) surface initially exposed to 40 langmuirs of molecular BrCN at 300 K and annealed to various temperatures for 1 min. The XPS intensities are relative.

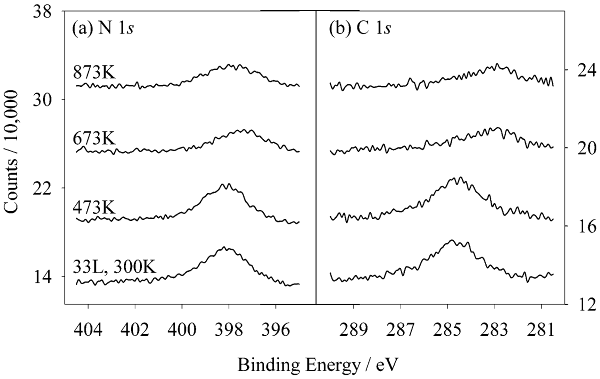

Figure 8. Nitrogen and carbon 1s XPS spectra from a Si(100) surface initially exposed to 33 langmuirs of molecular ClCN at 300 K and annealed to various temperatures for 1 min. The XPS intensities are relative.

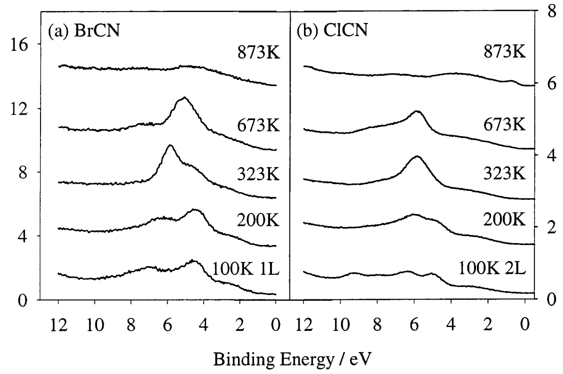

Figure 9. He(I) UPS spectrum from a Si(100) surface initially exposed to (a) 1 langmuir of BrCN and (b) 2 langmuir of ClCN at 100 K and annealed to various temperatures for 1 min. The surface is cooled to 100 K before each measurement. The UPS intensities are relative.

energies. This shift in binding energy is attributed to the increasing presence of atomic C and N surface species formed from partial decomposition of the surface CN groups. The initial decomposition of the CN groups at 473 K is similar to that found for ICN[1] and other comparable systems.[4] As the annealing temperature is further increased, the C 1s and N 1s peaks continue to broaden and shift toward lower energies as the concentration of adsorbed atomic C and N species increases with the simultaneous decrease in the concentration of adsorbed CN. Finally at around 873 K, the C 1s and N 1s peaks indicate only the atomic species with binding energies of 283 and 398 eV, respectively, remain on the Si(100) surface. At this temperature, all surface CN species are decomposed into Si−C and Si−N species. A similar decomposition temperature is found for ICN.[1]

The decomposition temperature of the adsorbed CN species on the Si(100) surface is similar to that found for other C and N containing compounds on the Si(100) surface.[3] The CN surface bonds created by HCN adsorption on Si(100) decompose between 600 and 800 K.[5] The C_2N_2 and $(HCN)_3$ molecules also decompose in the same temperature range.[6,8]

UPS Temperature-Dependent Studies. Figure 9a shows the UPS spectra measured after a 1-langmuir exposure of BrCN to Si(100) at 100 K and subsequent annealing at the indicated temperatures. As discussed above, the two peaks at 5.3 and 7.7 eV for the 1-langmuir BrCN exposed Si surface indicate the presence of molecular BrCN on the surface. At this exposure, XPS studies indicate the surface consists primarily of molecular BrCN with a very small concentration of surface Br and CN. With increasing annealing temperature, these two peaks slowly vanish as a fraction of the BrCN desorbs and the remaining dissociates into atomic Br and intact CN groups. At approximately 323 K, only a single peak appears at 6.0 eV with a shoulder at the lower binding energy, signifying the complete dissociation of BrCN into atomic Br and intact CN groups on the surface. This shoulder is similar to that observed for room-temperature adsorption and is due to atomic Br. When the annealing temperature is increased to 873 K, the peak at 6.0 eV disappears leaving only the contribution due to atomic Br at 5.0 eV. The XPS experiments show that the CN group is completely dissociated into atomic C and N at 873 K, while the Br 3d peak intensity drops by about 90%. Thus, the UPS photoelectron peak at 5.0 eV indicates the presence of atomic Br on the Si(100) surface after annealing to 873 K. For further increases in annealing temperature, this peak also vanishes, indicating the complete removal of surface Br.

Figure 9b shows the UPS spectra measured after a 2-langmuir exposure of ClCN to Si(100) at 100 K and subsequent annealing at the indicated temperatures. After a 2-langmuir ClCN exposure, the surface contains a mixture of molecular ClCN, atomic Cl, and CN functional groups. As this surface is annealed to increasing temperatures, the peaks due to the molecular ClCN species slowly vanish as some fraction of the molecularly adsorbed ClCN dissociates into adsorbed Cl and CN species and the remaining fraction desorbs from the surface. At approximately 323 K, a distinct peak at 6.0 eV is visible. This peak is similar to the peak found for a room-temperature exposure of ClCN and indicates the presence of CN groups on the surface. Similar to the room-temperature adsorption, this peak is broadened due to the contribution of adsorbed atomic Cl to this peak. The UPS spectrum of chemisorbed Cl contains many peaks between 3 and 9 eV.[27,28] Thus the broad feature at bonding energies higher than 6 eV is also attributed to adsorbed Cl. This feature also becomes more pronounced with the decreasing CN surface concentration as inferred by the XPS temperature-dependent measurements. Finally at 873 K, no Cl or CN is present on the surface and the UPS spectrum looks similar to that of clean Si(100).

Conclusions

The adsorption and decomposition of BrCN and ClCN on Si(100) are investigated utilizing XPS and UPS. For submonolayer exposures, XPS indicates that the CN triple bond remains intact upon adsorption at 100 K. The π-electrons in the CN triple bond contribute to two peaks (5.3 and 7.7 eV for BrCN and 6.5 and 9.5 eV for ClCN) in the UPS spectrum. The splitting of the π-system shows that some fraction adsorbs molecularly at low temperatures, while the rest adsorbs in a dissociated state. XPS analyses of the C 1s photoelectron peak following submonolayer exposure at low temperatures suggest that molecular adsorption for BrCN is higher (60%) than that of ClCN (40%). The fraction of molecular BrCN is larger than the 25% found for ICN adsorption on Si(100),[1] possibly due to the stronger Br−CN bond. However, this possibility does not explain the large degree of dissociation found for low-temperature ClCN adsorption on Si(100) with respect to BrCN. We propose, based on the low-temperature XPS uptake experiments, that molecular ClCN has a lower sticking probability with respect to ICN and BrCN and that this lower sticking probability results in the disproportional buildup of the dissociated species. The dissociated species forms due to the relatively weak X−CN bond. Consistent with this idea, the C_2N_2 and aromatic $(HCN)_3$ molecules adsorb without dissociation on the Si(100) surface at low temperatures.[6,8] For low-temperature HCN adsorption on Si(100), HCN, HCNH, and CN species could be identified along with HCN dimers.[5] In contrast, the Si(100) surface after low-temperature adsorption of BrCN and ClCN contains only the molecular and one dissociated species with an intact CN group on Si(100).

The C 1s and N 1s photoelectron peaks found after BrCN and ClCN exposure at room temperature on Si(100) are similar to those found for ICN and support the existence of intact CN function groups.[1] As in the case of ICN, no contributions are found from the molecularly adsorbed species. The UPS spectra of BrCN and ClCN are more complicated than that of ICN due to the contribution of adsorbed atomic Br and Cl on the surface. However, for both BrCN and ClCN, the CN species bonded to the Si(100) surface contributes only a single peak (6.0 eV) due to the π-electrons in CN bond to the UPS spectra. This result indicates that the Br−CN and Cl−CN bonds break, while the CN bond remains intact during room-temperature adsorption on Si(100). Upon annealing the CN saturated Si(100) surface to higher temperatures, the UPS and XPS spectra indicate that the CN triple bond starts to disappear at approximately 470 K. Simultaneous changes in the C 1s and N 1s photoelectron peaks between 470 and 800 K are consistent with the idea that CN bond cleavage is correlated with silicon carbide and nitride formation. By 800 K, all adsorbed CN species decompose completely into silicon carbide and nitride. These annealing results are similar with the results obtained for the CN-saturated Si(100) surface prepared by using ICN[1] and other analogous CN-containing systems.[5−7]

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