INTERACTION OF BORAZINE WITH A Re(0001) SURFACE, STUDIED BY LEED, TDS, AES AND ELS

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The interaction of borazine (N₃B₃H₆) with a Re(0001) surface has been studied by low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES) and electron energy loss spectroscopy (ELS). Two LEED patterns have been observed following borazine adsorption and annealing. One is the 2x2 structure, assigned to arise from atomic nitrogen. The other is the 3¹/₂x2¹/₂ pattern and is related to boron. The appearance of the two patterns indicates that borazine dissociates at 570 K. With a high exposure (> 6 L) of borazine and a subsequent annealing, only the well-formed 3¹/₂x2¹/₂ pattern is observed. Completion of this boron structure depends on both the surface boron coverage and the annealing temperature. Thermal desorption spectra show three states for borazine (α, β₁ and β₂) and three states for hydrogen (α, β₁, β₂). The α state in the borazine desorption spectrum is due to desorption of multilayers of borazine. The β state hydrogen is shown to correspond primarily to decomposition of borazine on Re(0001). Two desorption states of nitrogen are observed at T > 1300 K and also arise from the decomposition of borazine. AE data show that borazine decomposes to a boron–nitrogen compound when irradiated with a 2 keV e⁻-beam. Chemisorbed borazine, on the other hand, without e⁻-beam irradiation, dissociates into atomic nitrogen and boron upon annealing to T > 450 K. ELS results corroborate the LEED, TDS, and AES data that borazine adsorbs on Re(0001) non-dissociatively at 115 K and dissociates into N and B upon annealing to ~ 600 K.

1. Introduction

Borazine (N₃B₃H₆), whose structure is analogous to the Kekule structure of benzene due to a partial delocalization of the π electrons [1,2], has been suggested as a potential precursor to boron nitride [3]. An understanding of the interaction of borazine with single crystal metal surfaces is therefore important both fundamentally and practically. Recently, we have studied the adsorption of borazine on a Re(0001) surface, using the surface science techniques of low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES) and electron energy loss spectroscopy (ELS). The results of these studies are presented and discussed in this paper. This work was initiated because of the interest in the growth of high temperature, ordered ceramic films of boron nitride on solid substrates. Re was chosen as the substrate because of its high melting point (3453 K) which makes it practical to desorb boron decomposition products from the surface.

Gas phase borazine has been studied by AES [4] and ELS [5] previously. The AE spectrum of gas phase borazine was found to resemble that of solid hexagonal boron nitride or ammonia [4]. EL spectra have shown that the loss features of borazine are similar in many respects to those of benzene, suggesting that borazine is best described as an unsaturated π-electron system [5].

2. Experimental

The experiments were carried out in a conventional UHV chamber equipped with LEED, a double-pass cylindrical mirror analyzer (CMA) for AES and ELS, and a mass spectrometer for TDS. This system has been described in detail previously [6]. The sample was spot-welded to two 0.5 mm Ta wires permitting the sample to be heated.
to 1500 K and cooled to 110 K. A W–5%Re/W–26%Re thermocouple was spot-welded to the sample edge.

The Re(0001) surface was cleaned using a relatively simple procedure previously described [7,8]. Surface carbon was removed by maintaining the surface at 1200 K in oxygen (10⁻⁷ Torr) for several hours. After the oxidation process, the only surface impurity remaining was oxygen, which was then removed by flashing the sample to 1900 K. After this cleaning procedure, AES indicated a clean surface (<1 at% O, S, C) and LEED exhibited a sharp hexagonal pattern with low background intensity.

Borazine was obtained from a commercial vendor and used without further purification. It was, however, regularly degassed by freeze–thaw cycling and evacuation at liquid nitrogen temperature. Part of the gas exposures were carried out using a gas doser consisting of a stainless-steel nozzle positioned directly in front of the crystal face. This configuration resulted in a local gas pressure enhancement of approximately 20 compared to the background pressure.

EL spectra were obtained using the CMA with a primary electron beam energy of 110 eV and a peak-to-peak modulation voltage of 0.5 V. The spectra were recorded in the first derivative mode. All TD spectra were acquired using a ~10 K/s heating rate.

3. Results and discussion

3.1. Low energy electron diffraction (LEED)

3.1.1. High exposure (~ 40 L)

Exposure of ~40 L borazine (via the gas doser) to Re(0001) at 115 K yields no ordered LEED patterns. No integral beams of the substrate remain visible due to the formation of multilayers of borazine. Annealing this surface to 228 K results in the appearance of the integral spots with a high background intensity. This reappearance of the integral spots correlates with the desorption of physisorbed multilayers of borazine in the α state (see section 3.2). Further annealing this surface to 579 K causes the emergence of fractional spots near the integral ones along the (1120) direction. Annealing to 1194 K leads to the formation of a well-formed LEED pattern with fractional order spots almost as intense as the integral beams. Upon fully developing this structure by annealing to above 1500 K, AES showed no surface nitrogen, indicating that this structure is associated then only with dissociated boron from the borazine precursor.

Figs. 1b–1d show the gradual development of the LEED pattern as a function of annealing temperature. Fig. 1a presents the LEED pattern of the substrate as a reference. A schematic drawing of the structure in fig. 1d is presented in fig. 2a whereas fig. 2b represents the lattice in real space translated from fig. 2a. Fig. 2b shows that the two primitive vectors of the boron induced structure are along the (1010) direction and rotated 10.9° from the (1120) direction, respectively. The two lattice constants are 3\(1/2\) a and 2\(1/2\) a, respectively, where a is the lattice constant of the Re(0001) surface. Since this structure cannot be simply related to the substrate lattice, matrix notation, \((-1, 1, 1),\) is needed to name it on the base of the primitive vectors of the substrate unit cell. For simplicity, this structure will be referred to as a 3\(1/2\times\)2\(1/2\) structure. This structure corresponds to a boron coverage (\(θ_B\)) of 1/9 ML (1 ML = 1.52 \(×\) 10¹⁵ atoms cm⁻², the atomic density of the Re(0001) surface). It is also possible that the fractional spots are due to the effect of multi-scattering [9].

3.1.2. Low exposure (< 1 L)

Exposure of ~0.5 L borazine to Re(0001) at 115 K induces no new ordered LEED pattern, only the 1×1 pattern of the substrate being apparent. Subsequent annealing of this surface to 486 K generates lines along the (10\(\overline{1}\)0) direction with half order beams superimposed on the lines. Further annealing to 801 K produces a well-ordered 2×2 structure with the half order beam intensities much weaker than the integral ones and with lines along the (11\(\overline{2}\)0) direction. Annealing still further leads to the lines becoming spots which form the boron 3\(1/2\times\)2\(1/2\) structure. Completion of the 3\(1/2\times\)2\(1/2\) structure depends on both the initial exposure of borazine and the an-
nealing temperature. At a low exposure (< 0.5 ML), only lines along the $\langle11\bar{2}0\rangle$ direction are observed, indicating that boron forms only a one-dimensionally ordered structure on Re(0001). Exposure of ~1 L borazine leads to an incomplete $3^{1/2} \times 2^{1/2}$ LEED pattern, with only fractional spots near the integral beams being apparent.

As stated above, the $2 \times 2$ structure appears following exposure of the surface to ~0.5 L borazine and subsequent annealing to 801 K. Previous studies in our laboratories have shown that atomic nitrogen forms a $2 \times 2$ structure on Re(0001) [8]. (Hydrogen, on the other hand, forms a $2 \times 2$ pattern with missing spots [10].) Furthermore, the disappearance of the $2 \times 2$ structure in this study is associated with the desorption of nitrogen, as indicated by the AES and TDS results, suggesting that the $2 \times 2$ structure arises from adsorbed nitrogen atoms. The formation of the $2 \times 2$ nitrogen structure consequently indicates that borazine decomposes into atomic nitrogen and boron upon annealing. The dissociation of borazine on Re(0001) is further corroborated by the TDS, AES and ELS results which follow.

The possibility that the surface nitrogen was due to background nitrogen adsorption during the borazine exposure was excluded as follows: An exposure of 1 L borazine was carried out at a surface temperature of 320 K where the nitrogen dissociation sticking coefficient is known to be
very low ($<10^{-6}$) [7,8]. A subsequent anneal of the adsorbed borazine to 760 K leads to the appearance of the $2 \times 2$ structure. Therefore, the nitrogen in the $2 \times 2$ phase is not due to an accumulation of nitrogen from the background, but rather is from the dissociation of borazine on the surface during annealing. The $3^{1/2} \times 21^{1/2}$ structure annealed to $>1500$ K, as shown above, consists solely of boron as indicated by AES. Borazine therefore must be dissociated on Re(0001) upon annealing.

The formation of the $2 \times 2$ structure can provide further information about the dissociation temperature of borazine. Borazine exposure to Re(0001) at various sample temperatures was carried out. The $2 \times 2$ structure was seen following an exposure at $\geq 570$ K, indicating that dissociation of borazine must occur at $\sim 570$ K. It should also be noted that with a relatively high exposure of borazine ($>6$ L) to Re(0001) at 115 K, a subsequent exposure to $>570$ K, the $2 \times 2$ structure cannot be seen. This may be caused by either an increase in the nitrogen coverage or an increase in surface disorder by boron. Since the dissociation temperature and dissociation products are the two important issues in the present study of borazine on Re(0001), these points will be addressed further in the following sections.

### 3.2. Thermal desorption spectroscopy (TDS)

The thermal desorption spectra of borazine following various borazine exposures on Re(0001) at 115 K are shown in fig. 3. The TD spectra show three desorption states located at $-200$, $-500$, and $-700$ K. These states have been labeled as $\alpha$, $\beta_1$ and $\beta_2$, respectively. The intensity of the $\beta$ states has been amplified 125 times with respect to the $\alpha$ state. The $\alpha$ state desorbs at low temperature, behavior typically observed for physisorbed layers. The activation energy for borazine in the $\alpha$ state is estimated from the peak temperature to be 11.6 kcal/mol, using Redhead's formula [11], and assuming first-order kinetics and a frequency factor of $10^{13}$ s$^{-1}$. It is found that the $\alpha$ state cannot be saturated by a borazine exposure as high as 100 L, a result consistent with multilayer formation. The desorption temperature ($\sim 200$ K) of the $\alpha$ state is actually very close to the melting point of solid borazine (215 K) [1]. The peak maximum of
both $\beta$ states shifts toward higher temperature as the borazine coverage increases. This temperature shift is not likely caused by zero-order kinetics of the desorption since the desorption spectra (especially the $\beta_2$ peak) do not show a common leading edge. The shift of the $\beta$ states toward high temperatures may be caused by a stabilization of borazine by an accumulation of surface nitrogen and/or boron from the decomposition of borazine. By analogy, for example, the bond energy of CO to Re(0001) has been found to be strongly influenced by C and O impurities on Re(0001) [10].

Fig. 4 presents the thermal desorption spectra of hydrogen desorbed following the adsorption of borazine. The spectra also show three peaks, all correlating with the three states of the borazine TD spectra in fig. 3. In previous studies of hydrogen interacting with a Re(0001) surface [10,12], hydrogen was found to adsorb dissociatively and desorb as one peak between 300 and 700 K. Hydrogen induces a saturated phase, a $2 \times 2$ structure with missing spots, corresponding to a hydrogen coverage of 0.25 ML. The $\alpha$ state in fig. 4 is therefore unlikely due to desorption of hydrogen bonded to Re(0001). The mass 2 signal of the $\alpha$ state appears to be caused by the dissociation of desorbed borazine in the mass spectrometer.

The LEED studies of borazine on Re(0001) discussed above show that borazine dissociates below 570 K giving atomic B and N. N forms the $2 \times 2$ structure and B begins to form the $3\sqrt{2} \times 2$ structure. Hydrogen must also be released during the borazine decomposition and apparently desorbs as the $\beta$ states, since no further desorption features are observed between 700 and 1300 K. Fig. 5 shows the correlation between the desorption spectrum of hydrogen and borazine where...
both spectra were acquired simultaneously. Two differences between these spectra are noteworthy: (1) The peak temperature of the \( \text{H}_2 \) spectrum is \( \sim 24 \) K lower than that of borazine. (2) The desorption of hydrogen begins at \( \sim 260 \) K, whereas the onset of the borazine is at \( 340 \) K. The above two points quantitatively indicate that the \( \beta \) states (at least the \( \beta_2 \) state) do not arise merely from the cracking of borazine in the mass spectrometer, but rather likely consist of hydrogen recombination from surface sites. The ratio of the integrated areas of \( \text{H}_2 \) to those of borazine for the \( \beta \) states in fig. 5, \( \theta_{\text{H}_2}^\beta/\theta_{\text{Bor}}^\beta \), is estimated to be \( \sim 77 \). The corresponding ratio of the \( \alpha \) states (\( \theta_{\text{H}_2}^\alpha/\theta_{\text{Bor}}^\alpha \)) is, however, only \( \sim 1 \). Since the hydrogen in the \( \alpha \) state is caused solely by the dissociation of borazine in the mass spectrometer, the contribution of hydrogen from borazine in the gas phase to the \( \beta \) peaks of hydrogen in fig. 5 should be very small.

The \( \beta \) state hydrogen is therefore primarily a contribution of atomic hydrogen resulting from the dissociation of borazine on the Re(0001) surface. This hydrogen could, of course, also come from other products of the decomposition, for example, NH on the surface.

The spectrum of hydrogen from the clean Re(0001) surface was also acquired (fig. 5) and has been used to estimate the coverage of the chemisorbed borazine. In so doing it is assumed that the saturation coverage of atomic hydrogen on clean Re(0001) in the \( 2 \times 2 \) phase is 0.25 ML. Using this calibration the hydrogen desorbed in fig. 4c is found to be \( \sim 2.36 \) ML, corresponding to \( \sim 0.39 \) ML of borazine.

Fig. 6 shows the thermal desorption spectra of nitrogen following various exposures of borazine on Re(0001) at 115 K. Mass 14 was monitored in order to eliminate any influence from background CO. The desorption features are at \( \sim 150, 400-700, \) and \( > 1200 \) K. The desorption states below 700 K are obviously correlated with the desorption of borazine, nitrogen being generated from the dissociation of borazine in the mass spectrometer. The ratios of the borazine to nitrogen in the \( \alpha \) state and \( \beta_1 \) and \( \beta_2 \) states, \( \theta_{\text{H}_2}^\alpha/\theta_{\text{Bor}}^\alpha \) and \( \theta_{\text{H}_2}^\beta_1/\theta_{\text{Bor}}^\beta_1 \), are approximately the same. The desorption feature at \( T > 1200 \) K arises from adsorbed atomic nitrogen [7,8]. These desorption states correlate with the disappearance of the \( 2 \times 2 \) structure of nitrogen, as discussed in section 3.1. Compared to the desorption spectra of nitrogen from clean Re(0001) [7,8], we note that in the present study the desorption peak maximum of nitrogen in the high temperature state (\( \beta_3 \)) is shifted to a higher temperature and the TDS peak has more than one desorption feature. Unfortunately, no complete TD spectrum of nitrogen could be acquired in the present study because of sample heating limitations at these temperatures. These two differences are associated with the presence of surface boron on Re(0001), that is, the bonding of nitrogen to the substrate appears to be strengthened by the presence of boron.

3.3. Auger electron spectroscopy (AES)

The change in the Auger electron spectrum of a borazine covered Re(0001) surface as a function of annealing temperature is shown on fig. 7. The surface was exposed to 6 L borazine and then annealed to the indicated temperature. Fig. 8 presents the intensity change of the nitrogen peak at 381 eV versus annealing temperature. Fig. 7a shows that the Auger spectrum between 130 and 200 eV is significantly different from either that of Re or bulk boron [13]. Since the boron Auger peak at 179 eV overlaps that of Re at 176 eV, the
lineshape in fig. 7a might, at first glance, be ascribed to a composition of the two. However, the following two points strongly indicate that the difference is not caused by a simple superposition of these two features. First, the Auger spectrum from borazine adsorbed on a Cu surface, presented in fig. 7b, is very similar to the spectrum of borazine on Re (fig. 7a) although Cu has no interfering AES features near 179 eV. Secondly, the AE spectrum of bulk boron shows essentially one peak at 179 eV [13]. The superposition of a boron contribution with the Re peak at 176 eV should increase the peak intensity at 176–179 eV. Spectrum 7a shows no large AES peak in this kinetic energy range. The superimposed AES line is, however, clearly seen in spectrum 7g which is obtained from a boron covered Re(O001) surface after having completely desorbed all nitrogen. We therefore conclude that the spectrum in fig. 7a is not caused by a simple overlap of the Re and bulk boron spectrum.

Two additional points are worthy of mention in fig. 7:

1) The AES lineshape of boron in borazine is significantly different from that of solid boron. Upon annealing a borazine covered Re(O001) to 1780 K, where nitrogen is desorbed, the AES lineshape changes to that of bulk boron and Re. The AES lineshape of boron in fig. 7a therefore must be associated with a different chemical environment from that for bulk boron, consistent, for example, with boron bonded to nitrogen. Fig. 7a, therefore, very likely is an AE spectrum of either borazine or a boron–nitrogen compound. The AE spectrum of borazine in the gas phase has been reported previously [4]. The spectrum is presented in the integral mode making it difficult to compare directly with spectrum 7a; however, the features are qualitatively very similar. The modification of the AES lineshape of boron bonded to nitrogen compared to the AES lineshape of bulk boron is similar to the changes in the AE spectra of silicon in SiO2 relative to that of bulk silicon [14,15].

2) Upon annealing the borazine covered Re(O001) surface, the lineshape and the intensity of the boron and nitrogen features remain unchanged until 1550 K. At ~1780 K, nitrogen
desorbs with a concomitant alteration in the AES lineshape. On a nitrogen-free surface (fig. 7g), the peaks at ~179 eV are simply a superposition of Re lines and bulk boron lines. Heating to 2000 K causes a decrease in the boron features, correlating with the desorption of boron. Further heating to 2300 K leads to the recovery of a clean Re surface. The AES spectral lineshape change upon annealing to 1780 K suggests that nitrogen bonds to boron until this temperature is reached at which point nitrogen desorbs, likely as a result of the decomposition of the boron–nitrogen compound. This decomposition temperature is ~400 K higher than the desorption temperature of nitrogen on clean Re(0001) (see refs. [7,8] and section 3.2 of this paper).

Fig. 8 also shows that the nitrogen AES intensity is not changed upon annealing from 115 to 1550 K. The TD spectrum shows, however, considerable desorption of borazine at 200 K and desorption of nitrogen at 1250–1500 K. These results suggest that borazine can be dissociated or desorbed by the 2 keV incident AES electrons. Furthermore, the formation of a boron–nitrogen compound detected by AES is not consistent with the conclusion from 1.FFT and TDS that borazine dissociates on Re(0001) at or below 570 K. This apparent disagreement will be shown to be also caused by the influence of the e−-beam irradiation during the acquisition of the AES spectrum.

In order to check the e−-beam effect on the dissociation of borazine, the following experiment was carried out: A 6 L borazine exposure was given to Re(0001) at 115 K and the AE spectrum acquired (fig. 9a). The surface was then heated to 504 K and an AE spectrum taken from the annealed surface without moving the sample (fig. 9b). The sample was then shifted such that spectrum was taken from an area where no e−-beam irradiation had impinged with the resulting spectrum shown in fig. 9c. The smaller intensity of the nitrogen peak of fig. 9c, compared to 9b, indicates that the e−-beam has caused dissociation of borazine at 115 K. It can be estimated from figs. 9b and 9c that at least 35% of the nitrogen in spectrum 9b arises from e−-beam irradiation. The spectral lines at 179 eV in fig. 9c appear to be a combination of the Re substrate and of boron.

The corresponding lineshape in figs. 9a and 9b is, however, that from boron bonded to nitrogen. The Auger lineshape of nitrogen (at 350–400 eV) in fig. 9c is also different from that in fig. 9a or 9b. The lineshape of N in fig. 9c is of a metal nitride type, similar to that observed from nitrogen adsorbed on clean Re(0001) [8]. In previous studies of ammonia on Ru(0001) [16] and nitrogen on Fe and Mo surfaces [17], it was found that Auger spectra of dissociated nitrogen show pronounced KL1L2,3 and KL1L1 peaks at 368 and 358 eV. For non-dissociated nitrogen in NH3 or N2, only the KL2,3L2,3 peak at 381 eV is apparent. The Auger
spectra of figs. 9b and 9c, therefore, correspond to chemically bonded nitrogen and adsorbed atomic nitrogen on Re(0001), respectively.

From the above experiments, it is concluded that the boron–nitrogen compound detected by AES is due to e−-beam induced dissociation of borazine rather than by thermal dissociation of borazine. To further demonstrate this, the following two experiments were carried out: (a) Re(0001) was exposed to 0.5 L borazine at 115 K and then annealed to 783 K without e−-beam irradiation. LEED results have shown that this surface exhibits the 2 × 2 structure of atomic nitrogen and the 3′1/2 × 21′1/2 structure of boron (see section 3.1.2). The Auger spectrum (fig. 9d) was measured from the annealed surface and showed the Auger lines of Re substrate plus boron and atomic nitrogen. (b) The Re(0001) surface was exposed to 10 L borazine at 115 K, annealed to 513 K, cooled to 115 K and re-exposed to 8 L borazine and annealed again to 715 K. The Auger spectrum (fig. 9e) was then measured from the thermally cycled surface. From fig. 9e, it can be seen that no boron–nitrogen compound has been produced by the thermal cycling process. The nitrogen appears to be atomic N bonded to the Re substrate. Those experiments confirm that borazine does not form a boron–nitrogen compound on Re(O001) by mere exposure at 115 K and subsequent annealing, but rather dissociates into atomic nitrogen and boron upon annealing to > 500 K.

It is also interesting to see that spectra 9c and 9e show approximately the same amount of surface nitrogen, although 9c is from a surface exposed to 6 L at 115 K and then annealed whereas 9e is from a surface after two cycles of exposure and annealing. It appears that the chemisorbed borazine saturates the Re(0001) surface by a single process of exposure and annealing.

Spectrum 9c can be used to estimate the surface coverage of borazine. A previous study by us of nitrogen on Re(0001) [8] showed that 0.25 ML N on Re corresponds to the Auger ratio $I_N / I_{Re}$ of 0.25. The ratio in fig. 9c, using this calibration, corresponds to 0.68 ML N formed from 0.23 ML borazine, a value qualitatively similar to that estimated from the TDS experiments (0.39 ML). It is noteworthy that both TDS and AES results show the coverage of chemisorbed borazine to be well below 1 ML. For a borazine coverage of 1/3 ML, each borazine will occupy three Re atoms having an area of ~ 19.8 Å². This low saturation coverage, together with the relatively low dissociation temperature of borazine, suggest that the chemisorbed borazine likely bonds to the Re substrate with its plane parallel to the substrate surface.

3.4. Electron energy loss spectroscopy (ELS)

The electron energy loss spectra from a Re(0001) surface following borazine adsorption at 115 K and a subsequent anneal show complex loss structures. Although it is difficult to interpret every detail of the EL spectra, many of the loss features correlate well with the results of the TDS, LEED and AES experiments.

A 1 L exposure of borazine to Re(0001) at 115 K induces a small feature at 7.6 eV. This feature is diminished by annealing the surface to 220 K and, upon heating to 793 K, this loss structure is no longer observed.

In previous ELS studies of borazine in the gas phase [5], a sharp loss peak at 7.6 eV was obtained and interpreted to correspond to excitation between the π electronic levels in borazine. A similar loss feature is also observed with benzene [5]. In the present work, the 7.5 eV loss feature indicates that borazine is adsorbed nondissociatively on Re(0001) at 115 K. Upon flashing the borazine covered surface to ~ 230 K, the 7.6 eV loss peak is significantly attenuated and correlates with the desorption of molecular borazine as the π state. Heating this surface further to ~ 600 K eliminates the 7.6 eV loss feature entirely. The disappearance of this loss feature correlates with the TDS and LEED results, that is, the desorption of hydrogen (the β states) and the appearance of the 2 × 2 LEED pattern of nitrogen on Re(0001), respectively. The ELS results therefore support the TDS, LEED, and AES results that borazine dissociates on Re(0001) upon annealing to ~ 600 K.

The primary goal of this study of the interaction of borazine with a surface such as Re was to investigate the possibility of synthesizing ordered, ceramic films of boron nitride. In this regard, the
following questions are crucially important:
(a) Does borazine dissociate on the substrate?
(b) If dissociation does occur, what is the dissociation temperature and the dissociation products?

The results of LEED, TDS, AES and ELS in the present study of borazine on Re(0001) provide information toward answering the above questions. The $2 \times 2$ LEED structure of atomic nitrogen and the $3^{1/2} \times 21^{1/2}$ structure of boron indicate that borazine dissociates into atomic nitrogen and boron at 570 K. This result is corroborated by the following experimental results: (1) The disappearance of the intrinsic loss peak at 7.6 eV of molecular borazine following an anneal to 600 K, (2) the desorption of hydrogen at approximately this temperature, and (3) the detection of atomic boron and nitrogen by AE spectra of the Re(0001) surface exposed to borazine at 115 K and subsequently annealed to ~ 500 K without $e^-$-beam irradiation.

In summary, a physical picture for the interaction of borazine with a Re(0001) surface has emerged from these studies. Borazine apparently forms physisorbed multilayers on Re(0001) at 115 K. These multilayers desorb at ~ 200 K, leaving chemisorbed borazine at a surface coverage well below 1 ML. Further annealing to above room temperature causes the chemisorbed borazine to dissociate into atomic N and B which desorb at > 1200 and > 2100 K, respectively. There is no evidence for the formation of boron nitride on Re(0001) upon borazine exposure and annealing. However, if multilayer borazine at 115 K is irradiated with (2 keV) $e^-$-beam, a boron–nitrogen compound forms and is stable to 1500 K. Further investigations of $e^-$-beam and ion beam induced formation of boron–nitrogen compounds from borazine and its derivatives on surfaces are currently under investigation.

4. Conclusions

The conclusion of these studies of the interaction of borazine with a Re(0001) surface are as follows.

(1) Two LEED patterns have been induced upon adsorption of borazine at 115 K and subsequent annealing. One, the $2 \times 2$, is associated with surface nitrogen and the other, the $(\frac{3}{4}, \frac{1}{4})$ in matrix expression referenced to the substrate lattice (or the so-called $3^{1/2} \times 21^{1/2}$), is ascribed to surface boron.

(2) Three desorption states of borazine on Re(0001) have been detected. The low temperature one ($\alpha$ state) is due to desorption of physisorbed borazine, and the two $\beta$ states likely correspond to chemisorbed borazine. The TD spectra of hydrogen also show three states, the $\alpha$ state arising from the cracking of borazine in the mass spectrometer upon desorption, and the $\beta$ states, corresponding primarily to the decomposition of borazine on the Re(0001) surface. The two desorption states of nitrogen at $T > 1300$ K appear to be from atomic nitrogen on Re(0001) arising from the decomposition of borazine. The boron formed from the dissociated borazine desorbs at $T > 2200$ K.

(3) The AE spectrum from a borazine covered Re(0001) surface (~ 6 L) at 115 K is either a spectrum of borazine or of another boron–nitrogen compound. The surface exposed to borazine at 115 K and subsequently annealed to ~ 500 K without $e^-$-beam irradiation shows, however, an Auger spectrum of atomic boron and nitrogen.

(4) A 7.6 eV loss peak in the ELS of borazine adsorbed on Re(0001), diminished upon annealing to ~ 230 K and totally eliminated when annealed to ~ 600 K, is associated with chemisorbed borazine.

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