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6. AUTHOR(S)
D. W. Greve
Professor of Electrical and Computer Engineering

7. PERFORMING ORGANIZATION NAME(S) and ADDRESS(ES)
Carnegie Mellon University
Schenley Park
Pittsburgh, PA 15213

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13. ABSTRACT (*Maximum 200 words*)

Cubic boron nitride has proven to be a challenging semiconductor to grow epitaxially. In large part this is due to its chemical similiarity to diamond in that the hexagonal (or graphic) sp^2-bonded phase often forms at ambient conditions rather than the sp^3-bonded form. In this contract, we have investigated the possible formation of sp^3-bonded forms of BN on particularly suitable substrates. Both Ni(100) and AlN have been studied. A careful study of the Ni(100) surface has shown that the hexagonal phase is formed when diborane and ammonia react thermally (without ionic bombardment). Work on AlN substrates is less complete but so far no evidence for formation of the sp^3-bonded phase has emerged.

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Study of Surface Processes During Growth of Epitaxial Boron Nitride

Final Report
AFOSR Contract F49620-93-1-0387

June 1, 1994- May 31, 1997

D.W. Greve
Department of Electrical and Computer Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

Research Objectives

This contract is an Augmentation Award for Science and Engineering Research Training (AASERT) grant associated with a primary contract concerning the growth of epitaxial heterostructures for infrared detectors. The objective of this contract was to investigate the surface chemistry of various reactants suitable for growth of boron nitride, with particular emphasis on routes for synthesis of cubic material. The reactants which were explored were diborane (B_2H_6) and ammonia (NH_3) on various substrates The work has been performed in association with A.J. Gellman of the Chemical Engineering department at Carnegie Mellon University.

Summary of Research Performed

Considerable progress has been made in the last year in understanding the synthesis of BN on Ni(100) substrates. As noted in earlier reports, the start of work was delayed approximately a year due to difficulty in identifying an appropriate student, and consequently a no-cost extension was requested. Ryan Desrosiers joined the project in September, 1994 and completed his M.S. degree in May of this year. He has chosen to accept a position with the TRW Corp. in California. Charmaine Chan joined the project in June, 1996 and continued the work until the end of the contract date. There was a shift in emphasis when Charmaine Chan joined the project in order to investigate surface chemistry on a different substrate, AlN. Thus the summary below is divided into work performed by the two different students.

Research on Ni(100) substrates (1994-1996)

The objectives of this project were to study the initial stages of growth of boron nitride on nearly lattice-matched single- crystal metallic surfaces. We wished to determine whether any purely chemical route exists for the synthesis of cubic boron nitride. Initially our work was motivated by the near-lattice match (~2.5% mismatch) between cubic boron nitride and various single-crystal metallic surfaces, especially Ni(100). Additional encouragement came from two sets of recent publications, to wit:

1. A study of hot filament, plasma assisted CVD of BN showed that only the cubic phase is grown on polycrystalline nickel substrates, while mixed growth of cubic and hexagonal phases is seen on substrates such as silicon [1,2].

2. Observation that oriented diamond films could be grown by hot filament CVD on Ni(111) and Ni(100) substrates without graphite formation [3]. These results were attributed to formation of a molten Ni-C-H surface layer on oriented metastable Ni_4C nucleated on the surface [4].

It should be noted that the boron nitride results have met with some skepticism by researchers in the field. Nevertheless, these publications provided strong motivation for study of the initial surface reactions on metallic surfaces.

Details of our results to date on surface reactions during BN growth have been presented at three conferences [5-8] and three journal articles [9-11]. Briefly, the main results as follows:

1. When diborane is adsorbed on the Ni(100) surface at low temperature, some desorbs molecularly at 130 K. The remaining diborane decomposes on the Ni(100) with the desorption of hydrogen complete by 500 K.

2. Boron on the surface forms an Ni_2B phase between 700 and 900 K. At high temperatures, boron dissolves into the bulk of the crystal, with essentially no boron detectable at 1000 K.

3. When NH_3 and B_2H_6 are co-adsorbed on the Ni(100) surface at low temperatures, subsequent heating reveals changes in the hydrogen desorption spectrum and X-ray photoelectron (XPS) spectra. These changes indicate that a BN phase forms on the surface with submonolayer coverage. BN remains on the surface up to temperatures of about 1200 K.

4. Higher coverages of BN can be created by simultaneous exposure of the Ni(100) surface to NH_3 and B_2H_6 at high substrate temperatures (800- 950 K). Figure 1 below shows the XPS spectra observed after dosing at various temperatures. Growth is still limited to about a monolayer. These overlayers exhibited a (1x7) Low Energy Electron Diffraction (LEED) pattern which can be rationalized if the overlayer is hexagonal BN. This also is consistent with the near-zero growth rates after the first monolayer, as h-BN would not have any strong bonds protruding from the substrate.

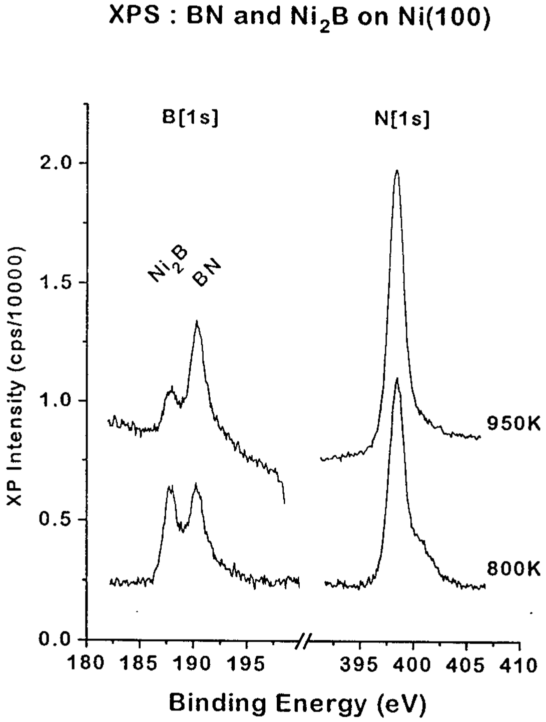

Figure 1. XP spectra observed after exposing the Ni(100) surface to NH_3 and B_2H_6 at various temperatures. BN has peaks clearly distinguishable from peaks associated with N and B bonded to nickel.

Collaborations with M. Skowronski of the Department of Materials Science and Engineering were also quite fruitful. His AFOSR-funded project [12] is directed at the growth of lattice-matched AlGaBN on SiC substrates. The two major results arising from this interaction are as follows:

1. BN overlayers with somewhat greater thickness were grown on prepared Ni(100) substrates by MOCVD using trimethylboron and ammonia as reactants. (The discovery that BN-coated nickel was passivated in air made this experiment possible). Approximately 10 ML of BN were grown, indicating that the growth rate of BN is small but not zero. XPS measurements on these layers show the π^* plasmon peak, confirming the identification of the overlayer as h-BN.

2. Growth of both AlBN and GaBN were performed by MOCVD. In the growth of GaBN, high boron concentrations cause the growth rate to go to essentially zero. XPS was used to verify the existence of boron in films grown below this threshold and tp verify that it was bonded to nitrogen as opposed to being present as elemental boron. These results have been submitted for conference presentation [13] and will appear in a journal article [14]. Surprisingly, other measurements provide evidence that under some conditions a BN phase appears which is sp^3-bonded. The explanation for the growth of sp^3-bonded BN in MOCVD but not on Ni(100) is still unclear. Possibilities include stabilization of the BN phase by incorporation of aluminum; the known catalytic effect of AlN on c-BN growth [15]; and high compressive stresses during growth.

Studies on AlN surfaces (1996-1997)

For the remaining contract period, we had identified two possible areas of investigation. One possibility was to pretreat the Ni(100) surface in order to obtain an Ni_4C surface layer, which would then provide a nucleation layer for c-BN. The second possibility was to follow up on the observation of an sp^3-bonded phase during AlBN growth by attempting to grow c-BN on AlN substrates. A summary of the work completed is presented below.

Since Ni_4C has been implicated as an importance surface phase in the growth of diamond on Ni surfaces [4] it was postulated that it might also serves to nucleate cubic BN growth (C-BN and diamond have similar geometric and electronic structures). Ni_4C films were grown from 2-butyne quite readily on the Ni(100) surface. Exposure to the reactant mixture of NH_3 and B_2H_6, however, revealed little reactivity and no evidence for the formation of BN.

AlN epitaxial layers approximately 1-2 μm thick grown by MOCVD were provided by Prof. Skowronski. The layers were grown on SiC substrates instead of sapphire in order to provide electrical conductivity which is desirable to prevent charging during surface science measurements. AlN MOCVD layers grown under similar conditions exhibit smooth surfaces with atomic steps by AFM indicating a high-quality ordered surface.

Our objectives were to (1) develop techniques for preparing AlN surfaces; and (2) to investigate the possibility of the development of sp^3-bonded BN phases on this surface. This work was motivated partially by our observation of sp^3-bonded BN during our MOCVD studies [13,14]. An sp^3-bonded phase has also been reported in MOCVD growth by one other group [16]. In addition, AlN is known to have a catalytic effect on c-BN growth [15].

1. AlN samples were mounted onto a Ta foil using a conducting, high temperature adhesive. This allowed heating to the temperatures needed to clean the sample surface (~1200K) and at the same time allowed study of the surface using XPS. The primary contaminant on the surface was oxygen, presumably in the form of Al_2O_3 generated by exposure to air. Oxygen was removed from the surface using cycles of Ar^+ bombardment (1.7 keV) and annealing to 1200K.

2. Two types of experiments were performed in order to attempt to grow BN on the AlN surface: exposure to B_2H_6 at high temperature, and exposure to a mixture of NH_3 and B_2H_6 at high temperature. Figure 2 illustrates the results of experiments in which the surface was exposed to B_2H_6 at 950K. The two peaks in XP spectrum a) are of the B[1s] region and are believed to arise from the presence of BN (192.5 eV) and some form of aluminum boride (189 eV). Subsequent exposure of this surface to NH_3 at 950K causes the reaction of the aluminum boride to BN and AlN (spectrum b).

Simultaneous exposure of the AlN surface to a mixture of NH_3 and B_2H_6 results in the formation of a layer of BN at the surface. Figure 3 shows the B[1s] region of the XP spectrum after 10 minute (a) and 30 minute (b) exposures ($P_{NH3} = 10^{-7}$ Torr, $P_{B2H6} = 10^{-8}$ Torr, 1050K). The single peak is due to B in the BN film. The fact that the amount of BN has saturated and cannot be increases suggests that it is in the form of h-BN rather than c-BN although there is no direct evidence yet for the structure of this surface film.

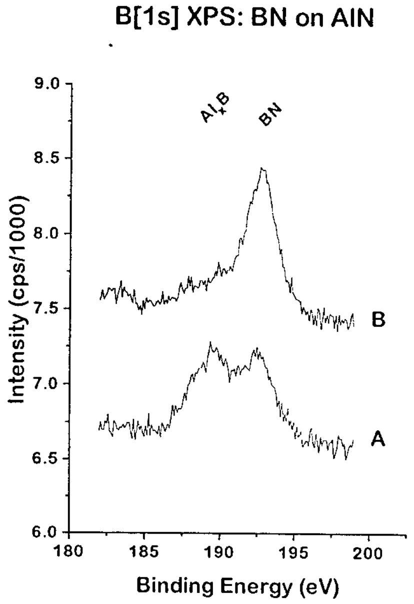

Fig. 2. a) XPS of the B[1s] level after exposure of the AlN surface to B_2H_6 at 10^{-8} Torr for 30 min. at 950K. The two species are assigned to an aluminum boride and BN. b) Exosure of this surface to NH_3 results in the conversion of the aluminum boride to BN.

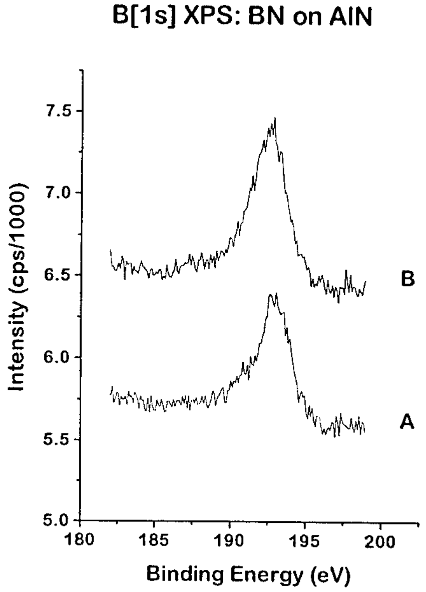

Fig. 3. a) XPS of the B[1s] level after exposure of the AlN surface to a mixture of 10^{-8} Torr B_2H_6 and 10^{-7} Torr NH_3 at 1050K for 10 min. b) Further exposure of the same surface to the same mixture for an additional 20 min. No further increase in the BN coverage is observed.

Summary

The investigations conducted during the course of this program have identified new surface reactions producing films of BN on the surfaces of Ni and AlN. The evidence to date suggests that these films are hexagonal in structure although that remains to b confirmed by STM experiments that are being conducted at the moment. Although the ultimate goal of the program is the synthesis of BN in its cubic form it is clear from this investigation that the Ni and AlN surfaces activate reactions between NH_3 and B_2H_6 which would not otherwise occur. Control of reaction conditions may be the key to selective generation of the cubic over the hexagonal phase.

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8. "Nucleation of Boron Nitride on Ni(100) Surfaces," R.M. Desrosiers, D.W. Greve, and A. J. Gellman, Symposium A. E-MRS Spring Meeting, Strasbourg, France, June, 1996).
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Conference Presentations

"Decomposition of Diborane and Ammonia on Ni(100) Surfaces," R.M. Desrosiers, A.J. Gellman, D.W. Greve, and C.F. McFadden, Electrochemical Society Spring Meeting, (Reno, NV, May, 1995).

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"Nucleation of Boron Nitride on Ni(100) Surfaces," R.M. Desrosiers, D.W. Greve, and A. J. Gellman, (*Thin Solid Films*, in press).

"Decomposition of B2H6 on Ni(100)," R.M. Desrosiers, D.W. Greve, and A.J. Gellman, (*J. Vac. Sci. Technol. A*, in press).

"Nucleation of boron nitride thin films on Ni(100)," R.M. Desrosiers, D.W. Greve, and A.J. Gellman, (*Surface Science*, in press).

"Growth of AlBN solid solutions by organometallic vapor phase epitaxy", A.Y. Polyakov, M. Shin, W. Qian, M. Skowronski, D.W. Greve, R.G. Wilson, (*J. Appl. Phys.*, in press).

Personnel

Faculty

D.W. Greve, Professor ECE, principal investigator

A.J. Gellman, Professor Chem. Eng., associate investigator

Graduate Students (August, 1994- May, 1997)

Ryan Desrosiers
(M.S. student ECE, supported by AASERT grant, US citizen)

Charmaine Chan
(M.S. student Chem. Eng., supported by AASERT grant, US citizen)

Interactions

M. Skowronski, Materials Science and Engineering, Carnegie Mellon (supply of AlN/ silicon carbide substrates).

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Nucleation of boron nitride on Ni(100) surfaces

R.M. Desrosiers[a], D.W. Greve[a,*], A.J. Gellman[b]

[a]*Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA*
[b]*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

Abstract

We report studies of the formation of boron nitride by decomposition of diborane (B_2H_6) and ammonia (NH_3) on the Ni(100) surface. Diborane decomposes on the Ni(100) surface and is accompanied by the desorption of hydrogen, with the decomposition complete at 500 K. In the absence of ammonia, the boron on the surface reacts with the substrate to form a Ni_2B phase. Boron nitride can be formed by heating ammonia and diborane multilayers from 100 K or by coadsorption of the two gases at temperatures above 800 K. The former procedure produces disordered, submonolayer coverages while the latter procedure produces ordered overlayers. A low energy electron difraction (LEED) pattern characteristic of an overlayer (1 × 7) is observed after growth at 950 K. This surface reconstruction appears to be consistent with the formation of a strained hexagonal boron nitride overlayer.

Keywords: Boron nitride; Adsorbtion; Films

1. Introduction

Cubic boron nitride (c-BN) is of considerable interest because it is a large bandgap semiconductor ($E_G = 6.3$ eV) which can be doped both n and p type. Like diamond, it is generally believed that formation of c-BN is only favored under conditions of high temperature and high pressure [1]. Epitaxial growth of c-BN has been hampered by the lack of a suitable lattice-matched substrate. Polycrystalline c-BN films can be grown on a variety of substrates but so far only under conditions of high energy ion bombardment [2]. The resulting films exhibit high compressive strain and a layered structure is observed with amorphous and hexagonal boron nitride at the initial growth interface followed by a transition to predominantly c-BN in the upper part of the film.

In this paper, we explore the possibility of the nucleation of epitaxial layers of c-BN directly on Ni(100) crystals. Ni(100) ($a = 3.50$ Å) is an excellent lattice match to c-BN ($a = 3.61$ Å) and an epitaxial c-BN film grown on this substrate would be compressively strained, which is thought to be favorable for the formation of c-BN. Ni(100) has been used as a substrate for c-BN growth using hot filament assisted plasma enhanced CVD [3] and ion assisted deposition techniques [4,5] and in one case was reported to yield nearly pure c-BN layers [3]. Finally, nickel is known to act as a catalyst in diamond synthesis [6]. Our approach is to use surface science techniques to explore the surface reactions of ammonia (NH_3) and diborane (B_2H_6) on the Ni(100) surface.

We first report studies of the decomposition of diborane on Ni(100). We then describe the results of coadsorption experiments in which diborane and ammonia react on the Ni(100) surface.

2. Experimental method

The experiments were performed in an ion pumped ultra-high vacuum chamber with a base pressure below 1.0×10^{-10} Torr. The chamber is equipped with an Extrel quadrupole mass spectrometer for thermal desorption spectrometry (TDS) experiments and a 150° hemispherical energy analyzer for X-ray photoelectron spectrometry (XPS) measurements. In addition, the chamber is equipped with electron optics for low energy electron diffraction (LEED) measurements. Diborane, ammonia and deuterated ammonia (ND_3) were introduced into the chamber through leak valves terminated with micro-capillary arrays. Doses reported are in effec-

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[*] Corresponding author.

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tive Langmuir exposures (1 L $= 10^{-6}$ Torr s^{-1}) taking account of the enhancement factor due to the microcapillary arrays. Before beginning experiments, the crystal was cleaned by argon sputtering followed by annealing at 1200 K.

3. Diborane decomposition on Ni(100)

First, TDS experiments were performed in order to determine the decomposition reactions of diborane. B_2H_6 was adsorbed onto the Ni(100) surface at 85 K, followed by temperature ramping at a rate of 2 K s^{-1}. Molecular diborane desorption was studied by monitoring the signal at $m/q = 27$ ($B_2H_5^+$). For small exposures (< 0.8 l), a broad feature was observed with a peak desorption temperature of 130 K, with a peak area which increases with exposure. For higher exposure (up to 2.5 l) an additional peak at 100 K appears and grows strongly with increasing exposure. These two peaks at 100 and 130 K were attributed to multilayer and monolayer desorption, respectively. The boron peak at $m/q = 11$ shows a similar behavior for exposures less than 2.5 L and there is no desorption of other boron-containing species up to at least 1000 K.

Fig. 1 shows the TDS spectra obtained for $m/q = 2$ (H_2^+) following B_2H_6 adsorption at 85 K. For low exposures, there is a single peak at 350 K. This peak shifts to a lower temperature and its area increases with increasing exposure. With increasing exposure additional peaks appear at 180 and 250 K. The total quantity of desorbed hydrogen saturates at 0.8 L; this exposure also corresponds to saturation of the $m/q = 27$ peak at 130 K.

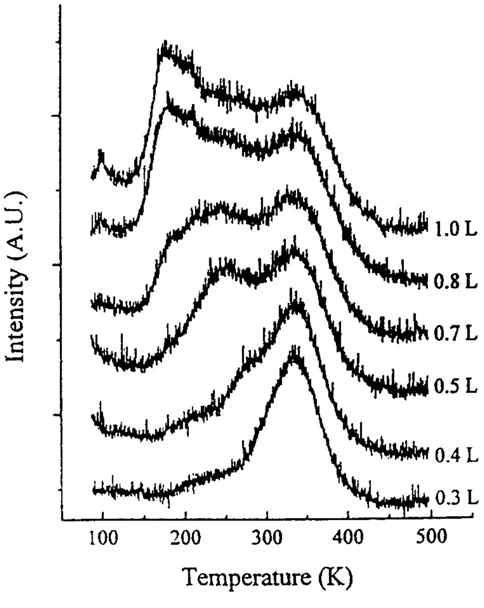

Fig. 1. H_2 ($m/q = 2$) thermal desorption spectra obtained vollowing various exposures of Ni(100) to B_2H_6 at 85 K (heating rate 2 K s^{-1}).

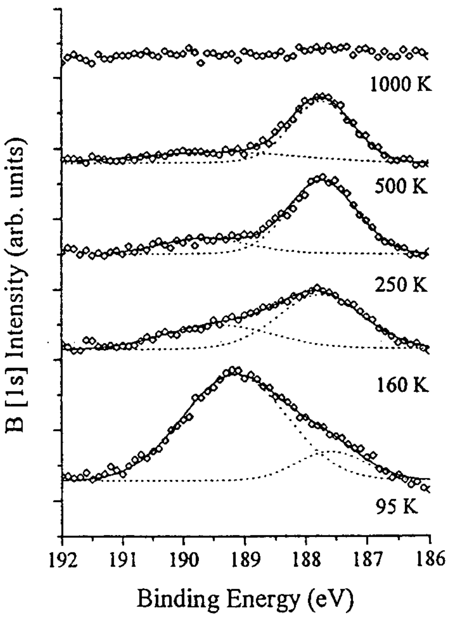

Fig. 2. X-ray photoelectron spectra for 15 L B_2H_6 adsorbed onto Ni(100) at 95 K. B[1s] spectra were taken after heating the crystal to the indicated temperature for several s.

Desorption of hydrogen indicates that diborane is decomposing on the surface. As no desorption of boron-containing species was observed above 130 K, it is evident that the only desorption product is hydrogen and that boron remains on the surface. (For larger exposures, above 2.5 L, the situation becomes more complex and higher boranes are produced [7]). The peak at 350 K is attributed to hydrogen desorbing from sites on the Ni(100) surface; the shift in this peak position with increasing exposure is consistent with the known second-order desorption kinetics of hydrogen on Ni(100) [8].

The quantity and bonding state of the boron remaining on the surface was monitored using XPS. Fig. 2 shows the observed XPS spectra after adsorption of 15 L of diborane at 95 K followed by heating cycles to 160, 250, 500 and 1000 K. After adsorption at 95 K, two peaks are visible at 187.6 and 189.2 eV. Following Fryberger et al. [9], who studied diborane condensed onto Mo(100), we attribute these peaks to B bonded to the metal surface and B_2H_6 or its fragments, respectively. As the temperature is increased to 500 K, the peak at 187.6 eV grows while the peak at 189.2 eV shrinks, consistent with the decomposition of B_2H_6 and BH_x fragments and the desorption of hydrogen. At 1000 K, the boron peak entirely disappears. As there is no desorption of boron observed in TDS, this indicates that boron has dissolved into the bulk.

The Ni–B phase diagram [10] indicates the existence a number of possible solid phases (NiB, Ni_2B, Ni_3B and Ni_4B_3) and thus it is possible that a crystalline nickel boride layer can be created on the surface, similar to the case of diamond growth. In order to explore this possibility, boron was deposited onto the Ni(100) surface by a 150 L exposure at a temperature of 500 K. Then, the ratio between the boron and nickel XPS signals $I_{B[1s]}/I_{Ni[2p_{3/2}]}$ was measured as a function of temperature. This ratio decreased between 500 and 700 K, was approximately constant from 700 to 900 K and then decreased rapidly above 900 K. This behavior is consistent with the formation of a thin layer of a single phase. The measured ratio $I_{B[1s]}/I_{Ni[2p_{3/2}]}$ at 800 K was compared with the measured value of this ratio for samples of three different nickel boride phases (NiB, Ni_2B and Ni_3B). The results suggest that the phase formed is Ni_2B [7]. This phase is unfortunately not a lattice match to Ni and c-BN (Ni_2B is tetragonal with $a = 4.989$ and $c = 4.246$ Å [10]). This is in contrast to the situation with diamond growth, where Ni_4C forms which is a good lattice match to diamond [11].

These results indicate that boron or BH_x fragments form on the Ni(100) surface at relatively low temperatures and well below the temperature at which boron diffuses into the bulk. So one possible approach for growth of boron nitride is the coadsorption of diborane and ammonia at low temperature followed by heating. Alternatively, the substrate can be simultaneously exposed to a flux of diborane and ammonia at a temperature low enough to limit the diffusion of boron into the bulk. We will discuss the results obtained from these two approaches below.

4. Growth and characterization of boron nitride overlayers

We first consider the consequences of adsorbing diborane and ammonia at low temperatures followed by heating. This approach was explored by Rodriguez et al. [12] for the Ru(0001) surface; they observed the formation of BN although the phase was not identified. In our experiments the Ni(100) sample was cooled below 100 K and then exposed to 5 L of ND_3 followed by 15 L of B_2H_6. Then a TPD experiment was performed, monitoring $m/q = 2$ (H_2^+), 3 (HD^+), 4 (D_2^+), 27 ($B_2H_5^+$) and 20 (ND_3^+). The following features were observed [13]:

(1) Large peaks for $m/q = 2$, 3, 4, 20 and 27 at 114 K. This is attributed to molecular desorption of ND_3 and B_2H_6.
(2) A peak at 500 K for $m/q = 4$. This indicates that some ND_3 has reacted with diborane, since it is known that NH_3 does not decompose but rather desorbs molecularly from Ni surfaces [14].
(3) For $m/q = 2$, no peaks were observed at 350 and 410 K, in contrast to the TPD results discussed above for diborane alone on Ni(100). This is also consistent with a reaction between B_2H_6 and ND_3.

XPS experiments were performed in order to study further the reaction between B_2H_6 and NH_3. Fig. 3 shows the observed XPS spectra after dosing a crystal at 100 K with 5 L NH_3 followed by 15 L B_2H_6 and annealing to various temperatures. At 100 K a strong N[1s] peak is observed at 400.3 eV, which is consistent with that previously observed for NH_3 multilayers on Ni(110) [15]. The B[1s] spectrum shows a peak at 189.7 eV with a shoulder at lower energy. This suggests that there is less diborane than ammonia on the surface and that it is predominantly B_2H_6 or BH_x with a smaller amount of B bound to nickel. Heating to 250 K results in desorption of the NH_3 multilayers while the 189.7 eV boron peak shrinks and the lower energy peak grows. At 600 K the nitrogen peak has shifted to 397.5 eV, while the boron spectrum is nearly unchanged. At 1000 K, the N[1s] peak shifts slightly to 398.5 eV and the boron peak attributed to boron bonded to nickel is reduced in intensity. A possible mechanism for the surface reaction which is consistent with these observations will be reported elsewhere [13]. Comparing the peak intensities with those obtained with known surface coverages of B and N, we obtain coverages of 0.3 ML of boron and 0.4 ML of nitrogen [13].

It is known from previous work that N desorbs from nickel below 800 K [14] and that boron diffuses into the crystal above 800 K [7]. So the persistence of B and N on the surface at 1000 K is evidence for formation of BN. The peak positions at 1000 K also agree well with those for c-BN and h-BN films [12,16–19]. The forma-

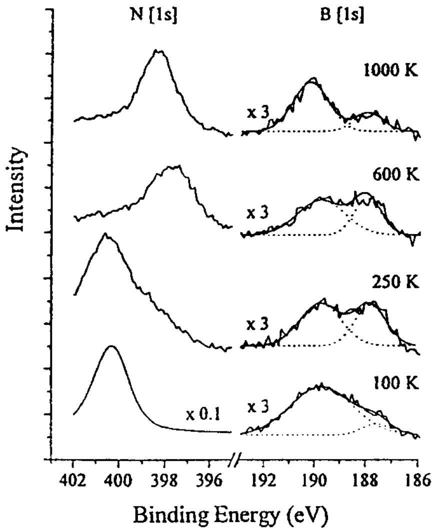

Fig. 3. N[1s] and B[1s] X-ray photoelectron spectra from the coadsorption of 5 L ND_3 followed by 15 L B_2H_6 on Ni(100) at 100 K. Spectra were taken after heating the sample to 250, 600 and 1000 K.

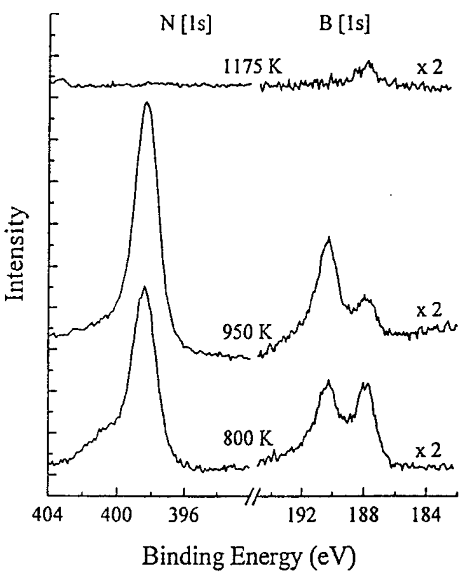

Fig. 4. N[1s] and B[1s] X-ray photoelectron spectra obtained after BN growth on Ni(100) at various substrate temperatures. Growth conditions were: 1 × 10^{-7} Torr NH_3, 1 × 10^{-8} Torr B_2H_6, and the growth time was 30 min.

tion of BN in similar experiments was previously observed on Ru(0001) by Rodriguez et al. [12], although the phase was not determined.

In order to obtain higher surface coverages and possibly to permit unambiguous identification of the BN phase, we also performed growth by coadsorption at higher temperatures. In these experiments, the Ni(100) crystal was exposed to 10^{-7} Torr of NH_3 and 10^{-8} Torr of B_2H_6 for 30 min. The temperature range explored was 800–1175 K.

The resulting XPS spectra are presented in Fig. 4. A boron peak at approximately 187.8 eV is visible in all spectra and decreases monotonically with temperature. This peak was attributed to nickel boride and is consistent with more rapid diffusion of boron into the substrate at higher temperatures. The position of the remaining boron peak and the nitrogen peak are consistent with the formation of either c-BN or h-BN. The greatest amount of BN is formed at 900 K; BN appears to decompose at approximately 1200 K. The amount formed at 950 K corresponds to approximately 1.0 ML B and 1.1 ML N. Growth for longer times (up to 120 min) showed essentially no change in the BN yield.

Growth at 950 K yielded a sharp (1 × 7) LEED pattern, indicating a well ordered BN layer. The LEED pattern became sharper upon annealing at 1100 K and disappeared entirely after annealing at 1200 K, upon which the (1 × 1) LEED pattern characteristic of a clean Ni(100) surface was observed. The (1 × 7) LEED pattern is difficult to rationalize for a c-BN overlayer. However, a slightly strained h-BN layer can be arranged on the Ni(100) surface to yield this periodicity. The identification of the overlayer as h-BN is also supported by the extremely low growth rates after the first monolayer is formed.

5. Conclusions

The reactions of B_2H_6 and NH_3 with the Ni(100) surface have been studied. B_2H_6 readily decomposes on the Ni(100) surface to yield a boron overlayer. Boron forms a Ni_2B phase at intermediate temperatures and diffuses into the crystal at 1000 K. BN overlayers can be formed either by reactions between condensed layers of B_2H_6 and NH_3 or by simultaneous exposure to B_2H_6 and NH_3 at temperatures of about 950 K. After growth of approximately 1 ML, the growth rate becomes quite slow. The overlayer formed consists of ordered h-BN.

Acknowledgements

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Decomposition of B_2H_6 on Ni(100)

Ryan M. Desrosiers and David W. Greve
Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Andrew J. Gellman
Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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TPD later?

The decomposition of diborane (B_2H_6) has been studied on the Ni(100) surface by means of thermal desorption spectrometry (TDS), x-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED). At low gas exposures, decomposed B_2H_6 on the Ni(100) surface at low temperatures produces several peaks in the H_2 TDS spectra. At high gas exposures, B_4H_{10} was observed desorbing from the surface. The TDS spectra and XPS results for low gas exposures indicate that heating to 500 K results in complete decomposition of B_2H_6, leaving B bonded to the Ni(100) surface. Heating a thick boron film to 700 K results in a significant shift in the B $[1s]$ and Ni $[2p_{3/2}]$ XPS peak positions, indicating that adsorbed B reacts with Ni(100) to form a nickel boride phase. This nickel boride phase is stable on the surface at temperatures up to 900 K. Nickel boride standards (NiB, Ni_2B, Ni_3B) were used for comparison with the surface nickel boride phase. XPS analysis of the standards led to the determination that the phase forming on the surface at 700 K was Ni_2B. As the temperature is increased above 900 K, XPS results indicate that the boron diffuses rapidly into the bulk. It has also been found that high-temperature annealing in the presence of B_2H_6 results in the formation of a sharp (3×3) LEED pattern produced by 2/9 ML of B on the Ni(100) surface. © *1997 American Vacuum Society.* [S0734-2101(97)02904-7]

I. INTRODUCTION

Nickel has long been known to serve as a catalyst for high-pressure; high-temperature synthesis of diamond and cubic boron nitride (*c*-BN).[1,2] Recently, however, there has been interest in the use of single-crystal nickel as a substrate FoR ~~in~~ low-pressure epitaxial growth of diamond and *c*-BN.[3–6] This interest stems primarily from the excellent lattice match between the Ni(100) surface ($a_{\mathrm{Ni}}=3.52$ Å) and the (100) planes of diamond ($a_{\mathrm{dia}}=3.57$ Å) and *c*-BN ($a_{\mathrm{BN}}=3.62$ Å).

The growth of semiconductor materials on metal substrates presents new and interesting problems not previously encountered with epitaxial growth on Si, III–V, and II–IV surfaces. For instance, in the initial stages of growth, one must consider the possibility of the formation of compounds other than the desired semiconductor. The compound formed may or may not retain the desired lattice match. In the most desirable case, the compound will act as a lattice-matched buffer layer between the substrate and the desired thin film. As an example, in the growth of diamond on Ni(100), it has been shown that high-temperature annealing during the initial stages of growth leads to the formation of a Ni_4C buffer layer.[7] This Ni_4C buffer layer is lattice matched to diamond and has been found to play an important role in diamond nucleation.

Diborane (B_2H_6) is a common group III reactant in chemical-vapor deposition of *c*-BN films.[4,8] Thus, in order to effectively grow *c*-BN on Ni surfaces, a sound understanding of the interaction of B_2H_6 with Ni(100) is desired. Of the few studies of the surface chemistry of B_2H_6 on metal surfaces, only refractory metals such as Ru(0001) and Mo(100) have been investigated.[9,10] In this article, we present the results of our study of the surface chemistry of B_2H_6 on Ni(100). The results indicate that B_2H_6 interacts with the Ni(100) surface in a variety of ways. Condensed multilayers of B_2H_6 adsorbed onto the Ni(100) surface at low temperatures appear to react to form a higher molecular weight borane, B_4H_{10}. On the other hand, dosing B_2H_6 at high temperatures leads to the formation of a nickel boride compound, Ni_2B, on the surface. These results indicate that growth of BN films on Ni(100) using B_2H_6 as the group III reactant may be hampered by competing reactions between the substrate Ni atoms and the group III reactant.

II. EXPERIMENT

The experiments described in this article were performed in an ion-pumped stainless steel ultrahigh vacuum (UHV) chamber with a base pressure below 1.0×10^{-10} Torr. The chamber is equipped with an Extrel quadrupole mass spectrometer for thermal desorption spectrometry (TDS) experiments and a 150° hemispherical electron energy analyzer for x-ray photoelectron spectrometry (XPS) measurements. In addition, the chamber is equipped with electron optics for low energy electron diffraction (LEED), a 5 keV argon ion gun for secondary ion mass spectrometry (SIMS), and leak valves for the introduction of gases into the chamber.

The Ni(100) crystal was obtained from the Monocrystals Company and was electromechanically polished to a mirror finish. The crystal was mounted in the chamber by spot welding it between two tantalum wires attached to a sample holder on a UHV manipulator. The sample manipulator was equipped with a liquid nitrogen reservoir for cooling purposes and a chromel–alumel thermocouple for temperature measurements. With this system, the crystal could be cooled to 85 K, and heated to 1200 K at a constant rate of up to 10 K/s. Prior to experiments, the sample surface was prepared by performing 20 min sputter and 1200 K anneal cycles until the coverage of surface contaminants (oxygen, sulfur, carbon, chlorine) fell below the detection limit of the XPS system. Typically, 6 h of sputtering at 5 μA/cm^2 crystal current density was required to clean the surface after exposure to atmosphere.

X-ray photoelectron spectra were recorded with a Fisons CLAM II hemispherical energy analyzer operating in constant analyzer energy mode with a pass energy of 35 eV. Under these conditions, the analyzer has an energy resolution of better than 0.7 eV. The x-ray source used was an 800 W Fisons XR3E2-HP fitted with an Al anode ($h\nu=1486.6$ eV). Prior to cleaning the crystal surface, the x-ray source was degassed such that its operation did not raise the base pressure above 3×10^{-10} Torr. The source-to-analyzer angle for this XPS system is fixed at 45°, however, the sample could be rotated to measure XP spectra at different takeoff angles. Unless otherwise stated in this article, XPS measurements were acquired for electron emission normal to the crystal surface.

The B_2H_6 gas used for this study was obtained from Voltaix and was kept in cold storage to prevent thermal decomposition of B_2H_6 in the canister. Gas exposures in this article are given in terms of langmuirs ($1\ \text{L}=10^{-6}$ Torr s). The gas was introduced into the UHV system using leak valves terminated with microcapillary arrays. During gas exposures, the sample was placed 2 cm from the end of the doser. These capillary arrays led to an enhancement factor of ~5 for gas exposures. This enhancement factor was taken into account when quoting gas exposures in this article.

Several nickel boride compounds were obtained for use as standards for comparison to the nickel boride phases formed by the reaction of B_2H_6 with the Ni(100) surface. NiB and Ni_2B powders (99% pure) were obtained from Alpha Aesar, and Ni_3B powder (99% pure) was obtained from All-Chemie Ltd. The powders were pressed into indium foil, which was in turn mounted onto a piece of tantalum foil spot welded to a sample holder. By mounting the powders in this manner, the samples could be cleaned by Ar ion sputtering and repositioned in the chamber to perform XPS measurements. Heating was not possible due to the low melting point of In. While cleaning the powder samples with 5 keV Ar ions, SIMS was performed to monitor the sputtered species. XPS and SIMS measurements indicated that the primary surface contaminant was oxygen in the form of nickel and boron oxides. The samples were considered clean when the ratio of the O ($m/q=16$) to the Ni ($m/q=58$) signal reached a minimum. This cleaning process typically required 4 h of sputtering with an ion flux of 5 μA/cm^2. To determine if any preferential sputtering was occurring that would leave the surface concentrations of the powders nonstoichiometric, Xe and He gases were used in addition to Ar to sputter the samples for several hours. Subsequent XPS analysis of the powder composition indicated no differences in the Ni:B ratio, which could be attributed to preferential sputtering of Ni or B. Thus, Ar ion sputtering was considered adequate for sample cleaning and was used for all nickel boride standards used in this study.

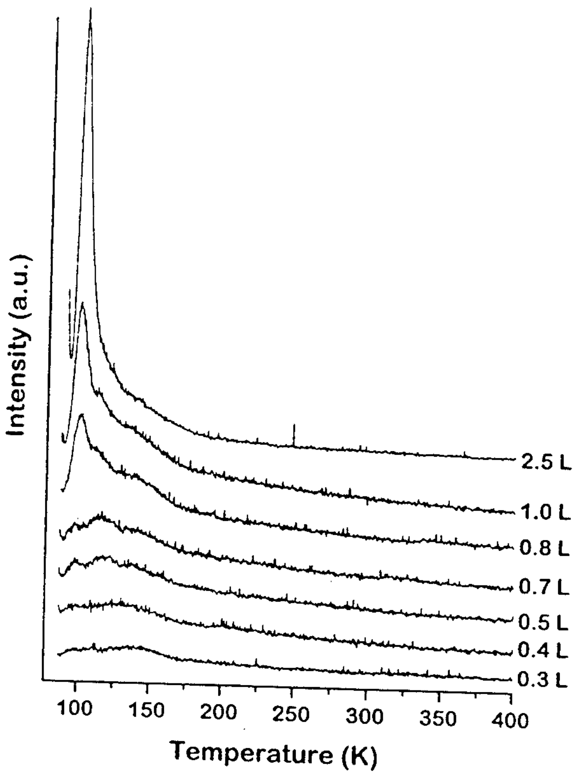

FIG. 1. Thermal desorption spectra ($m/q=27$, $B_2H_5^+$) obtained following increasing exposures of Ni(100) to B_2H_6 at 85 K. (Heating rate=1 K/s).

III. RESULTS

A. Decomposition of B_2H_6 on Ni(100) at low temperatures

A series of TDS experiments were performed to study any decomposition reactions of B_2H_6 occurring on the Ni(100) surface. Figure 1 shows the resulting $m/q=27$ ($B_2H_5^+$) thermal desorption spectra for different exposures of B_2H_6 adsorbed with the sample at 85 K. For these thermal desorption spectra, $m/q=27$ was monitored for thermal desorption of B_2H_6 rather than the parent mass $m/q=28$ ($B_2H_6^+$). This procedure was employed to prevent any ambiguity in identifying B_2H_6 against a background containing small amounts of CO. As the B_2H_6 exposure is increased from 0.3 to 2.5 L, two desorption features can be identified in Fig. 1. At low exposures, less than 0.8 L, one broad feature appears with a peak desorption temperature of about 130 K. The area of this feature increases with exposure and saturates between 0.7 and 0.8 L. For exposures below 0.8 L, a fraction of the B_2H_6 decomposes to yield hydrogen, which then desorbs as shown below. The second feature in Fig. 1 appears at exposures greater than 0.8 L, has a fixed peak desorption temperature of 100 K, and increases until the exposure reaches 2.5 L.

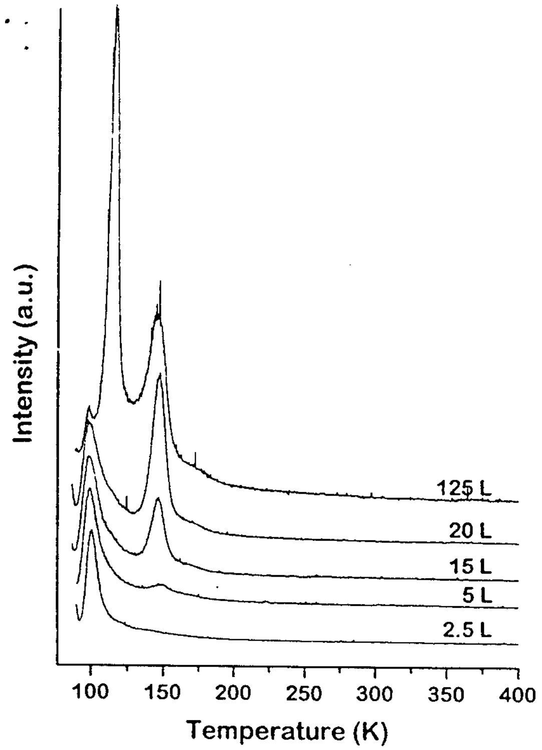

FIG. 2. Thermal desorption spectra ($m/q=11$, B^+) obtained following increasing exposures of Ni(100) to B_2H_6 at 85 K. (Heating rate = 1 K/s).

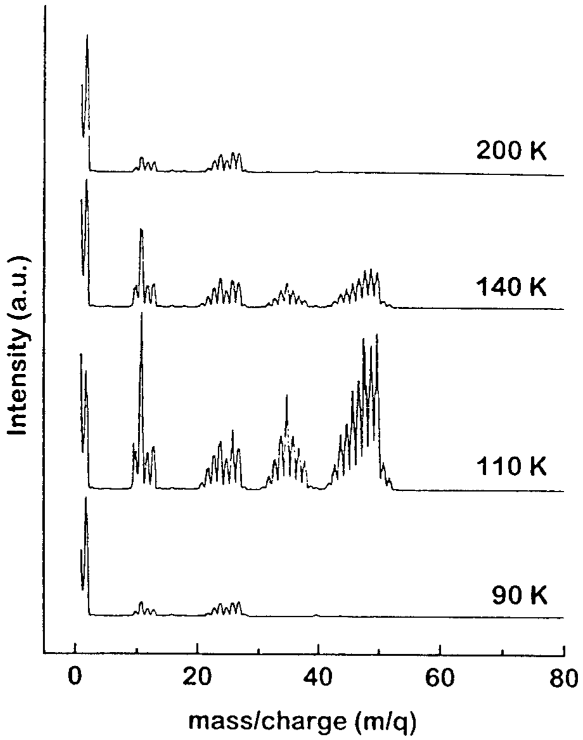

FIG. 3. Mass spectra for a 125 L exposure of B_2H_6 adsorbed on Ni(100) at 85 K followed by heating at 1 K/s. While the sample was heated, the spectra were acquired at 90, 110, 140, and 200 K. Each spectrum required 7 s to acquire.

For monolayer desorption, a peak temperature of 130 K is quite low compared to previous studies of B_2H_6 on refractory metals such as Mo(100)[9] ~~Ref. 9)~~ and Ru(0001).[10] On Ru(0001) and Mo(100), multilayer desorption was found to occur between 150 and 160 K, and the monolayer was found to desorb at around 300 K. The difference in the monolayer peak desorption temperature warranted an experiment to verify the accuracy of the temperature measurement system used in this study. In atmosphere, the temperature was measured with the sample placed in a liquid N_2 bath and with the sample placed in an ice water bath. The results of these two calibration points indicated an accuracy of ±2 K in the temperature measurement system.

In the course of the TDS experiments, it was found that as the B_2H_6 exposure is increased above 2.5 L, the 100 K peak present in Fig. 1 saturates. This is followed by the appearance of two new peaks at 115 and 147 K in the $m/q=11$ (B^+) thermal desorption spectra. Figure 2 shows the $m/q=11$ TD spectra for B_2H_6 exposures between 2.5 and 125 L. It can be seen that there are three peaks present in the thermal desorption spectra. The first peak is centered at 100 K and has an area that becomes saturated at B_2H_6 exposures above 2.5 L. The second peak is centered at 147 K, and has an area that becomes saturated at B_2H_6 exposures above 20 L. Finally, the third peak present in Fig. 2 is centered at 115 K, and it was found that its area increases without an observed limit as exposure is increased. A comparison of the peak height ratios of the $m/q=11$ and $m/q=27$ peaks at 100 K indicate that this peak is the result of B_2H_6 desorption and cracking in the mass spectrometer. However, the two peaks at 115 and 147 K, which appear in both the $m/q=11$ and $m/q=27$ spectra, do not match the cracking pattern of B_2H_6. For both peaks, the ratio of $m/q=11$ to $m/q=27$ (not shown in Fig. 1) is over twice the value observed for the cracking of pure B_2H_6 in the mass spectrometer.

In order to identify the compound desorbing from the surface at 115 and 147 K, the mass spectrometer used for the ~~temperature-programed desorption (TPD)~~ TDS experiment was used in residual gas analysis (RGA) mode rather than in single mass mode. At 85 K, 125 L B_2H_6 was exposed to the Ni(100) surface, and the sample was heated at 1 K/s from 90 to 400 K. At 90, 110, 140, and 200 K, the mass spectrometer was used to perform a RGA from 1 to 100 amu ~~in~~ of the desorbing species. The process of acquiring the RGA data takes 7 s, thus, the RGA spectra correspond to a temperature range of 7 K. Since the peaks at 115 and 147 K in Fig. 2 have a full width at half-maximum greater that 7 K, it is possible to take a "snap shot" RGA of the species desorbing from the surface. Figure 3 shows the RGA spectra resulting from this procedure. At 90 K, the RGA spectrum indicates the presence of B_2H_6 gas resulting from the large 125 L dose, along with a small amount of background gasses (CO_2, CO, H_2O, H_2) normally present in a UHV system. As the 90 K spectrum clearly shows, the cracking of B_2H_6 generates fragments ranging from $m/q=1$ (H^+) to $m/q=27$ ($B_2H_5^+$). At 110 K, the RGA spectrum indicates a new compound desorbing from the surface. The cracking pattern of this new

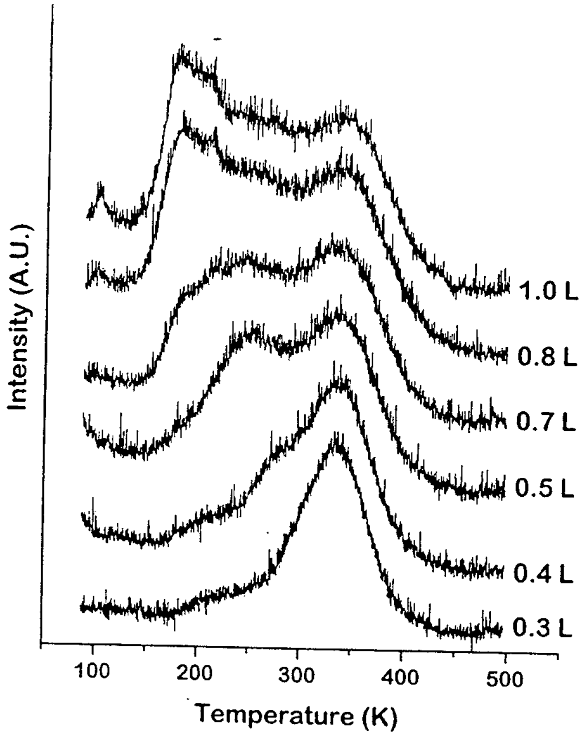

FIG. 4. Thermal desorption spectra ($m/q=2$, H_2^+) obtained following increasing exposures of Ni(100) to B_2H_6 at 85 K, (Heating rate=1 K/s).

compound contains masses ranging from $m/q=1$ to $m/q=53$. The RGA spectrum taken at 140 K contains the same cracking pattern as the 110 K spectrum although the intensity has decreased. Finally, at 200 K all boron containing species have desorbed from the surface, and the RGA spectrum is nearly identical to the spectrum taken at 90 K. These results suggest that the multilayers of B_2H_6 on the Ni(100) surface are reacting to form a new borohydride compound (B_4H_{10}), which has a mass greater than B_2H_6 and desorbs from the Ni(100) surface at 115 and 147 K. This B_2H_6 multilayer reaction was not observed previously in studies of B_2H_6 on Mo(100)[9] ~~(Ref. 9)~~ and Ru(0001)[10] ~~(Ref. 10)~~ surfaces, although these studies did not report B_2H_6 exposures above 8 L. The formation of this new borohydride will be discussed in Sec. IV of this article.

While the B_2H_6 TDS results indicate that there is no desorption of boron containing species at temperatures above 160 K, $m/q=2$ (H_2^+), thermal desorption spectra reveal several peaks at higher temperatures indicating that decomposition of B_2H_6 is occurring. Figure 4 shows the thermal desorption spectra for H_2 desorption following various exposures to B_2H_6. For exposures between 0.3 and 0.8 L, the spectra show three desorption features at 340, 250, and 180 K. At low exposures (below 0.4 L), there is one peak in the TDS with a desorption temperature of 350 K. This peak shifts to a slightly lower temperature (340 K) and the area becomes saturated as the B_2H_6 exposure is increased to 0.4 L. The peak location and second-order desorption kinetics of this feature are the same as those observed for hydrogen

hydrogen desorbing from sites directly on the Ni(100) surface. At 0.4 L, a new peak at 250 K begins to grow out of the 350 K peak, and at 0.7 L another desorption feature appears at 180 K. From Fig. 4, it is apparent that all three peaks are saturated at exposures above 0.8 L. The saturation exposure of 0.8 L coincides with the saturation of the 130 K $m/q=27$ peak presented in Fig. 1. The final peak in the H_2 TDS spectra occurs at 100 K and coincides with the large 100 K B_2H_6 desorption peak. As in the case of the 100 K $m/q=11$ peak in Fig. 2, this H_2 peak is consistent with B_2H_6 cracking in the mass spectrometer. The fact that H_2 TDS peaks appear at temperatures where no boron containing compounds are observed to desorb, indicates that the H_2 desorption is caused by a fraction of the B_2H_6 monolayer decomposing on the Ni(100) surface. This hypothesis is further supported by XPS data, which indicates that boron remains on the surface after TPD experiments.

Comparison of these H_2 TDS spectra to previous TDS studies of B_2H_6 on Ru(0001) reveals several similarities. Rodriguez *et al.*[10] reported two H_2 TDS desorption peaks at 280 and 380 K, which were attributed to the decomposition of the B_2H_6 monolayer and desorption of H_2 from the metal surface. However, Rodriguez *et al.* did not observe the 190 K low-temperature peak observed in our study.

In addition to the TDS experiments, XPS was used to study the decomposition of B_2H_6 on the Ni(100) surface. Figure 5 shows the B [1*s*] XP spectra for 15 L B_2H_6 exposed to the Ni(100) surface at 95 K, followed by heating cycles to 160, 250, 500, and 1000 K. Between heating cycles, the sample was cooled to <100 K before taking the XP spectrum. The XP spectrum of the condensed B_2H_6 at 95 K is composed of two peaks at 187.6 and 189.2 eV. The higher binding energy peak is associated with molecular B_2H_6 and partially decomposed B_2H_6 fragments while the lower binding energy peak is attributed to boron bonded to the Ni(100) surface. These peak locations are close to the values of 187.7 and 189.6 eV reported for B bonded to Mo and B_2H_6 multilayers condensed onto Mo(100).[9] The existence of the two peaks at 95 K is strong evidence for the fact that at low temperatures, a fraction of the B_2H_6 on the surface immediately decomposes, leaving either B or BH_x species bonded to Ni(100). As the surface is heated from 95 to 160 K, borohydride compounds desorb while the remaining BH_x fragments on the surface decompose further. At 160 K, the higher binding energy peak has decreased in size (due to desorption of the borohydrides) and has shifted by 0.2 to 189.4 eV. At this temperature, this 189.4 eV peak can be attributed entirely to BH_x fragments left on the surface following borohydride desorption. Also at 160 K, the lower binding energy peak has shifted by 0.1 to 187.7 eV, and has doubled in size. This clearly indicates that during the heating cycle, BH_x fragments decompose leaving additional B bonded to the Ni(100) surface. After heating to 250 K, the area of the lower binding energy peak has increased once more, with the peak location remaining fixed at 187.7 eV. The higher binding energy peak has decreased in size again,

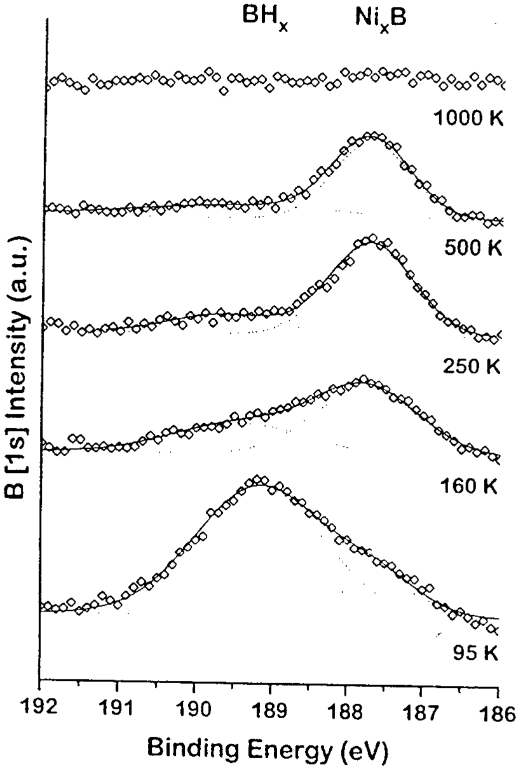

FIG. 5. XP spectra for 15 L B_2H_6 adsorbed onto Ni(100) at 95 K. B [1s] spectra were taken after heating the crystal to the indicated temperature for several seconds.

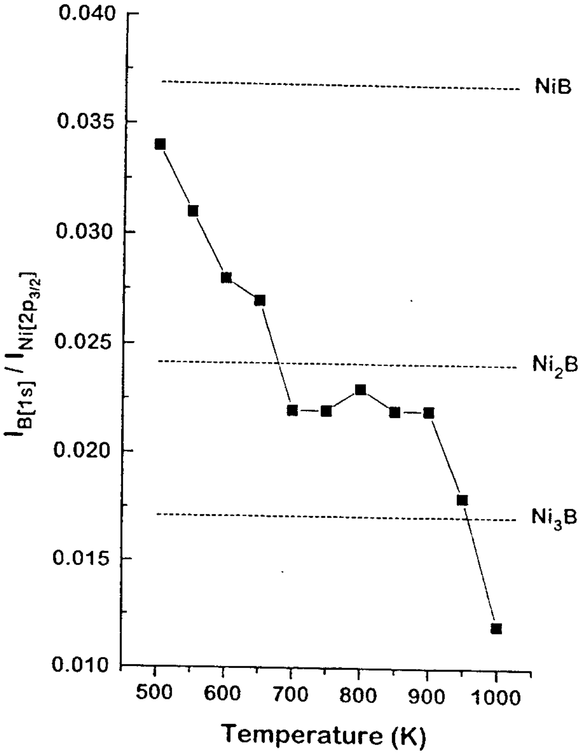

FIG. 6. Ratio of B [1s] peak height to Ni [$2p_{3/2}$] XPS intensities as a function of annealing temperature. The initial surface was prepared by dosing 150 L B_2H_6 onto the Ni(100) surface at 500 K.

and remains fixed at 189.4 eV. From the TDS results, we know that heating to 500 K results in complete decomposition of the B_2H_6 on the surface due to the fact that H_2 desorption ceases at 450 K. The XP spectrum obtained after heating to 500 K shows the lower binding energy peak at 187.7 eV in addition to a very small higher binding energy peak. The peak at the higher binding energy may be attributed to a small amount of B_2H_6, which readsorbed from the background onto the surface during the cooling cycle. Heating the surface to 1000 K resulted in complete disappearance of the B [1s] peak.

B. Decomposition of B_2H_6 on Ni(100) at high temperatures

XPS was used to further investigate the interaction of B_2H_6 on Ni(100) at temperatures exceeding 500 K. Saturated B/Ni(100) surfaces were prepared by exposure to B_2H_6 at 500 K. At this temperature, the adsorbed molecule completely decomposes on the surface, producing hydrogen gas and leaving boron bonded to the Ni(100) surface. While dosing, the B/Ni ratio was determined by comparing the B [1s] peak height to the Ni [$2p_{3/2}$] peak height. It was found that after dosing 150 L B_2H_6 at 500 K, the B/Ni peak height ratio became saturated at a value of 0.035. Angle-resolved XPS measurements of this saturated B/Ni(100) surface were performed ~~for~~ using takeoff angles of 90°, 40°, and 15°. These angle-resolved XPS measurements showed an increase of 8% and 18% in the B/Ni peak height ratio for the 40° and 15° angles, respectively, relative to the measurement at 90°. This data indicates that the saturated B/Ni(100) surface is boron rich, however, the XPS peak positions did not change as a function of angle, indicating uniform chemical composition.[12]

In order to monitor the diffusion of B into the Ni(100) substrate, a saturated B/Ni(100) surface was prepared as described above, and heated from 500 to 1000 K in 50 K increments. The crystal was held at the elevated temperature for a few seconds, and then allowed to cool to below 250 K prior to XPS measurements. After each heating cycle, XP spectra were obtained and the B/Ni peak height ratio was calculated. Figure 6 is a plot of the resulting B/Ni peak height ratio as a function of temperature for this experiment. As Fig. 6 shows, the B/Ni ratio starts at the saturated value of 0.035, and then decreases sharply as the temperature is increased to 700 K. Between 700 and 900 K, the B/Ni ratio is constant at 0.022, and then decreases sharply again as the temperature is increased above 900 K. Angle-resolved XPS measurements were performed on the saturated B/Ni(100) surface, which had been heated to temperatures corresponding to those of the plateau region in Fig. 6 (700–900 K). In this plateau region, it was found that takeoff angles of 90°, 70°, and 40° had little effect (less than 4%) on the B/Ni ratio. This is strong evidence that a homogenous three-dimensional nickel boride phase forms on the Ni(100) surface in this temperature range. This hypothesis is supported not only by the constant B/Ni ratio with respect to the takeoff angle, but also by the fact that there is a decrease of 0.3 eV in the B [1*s*] peak and a decrease of 0.5 eV in the Ni [$2p_{3/2}$] peak as the saturated B/Ni(100) surface is heated from 650 to 700 K. This shift in the XPS signal indicates that a chemical reaction occurs as the surface temperature reaches 600–700 K. Figure 7 shows the B [1*s*] XP spectra for a saturated B/Ni(100) surface prepared at 500 K, and heated to 800 and 1000 K. At 500 K, Fig. 7 shows the B [1*s*] XPS peak position is 187.7 eV. Heating to 800 K results in a peak shift to a lower binding energy of 187.4 eV, where it remains at temperatures up to 1000 K. The formation of a metal boride phase had been observed before on Mo(100), where the formation of MoB_2 coincided with the B [1*s*] signal splitting into two peaks.[13] It should be noted that due to the large 150 L dose, there was still a B [1*s*] peak present in the XP spectrum at 1000 K. This residual peak, however, was not observed for small doses (<10 L), where the boron dissolved completely into the bulk at 1000 K.

In order to identify the nickel boride phase forming on the Ni(100) surface, several nickel boride standards were obtained. NiB, Ni_2B, and Ni_3B samples were mounted in the UHV system and prepared as described in Sec. 2. Table I shows the results of the XPS analysis for these samples, which includes the peak location for the B [1*s*] and Ni [$2p_{3/2}$] signals, as well as the B/Ni peak height ratio. As the Ni:B stoichiometry increases from 1:1 to 3:1, several distinct trends are observed. The B [1*s*] peak position decreases from 187.7 to 187.5 eV, the Ni [$2p_{3/2}$] peak position decreases from 853.1 to 852.8 eV, and the B/Ni peak height ratio decreases as the nickel fraction increases. Similar trends have been observed in iron boride systems, where the Fe [$2p_{3/2}$] signal decreases as the Fe fraction increases, and the B/Fe peak height ratio follows the same decreasing trend observed here.[14]

C. (3×3) LEED pattern for B on Ni(100)

In the course of the experiments, it was found that an ordered (3×3) LEED pattern could be formed on the Ni(100) surface while dosing at high temperatures. The (3×3) surface was prepared by annealing the Ni(100) crystal at 1175 K in 1×10^{-8} Torr B_2H_6 for 30 min. At this temperature, the B_2H_6 completely decomposes on the surface, and most of the remaining B diffuses into the bulk. However, after this procedure, a sharp (3×3) LEED diffraction pattern was observed. Subsequent XPS analysis of this surface shows a small amount of B with no other adsorbates detected. Thus, the (3×3) LEED pattern must be caused by the small amount of B remaining on the surface. The size of the B [1*s*] peak led to the determination that the (3×3) LEED pattern corresponded to 2/9 ML of B on the Ni(100) surface. Figure 8(a) shows a photograph of the (3×3) LEED pattern produced by the procedure described above, while for reference, Fig. 8(b) shows the (1×1) pattern produced by a clean Ni(100) surface.

The XPS calibration used to calculate the absolute coverage of B on the Ni(100) surface was obtained in the following manner. First, NH_3 was dosed onto a clean Ni(100) surface at 500 K until the N [1*s*] signal in the XP spectra saturated. This procedure results in a sharp (2×2) LEED

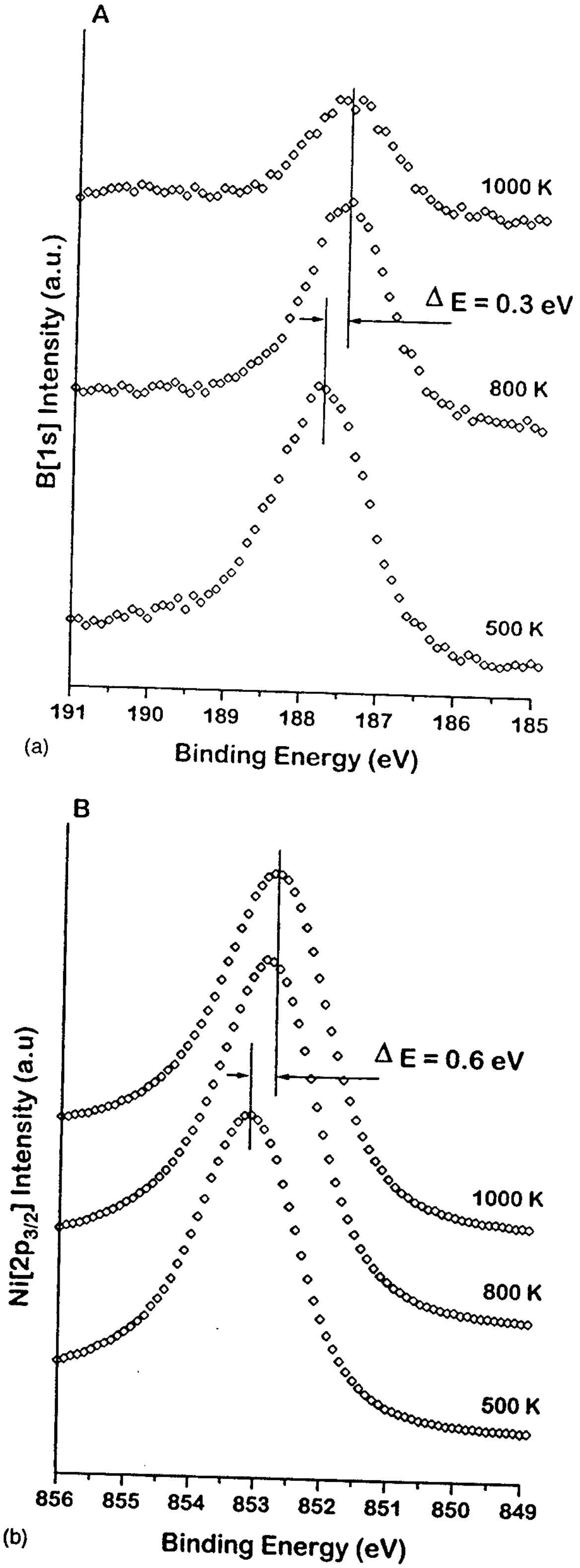

FIG. 7. (a) B [1*s*] and (b) Ni [$2p_{3/2}$] XP spectra for a boron saturated surface prepared by dosing 150 L B_2H_6 at 500 K. The spectra were taken after heating the sample to the indicated temperature.

TABLE I. XPS results for the nickel boride standards, surface nickel boride phase at 500 and 800 K, and a clean Ni(100) surface. The table contains the B [1*s*] and Ni [$2p_{3/2}$] peak positions as well as the B [1*s*] to Ni [$2p_{3/2}$] peak height ratio.

Sample	B [1*s*] (eV)	Ni [$2p_{3/2}$]	Peak ratio
Ni(100)	···	852.7	···
B/Ni(100) (500 K)	187.7	853.2	0.034
B/Ni(100) (800 K)	187.4	852.8	0.022
NiB	187.7	853.1	0.037
Ni_2B	187.5	852.9	0.024
Ni_3B	187.5	852.8	0.017

pattern, which is known to correspond to 0.5 ML of N and allows a confident calibration of the N [1*s*]/Ni [$2p_{3/2}$] XPS peak intensity ratio in terms of N coverage.[15] The intensity ratio of ~~N/Ni~~ N[1s]/Ni[$2p_{3/2}$] on the (2×2) Ni(100) surface was measured to be 0.021, thus, for 1 ML of N on Ni(100)~~. a N/Ni~~ ratio of 0.042 would be expected. ~~Next~~, hexagonal BN powder was pressed into In foil and placed in the UHV system for analysis. The XP spectra for the *h*-BN was found to be quite pure, with no contaminants (C, O, S) detected in the spectra. The intensity ratio of the N [1*s*] signal to the B [1*s*] signal for the h-BN powder was measured to be 0.26. Thus, for 1 ML of B on the Ni(100) surface, the expected B [1*s*]/Ni [$2p_{3/2}$] intensity ratio would be 0.26 times the calculated monolayer N/Ni intensity ratio. This leads to a calculated value of 0.011 for the B/Ni intensity ratio, which corresponds to 1 ML of B on Ni(100). For the Ni(100)–(3×3)–B surface, the B [1*s*]/Ni [$2p_{3/2}$] intensity ratio was measured to be 0.0024, which is about (2/9)·(0.011). Thus, we conclude that the (3×3) LEED pattern on the Ni(100) surface is caused by 2/9 of a monolayer of B on the surface.

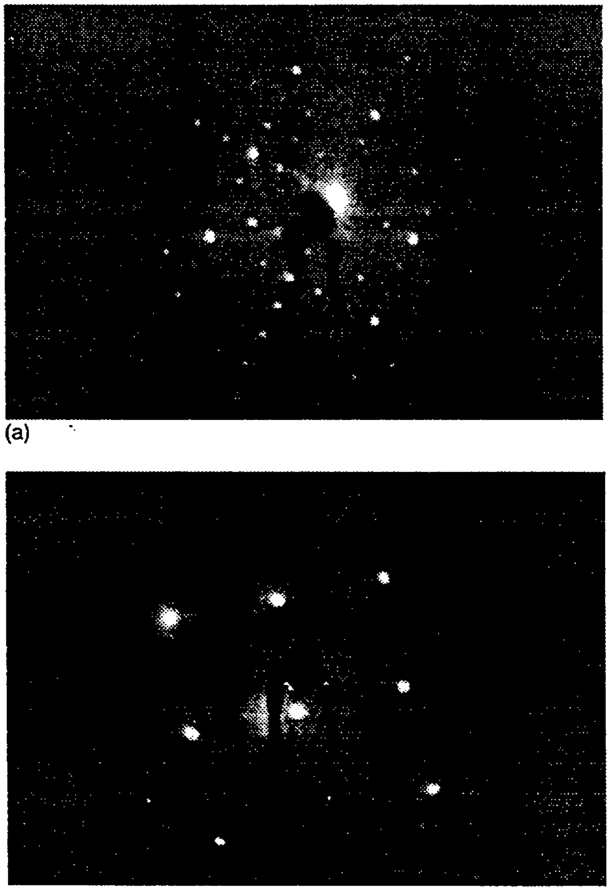

FIG. 8. (a) LEED pattern showing (3×3) structure of boron on Ni(100). The surface was prepared by saturating a Ni(100) surface with boron and annealing at high temperatures for long periods. (Beam voltage=161 eV.) (b) LEED pattern showing the (1×1) diffraction pattern obtained after cleaning the Ni(100) surface as described in the text. (Beam voltage=164 eV.)

IV. DISCUSSION

A. Reaction of B_2H_6 multilayers at low temperatures

The RGA data presented in Fig. 3 and the TPD data in Fig. 2 suggest that following large doses of B_2H_6, the B_2H_6 multilayers react form a new compound that desorbs from the surface at 115 and 147 K. The thermal decomposition of B_2H_6 under various conditions has been studied previously by several researchers and is well documented.[16,17] For instance, pyrolysis of B_2H_6 in sealed vessels at 373 K is known to produce B_4H_{10}, B_5H_{11}, and H_2 with BH_3, B_3H_7, and B_3H_9 as unstable intermediates.[16] At room temperature, in a pressurized vessel, 15% of B_2H_6 is known to decompose to form B_4H_{10} and H_2.[17] These two decomposition reaction schemes occur at temperatures and pressures that differ significantly from the UHV conditions of this study. However, these decomposition reaction schemes do suggest possible reaction products (B_4H_{10}, B_5H_{11}) resulting from B_2H_6 multilayers reacting on the Ni(100) surface.

The identity of the high molecular weight borane can be determined on the basis of its fragmentation pattern in the mass spectrometer. The mass spectrum resulting from B_5H_{11} would be expected to contain masses as high as $m/q = 65$ ($B_5H_{10}^+$), while the B_4H_{10} mass spectrum would be expected to contain masses as high as $m/q = 53$ ($B_4H_9^+$). The mass spectra in Fig. 3 taken at 110 and 140 K indicate the compound desorbing from the Ni(100) surface has a cracking pattern, which produces masses up to $m/q = 53$. Thus, the mass spectra in Fig. 3 are consistent with the cracking pattern expected from B_4H_{10}. It is important to note that the B_2H_6 used in this work does have an unavoidable, low level contamination of B_4H_{10}. A residual gas analysis of the gas exposed to the Ni(100) surface shows a contribution of <2% to the signal at $m/q = 11$ from the B_4H_{10} contaminant. We also note that in the $m/q = 11$ spectra of Fig. 2 the B_2H_6 desorption at 100 K saturates at an exposure of 2.5 L. A further increase in the exposure by a factor of 8 to a total of 20 L results in a considerable increase in the desorption of B_4H_{10} at 147 K. The size of the signal is a factor of 5–10 times greater than that expected from the amount of B_4H_{10} in the source gas. On this basis, we suggest that following large exposures of B_2H_6 the multilayers react to form B_4H_{10}, which desorbs from the surface at 110 and 147 K. At this time, the role of the Ni(100) surface in the reaction is uncertain and the exact source of the B_4H_{10} is not critical to the conclusions of this work. The observation of B_4H_{10} desorption is an interesting result that warrants further investigation and is mentioned here as a caveat to those studying the surface chemistry of B_2H_6 in the future.

B. B_2H_6 decomposition on Ni(100)

The XPS results presented in Fig. 5 clearly indicate that decomposition is occurring upon adsorption of B_2H_6 at 95 K. The extent of this decomposition was determined by analyzing the area of the B [1*s*] peak associated with the decomposed B_2H_6 (BE=187.7 eV in Fig. 5). From this analysis, it was determined that at 95 K, 0.8 ML of B is adsorbed on the Ni(100) surface, resulting from the decomposition of 0.4 ML of B_2H_6 during exposure ~~at 95 K~~. As the crystal is heated to 250 K, further decomposition of B_2H_6 occurs, and the B coverage increases to 1.8 ML. Further heating to 500 K results in a reduction in the amount of B on the surface, with the area of the B [1*s*] peak corresponding to 1.2 ML. Finally, as the crystal is heated to 1000 K, the B [1*s*] peak disappears entirely. Given this information, and the fact that TPD results indicate no B containing species desorbing from the surface in the 150–1000 K range, we conclude that the boron is diffusing into the bulk at high temperatures. The diffusion of B into Ni is not at all ~~that~~ surprising, considering the fact that the diffusivity has been measured to be on the order of 10^{-12} cm^2/s at 1000 K.[18] For a diffusion length of 50 Å, this diffusivity leads to a diffusion time of 0.25 s.[19] Thus, at 1000 K, B is highly mobile in Ni.

C. Formation of the nickel boride phase on Ni(100)

In addition to the XPS results for the nickel boride standards, Table I also shows the XPS results for a clean Ni(100) sample and a saturated B/Ni(100) surface heated to 500 and 800 K. As Table I shows, the XPS peak locations alone are not sufficient to unambiguously determine the phase of the surface compound. The B [1*s*] and Ni [2$p_{3/2}$] peak positions for the saturated B/Ni(100) surface at 500 K agree well with the peak positions for the NiB sample, having B [1*s*] and Ni [2$p_{3/2}$] positions at 187.7 and 853.2 eV, respectively. For the saturated B/Ni(100) surface at 800 K (at temperatures above 700 K, where the nickel boride phase is believed to form), XPS peak positions agree well with both the Ni_2B and the Ni_3B sample, having B [1*s*] and Ni [2$p_{3/2}$] positions at 187.4 and 852.8 eV, respectively. From Fig. 6, it can be seen that the B/Ni peak height ratio is 0.022 for the phase that forms in the temperature range 700–900 K. Comparing this value to the B/Ni peak height ratios for the standards in Table I, it is clear that the Ni_2B sample (~~B/Ni~~=0.024) is closest to this value. Thus, we conclude that the nickel boride phase forming on the Ni(100) surface at temperatures above 700 K is Ni_2B. The phase diagram for B–Ni shows that Ni_2B is one of several compounds (NiB, Ni_2B, Ni_3B, Ni_4B_3) that can form under the conditions of the experiment, thus, the formation of Ni_2B is not unreasonable.[20] In addition, it has been observed that following the chemical-vapor deposition of near stoichiometric NiB films, annealing at 1000 K results in the formation of Ni_2B crystallites, indicating the stability of this phase.[21] It should be noted that in the course of these experiments, no LEED pattern was observed for the Ni_2B phase on the surface, indicating that there was no long-range order in the film.

1s]/Ni:[2$p_{3/2}$]

D. Implications of B_2H_6 decomposition on BN growth

The prospects of epitaxial growth of cubic boron nitride on the lattice-matched Ni(100) surface provides the primary motivation for this study. In order to understand the initial stages of *c*-BN growth, knowledge of how B_2H_6 and B interact with the Ni(100) surface is of vital importance. In this study, we have found that at temperatures above 700 K, B reacts with the Ni(100) surface to form a layer of Ni_2B. In the initial stages of *c*-BN growth, the formation of this layer of Ni_2B would be highly undesirable as it has a body-centered tetragonal unit cell (a=4.99 Å, c=4.25 Å) and is not lattice matched to *c*-BN.[20] To suppress the formation of this Ni_2B phase on the surface, a growth temperature above 1000 K could be used. At this temperature, the Ni_2B phase does not form on the surface because the diffusion of B into the bulk is extremely high. However, while the diffusion of B into the bulk prevents the formation of Ni_2B on the surface, at the same time it depletes the surface of the required group III element. Clearly, in the initial stages of *c*-BN growth on Ni(100), the substrate temperature is critical to maintaining the desired lattice match *and* maintaining the required B source on the surface to react with the nitrogen precursor.

V. SUMMARY

TDS experiments suggest that at high exposures, B_2H_6 multilayers on the Ni(100) surface react to form B_4H_{10}. TDS experiments have also shown that a fraction of the B_2H_6 monolayer on Ni(100) decomposes at low temperatures. As the temperature is increased to 500 K, TDS and XPS results indicate that B_2H_6 completely decomposes leaving B bonded to the Ni(100). As the surface is heated past 700 K, a decrease in the B [1*s*] and Ni [2$p_{3/2}$] XPS peak positions is observed, indicating that a chemical reaction has occurred to form a nickel boride phase on the surface. Comparison of this surface nickel boride phase to standards (NiB, Ni_2B, Ni_3B) led to the determination that Ni_2B was forming on the surface at 700 K. As the temperature is increased above 900 K, the B dissolves into the bulk. Annealing the Ni(100) crystal at 1175 K in 10^{-8} Torr of B_2H_6 results in the formation of a (3×3) LEED pattern. It was determined that this (3×3) LEED pattern was caused by 2/9 of a monolayer of B remaining on the surface.

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DECOMPOSITION OF DIBORANE AND AMMONIA ON Ni(100) SURFACES

R.M. Desrosiers[1], A.J. Gellman[2], D.W. Greve[1] and C.F. McFadden[2]
[1]Department of Electrical and Computer Engineering
[2]Department of Chemical Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

ABSTRACT

The decomposition of diborane (B_2H_6) and ammonia (NH_3) has been studied on Ni(100) by means of Thermal Desorption Mass Spectrometry (TDS), Auger Electron Spectroscopy (AES), and X-ray Photoelectron Spectroscopy (XPS). NH_3 desorbs from Ni(100) during heating and was found to decompose on the Ni(100) surface only under the influence of an electron beam. B_2H_6 was found to thermally decompose on Ni(100), leaving only boron on the surface at temperatures above 400 K. XPS and AES indicate that atomic boron on the surface dissolves into the bulk at temperatures between 500 K and 1000 K. Coadsorption of B_2H_6 and NH_3 was performed under various dosing conditions, and it was found that a reaction between NH_3 and B_2H_6 could be activated both thermally and through the use of an electron beam. XPS peak locations of the product agree well with previously reported values for boron nitride.

INTRODUCTION

Cubic boron nitride (c-BN) is of considerable interest as a high temperature, wide band gap semiconductor. It is similar to diamond in that the hexagonal (graphitic) phase (h-BN) is thermodynamically favored at room temperature. In addition, the lack of a practical, lattice- matched semiconductor substrate makes epitaxial growth challenging.

While there are no suitable semiconductor substrates, there is an excellent lattice match (≈2.5% mismatch) between c-BN (a = 3.615 Å) and the Ni(100) surface (a = 3.524 Å). Recent experiments on hot filament, plasma assisted CVD of BN have shown that only the cubic phase is grown on polycrystalline nickel substrates [1], in contrast to mixed growth of both hexagonal and cubic phases on other substrates such as silicon [2]. While these experiments are encouraging, the roles of surface chemical reactions, ion bombardment, and plasma chemistry cannot be easily separated and thus the mechanism by which the cubic phase is nucleated is unclear.

In order to better understand the reaction pathway to form BN, we have utilized surface science techniques to investigate the interaction of NH_3 and B_2H_6 on the Ni(100) surface. Assuming that the first steps in BN growth require decomposition of reactants, experiments were performed to study the decomposition of both NH_3 and B_2H_6 on the Ni(100) surface. Experiments were also performed to identify the products of the reaction between B_2H_6 and NH_3 when coadsorbed onto the Ni(100) surface. Our results indicate conditions under which a reaction between B_2H_6 and NH_3 can be thermally activated to form BN films.

EXPERIMENTAL

Experiments were performed in an UHV system (base pressure ~2×10^{-10} Torr) equipped with XPS, AES, and a quadrupole mass spectrometer. The 12 mm diameter Ni(100) substrate was prepared by 5 kV Ar^+ ion sputtering followed by an anneal to 1000 K. This process was performed until surface contaminants (sulfur, carbon, oxygen) were below the limit detectable by AES. XPS experiments were carried out using a Fisons Clam 2 150° concentric hemispherical analyzer with constant pass energy set to 35 eV. X-rays were produced by an 800 Watt Al K_α source (hν = 1486.6 eV). Gas exposures were made by bleeding gas into the chamber through leak valves. The NH_3 entered the system through a microcapillary array, and the B_2H_6 entered the system through a 1/2" dosing line. The gas exposures presented in this paper are given in units of effective langmuirs. The effective langmuir dose was calculated from the product of the real dose (in langmuirs) and a multiplication factor. The multiplication factors for the microcapillary array and 1/2" doser were estimated as 20 and 3 respectively.

RESULTS

In the course of the experiments, it was found that NH_3 did not decompose on the Ni(100) surface unless the NH_3 multilayers were exposed to a significant electron flux. Under conditions where care was taken to ensure that no stray electron beams were irradiating the surface, only background hydrogen was observed to desorb from the surface at 350 K indicating that the NH_3 was not decomposing. Figure 1 shows the m/q = 2 amu data for various exposures of NH_3 followed by electron beam irradiation at 100 K. For each spectrum, the NH_3 multilayers were exposed to 0.25 $\mu A/cm^2$ prior to and during the TDS experiment. Two distinct desorption features are present at 320 K and 450 K. The observed peak temperatures agree well with the Ni(110) β and γ_1 desorption peaks reported by Klauber et al. [3] and Bassignana et al. [4] which have been attributed to the decomposition of NH_3 and NH_2 respectively. On Ni(100) we did not observe the third (γ_2) peak associated with the decomposition of NH nor did we observe any N or NH_3 desorption above 300 K. XPS indicated the presence of a significant amount of N on the surface at temperatures above 600 K which disappeared after annealing to 1000 K. We thus conclude that NH_3 decomposition on Ni(100) is similar to that reported on Ni(110).

Figure 2 shows the B [1s] XPS spectra obtained following exposure to 15 L B_2H_6 at 100 K. The spectrum taken at 100 K is consistent with the sum of two peaks centered at 187.4 eV and 189.3 eV. The lower binding energy peak agrees well with reported values for atomic B [5], and indicates that B_2H_6 has decomposed to B on the surface. The higher binding energy peak at 189.3 eV remains in the spectra up to 160 K. TPD data for 5 L doses of B_2H_6 show a very distinct hydrogen desorption peak at 200 K, followed by a broad desorption feature extending to 400 K. The disappearance of the 189.3 eV XPS peak in the temperature range 160 K to 250 K and the TPD data suggest that the XPS peak at 189.3 eV is caused by BH_x species on the surface which decomposes as the temperature is increased above 200 K. Upon heating the sample to 1000 K, the XPS peak at 187.4 eV present in the 500 K spectrum disappears. Our TPD analysis showed no B containing compounds (B, BH, BH_2, BH_3, B_2H_6) desorbing from the surface at temperatures above 120 K. Thus the remaining B on the surface must dissolve into the bulk at temperatures between 500 and 1000 K. It was found that multilayers of B could be produced by dosing B_2H_6 at 500 K.

We conclude that some fraction of the B_2H_6 monolayer on the Ni(100) surface decomposes completely at 100 K while the remainder partially decomposes, followed by multilayer buildup. As the sample is heated, the multilayers desorb at 120 K. Further heating decomposes the BH_x species on the surface to atomic B. Finally, heating to 1000 K causes the B remaining on the surface to dissolve into the bulk. The phase diagram for B-Ni suggests several possible compounds (NiB, Ni_2B, Ni_3B, Ni_4B_3) which could form on the Ni(100) surface.

Following a procedure reported by Rodriguez et al. [6] for the formation of BN, NH_3 multilayers were formed on the Ni(100) surface followed by adsorption of B_2H_6 multilayers. Figure 3 shows the N [1s] and B [1s] XPS spectra for 5L NH_3 coadsorbed with 15L B_2H_6 dosed at 100 K. The different spectra were taken after the sample was heated to 100 K, 250 K, 600 K, and 1000 K. At 100 K, the N [1s] peak position at 400.3 eV agrees well with results from NH_3 on other NH_3/metal systems [7]. The B [1s] peak at 189.7 eV agrees well with our previous results for the B [1s] signal from B_2H_6 multilayers. At 250 K, the multilayers of NH_3 and B_2H_6 have desorbed, and the N [1s] signal shows little change. The B [1s] spectrum at 250K shows peaks at 187.7 and 189.6 eV indicating the presence of both B and BH_x on the surface. At 650 K, the N [1s] signal shifts to 397.5 eV while the B [1s] peak position remains relatively unchanged. When the sample is finally heated to 1000 K, the N [1s] signal peak shifts back slightly to a higher binding of 398.4 eV. At 1000 K, the 187.7 eV B [1s] peak has reduced intensity, and a new peak has appeared at 190.1 eV. The disappearance of the lower energy peak is not surprising from our previous results indicating boron dissolving into the bulk at high temperatures. The fact that both B and N remain on the surface at temperatures up to 1000 K is strong evidence that a reaction has occurred between the two. The B [1s] peak at 190.1 eV and the N [1s] peak at 398.5 eV agrees well with previously reported values for both c-BN and h-BN films (B [1s] = 191.1 eV, N [1s] = 398.4 eV) [8].

During the course of the coadsorption experiment described in the previous paragraph, the sample was exposed to a considerable flux of X-rays, and corresponding photo-emitted electrons. Previous work by Strongin et al. on growth of BN thin films by exposing condensed layers of NH_3 and B_2H_6 to synchrotron radiation prompted us to examine the role of X-rays and photo-emitted electrons in three different coadsorption experiments [9]. In the experiments, steps were taken to protect the surface from stray electron beam irradiation while the precursor gasses were dosed and the sample was heated from 100 to 1000 K. An XPS spectrum was taken after heating the sample to 1000 K. Figure 4, spectrum *a* shows the results of dosing 5L NH_3 followed by 15L B_2H_6 at 100 K. The results show B [1s] and N [1s] peak locations at 190.3 eV and 398.6 eV respectively. When compared with the data in figure 3, both peak locations and intensities agree quite well indicating that a similar amount of BN had formed on the surface without the influence of the x-ray source. Thus the reaction between NH_3 and B_2H_6 on the Ni(100) surface can be a thermally activated process. In contrast, figure 4, spectrum *b* shows the results of dosing 15L B_2H_6 followed by 5L NH_3 at 100 K. Under these conditions, with the dosing order reversed, the decrease in the XPS peak intensities suggest that the BN yield was reduced. Figure 4, spectrum *c* shows the results of dosing 5L NH_3 onto B multilayers at 100 K. Under these conditions, the absence of a N [1s] peak at 398 eV and a B [1s] peak at 190 eV indicate that there was no BN yield.

In order to determine the effect of the x-ray source on BN yield, the three coadsorption experiments were repeated with the surface exposed to the x-ray source during heating. Figure 5, shows the XPS spectra after heating the sample to 1000 K with the same dosing conditions as described for figure 4. If the x-ray source had no effect on the formation of BN, then the spectra in figure 5 would be the same as the spectra in figure 4. However, inspection of figures 4 and 5 show that not to be the case. The intensity of the N [1s] peak at 398 eV appears to be independent of the dosing conditions as does the B [1s] peak at 190 eV. Thus the presence of the x-rays (and corresponding photo-emitted electrons) significantly effects the interaction between B and N and results in equivalent amounts of BN yield.

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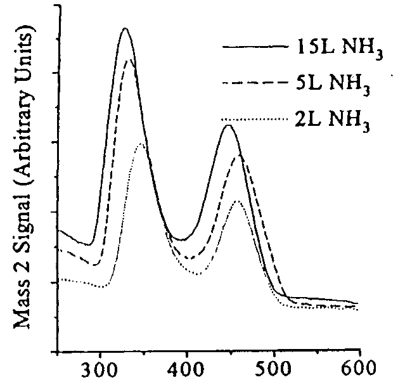

Figure 1. H$_2$ thermal desorption spectra obtained from various exposures of NH$_3$ dosed at 100 K on clean Ni(100)

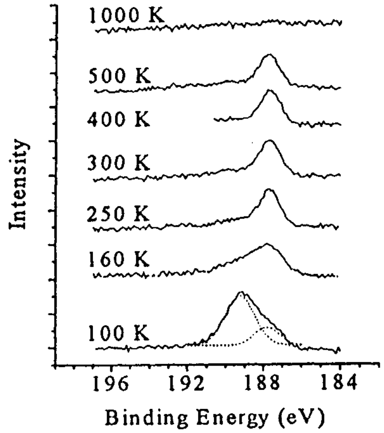

Figure 2. XP spectra from 15L B$_2$H$_6$ dosed at 100K. B [1s] spectra were taken after heating the sample to the indicated temperature.

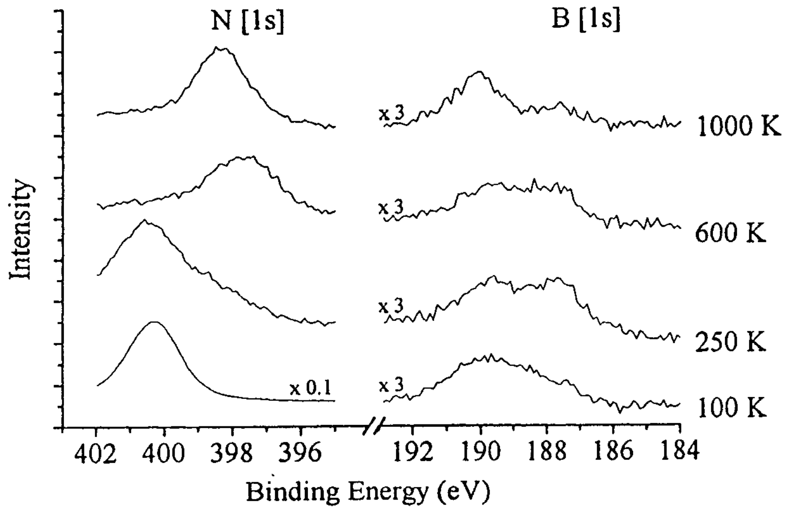

Figure 3. XP spectra from the coadsorption of 0.25L NH$_3$ and 15L B$_2$H$_6$. Spectra were taken after heating the sample to the indicated temperature.

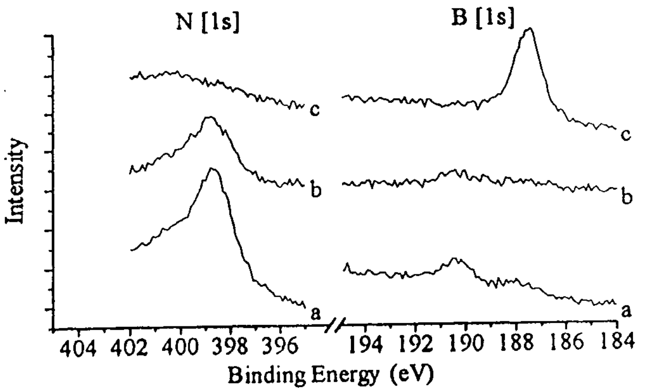

Figure 4: XP spectra showing the effects of dosing conditions on the formation of BN compounds on the Ni(100) surface. The spectra were taken after heating to 1000 K in the absence of X-ray or electron radiation. Dosing conditions were (a) 5L NH$_3$ followed by 15L B$_2$H$_6$ at 100K (b) 15L B$_2$H$_6$ followed by 5L NH$_3$ at 100K (c) 5L NH$_3$ dosed onto B multilayers at 100K.

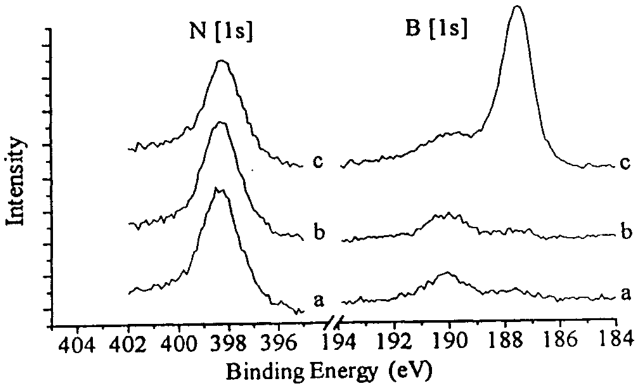

Figure 5: XP spectra showing the effects of X-ray and electron radiation on the formation of BN compounds on the Ni(100) surface. Spectra were taken after heating to 1000 K while illuminating the surface with X-rays. Dosing conditions were (a) 5L NH$_3$ followed by 15L B$_2$H$_6$ (b) 15L B$_2$H$_6$ followed by 5L NH$_3$ (c) 5L NH$_3$ dosed onto B multilayers.