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| 13. ABSTRACT (Maximum 200 words) The surface reactions of diborane and ammonia with the Ni(100) substrate have been studied. Diborane decomposes to boron on the surface and upon annealing forms an Ni ₂ B phase on the surface. Under appropriate conditions, BN can be formed when the surface is doped with both diborane and ammonia. The boron nitride so formed has been identified as the hexagonal phase of boron nitride. Additional studies on other substrates are planned in order to look for circumstances in which cubic BN can be formed. | | | |
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Study of Surface Processes During Growth of Epitaxial Boron Nitride

~~Annual~~ ^{FINAL} Report
AFOSR Contract F49620-93-1-0387

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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 is to investigate the surface chemistry of various reactants suitable for growth of boron nitride. The reactants explored so far are diborane (B_2H_6) and ammonia (NH_3). The work is to be performed in association with A. Gellman of the Chemical Engineering department at Carnegie Mellon.

Status of the Research Effort- Summary

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. Unfortunately, he has chosen to accept a position with TRW in California. We have identified a new student, Charmaine Chan, who will continue the work of this project beginning in June, 1996.

In the past year, the decomposition of B_2H_6 has been studied in detail, both by itself and when coadsorbed with NH_3 . BN has been formed under a range of different conditions

although growth appears to be very slow after the first monolayer is formed. We have identified the phase formed as hexagonal boron nitride. This phase forms despite the excellent lattice match between cubic BN and Ni(100). The experiments did suggest, however, some other routes to BN synthesis which will be explored in the remaining period. An interesting byproduct of this work is the discovery that BN layers formed in this way provide a nearly ideal passivation of the Ni(100) surface.

In the last year, we have had growing interactions between this effort and the AlGaBN growth project of M. Skowronski of the Department Materials Science and Engineering, also funded by AFOSR. This has involved surface science measurements (performed under this contract) on AlGaBN samples grown by MOCVD and the growth of BN samples by MOCVD growth under the other contract.

Summary of specific results from this work

The objectives of this project are to study the initial stages of growth of boron nitride on nearly lattice- matched single- crystal metallic surfaces. Our objectives are 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 ($\approx 2.5\%$ 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 submitted journal articles [9-11]. Copies of these papers will be sent under separate cover. 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 coadsorbed on the $\text{Ni}(100)$ 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 sub-monolayer coverage. BN remains on the surface up to about 1200 K.

4. Somewhat more BN can be created by coexposure 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 (1×7) 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.

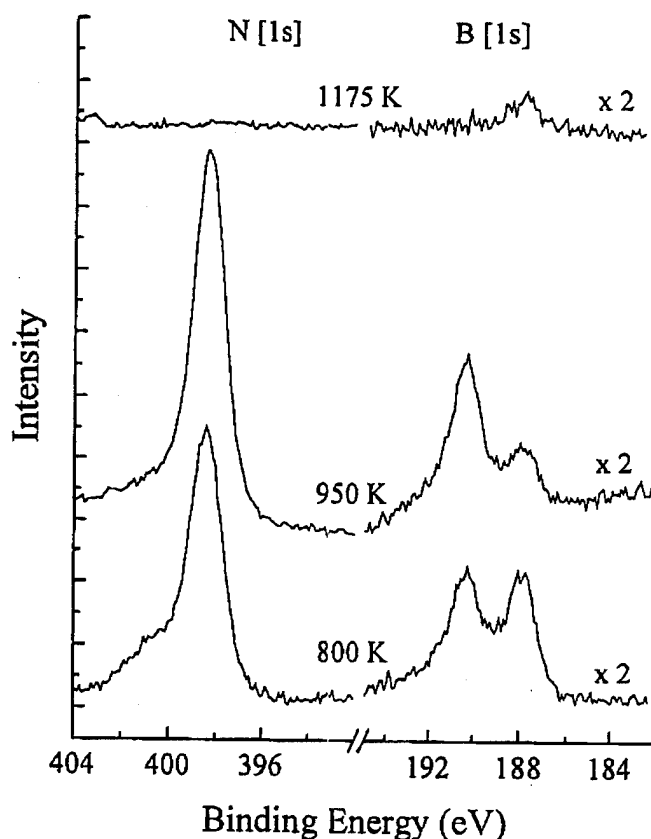


Figure 1. XPS spectra observed after dosing with NH_3 and B_2H_6 at various temperatures. BN has B[1s] peak at 190 eV and an N[1s] peak at 398.4 eV, clearly distinguishable from peaks associated with N and B bonded to nickel.

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. Growths 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 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.

Future objectives

While the fact that c-BN does not grow on Ni(100) is disappointing, there remain some opportunities to be explored for purely thermal synthesis of this material. Indeed, there continue to be tantalizing hints that such a route exists. Prior to our work on AlBN, one group [16] reported the growth of wurtzite BN under MOCVD conditions somewhat different from those we used. Wurtzite BN is an sp^3 -bonded variant of BN analogous to the hexagonal diamond structure. Another interesting result recently is the work of Davis and coworkers [4] which showed that Ni_4C formed on Ni(100) was an excellent nucleating layer for diamond growth. (Unfortunately the Ni_2B phase we observed, unlike Ni_4C , is not lattice-matched to the Ni(100) substrate). So we see some remaining lines of investigation which should be pursued. To summarize them briefly:

1. We believe we have formed the Ni_4C phase on Ni(100) by exposing the surface to hydrocarbons. We will try to confirm the growth of this phase and explore the growth of BN on it, if confirmed. Note that a procedure for easily forming this phase would be valuable also in diamond growth.
2. Our MOCVD results suggest that c-BN or w-BN might form by thermal

decomposition on AlN substrates. As we can now readily prepare such substrates by MOCVD, examination of AlN substrates appears to be an attractive option. In addition to the known catalytic effect noted earlier [15], AlN would have more directional bonds than a metal substrate.

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9. "Nucleation of Boron Nitride on Ni(100) Surfaces," R.M. Desrosiers, D.W. Greve, and A. J. Gellman, (submitted to *Thin Solid Films*).
10. "Decomposition of B₂H₆ on Ni(100)," R.M. Desrosiers, D.W. Greve, and A.J. Gellman, (submitted to *J. Vac. Sci. Technol. A*).
11. "Nucleation of boron nitride thin films on Ni(100)," R.M. Desrosiers, D.W. Greve, and A.J. Gellman, (submitted to *Surface Science*).
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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).

"Decomposition of Diborane and Ammonia on Ni(100) Surfaces," R.M. Desrosiers, A.J. Gellman, D.W. Greve, and C.F. McFadden, presented at the North Coast AVS Symposium (winner of first prize in student paper competition).

"Growth and Characterization of Boron Nitride Films on Ni(100)," D.W. Greve, A.J. Gellman, and R.M. Desrosiers, 42nd American Vacuum Society Meeting, (Minneapolis, MN, November, 1995).

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

"Decomposition of B_2H_6 on Ni(100)," R.M. Desrosiers, D.W. Greve, and A.J. Gellman, (submitted to *J. Vac. Sci. Technol. A*).

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

A.Y. Polyakov et al. (in preparation).

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Interactions

None to date.

Inventions/ Patent Disclosures

None to date.