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Effect of temperature on Ti and TiN films deposited on a BN substrate

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Nitrides (such as BN and TiN) are widely used in various industrial applications because of their excellent wear and corrosion resistance and their thermal and electronic properties. The structural and chemical features formed during plasma vapor deposition of Ti/TiN on BN substrates have been studied using synchrotron radiation near edge absorption spectroscopy (NEXAFS). Various phases of interest have been formed with different annealing temperatures. Diffusion of the nitridation and the interference from oxidation (e.g., TiO₂) and boride formation are of particular concern. X-ray photoelectron spectroscopy and secondary ion mass spectroscopy measurements complement our NEXAFS data. Phase formation and chemical bonding between the coating and the substrate are shown to be determining factors for the microhardness. © 1998 American Vacuum Society. [S0734-2101(98)55703-X]

I. INTRODUCTION

The manufacturing of wear and corrosion resistant thin film coatings is an important area of modern technology. Many of these films also exhibit improved hardness and better electrical conductivity. Cubic boron nitride (*c*-BN), similar to diamond in structure, is thermodynamically stable under high pressure and temperature.¹ The incorporation of a transition metal (Ti) into the BN system introduces metallic bonding which may increase better adhesion between the coating and the substrate thus enhancing the wear properties of these metal nitrides. The potential applications of these nitrides vary from a high temperature, a radiation hard semiconductor or an efficient heat-dissipating semiconductor substrate to its use in optics, cutting tools, and protective coatings.²⁻⁵

Various researchers have adopted plasma vapor deposition (PVD) and chemical vapor deposition (CVD) techniques for processing Ti–B–N composite coatings.⁵⁻¹² The Ti–B–N phase diagram (Fig. 1) gives the composition for a

particular stoichiometry at thermodynamic equilibrium.¹³ However coatings deposited by the PVD technique are considered to be in a nonequilibrium state due to the high quenching rates occurring during the deposition process.¹⁴ Some of the important physicochemical properties of these thin films are due to the formation of various phases such as TiN, TiN_x, TiB₂, BN, and TiB_xN_y.¹³ These multiphase compounds provide improved hardness, wear resistance, and toughness compared to that of single-phase materials. Several spectroscopic techniques, such as Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and cross-sectional transmission electron microscopy (XTEM) combined with electron energy loss spectroscopy (EELS) have been used to characterize the surfaces and interfaces of metal nitrides.^{15,16} It is apparent from these studies that the nature of any adhesion is strongly related to the extent of any physicochemical interactions that occur at the interfaces,¹⁷ but information is often incomplete or conflicting from the point of view of material characterization and composition. The influence of postdeposition annealing on the chemical and microstructural properties of these films is also relatively unexplored. For example, in the cutting tool industry TiN coated cutting tools subjected to harsh and ag-

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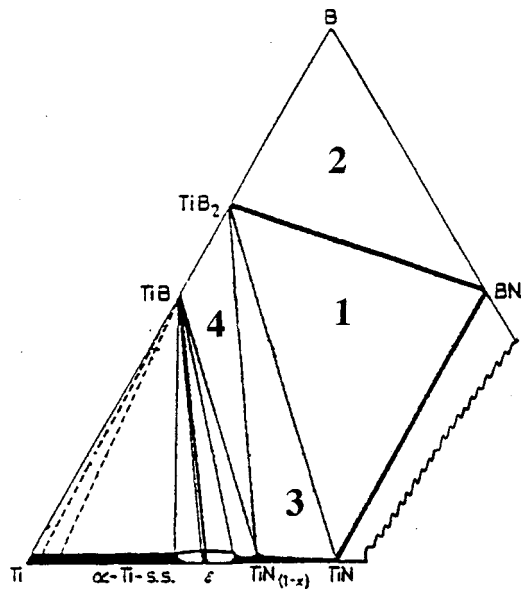


FIG. 1. Phase diagram of Ti-B-N (Ref. 13). Numbers circled are 1: $\text{TiB}_2 + \text{TiN} + \text{BN}$, 2: $\text{TiB}_2 + \text{B} + \text{BN}$, 3: $\text{TiN}_{1-x} + \text{TiB}_2$, and 4: $\text{TiB} + \text{TiB}_2 + \text{TiN}_{1-x}$.

gressive tribological environments normally reaching high temperatures due to frictional heating. Recently we have demonstrated that the core-level x-ray photoelectron spectroscopy can be used to characterize the bonding and structure of the Ti coated BN substrate.¹⁸ In this study, we take advantage of the local sensitivity of core level photoabsorption spectroscopy to identify the presence and formation of various Ti and B containing phases related to TiN film growth on BN substrates and to address some questions concerning the bonding structure of ternary Ti-B-N systems. These phases are obtained by different annealing treatments of Ti/TiN coated BN thin films. In addition, supporting data have been obtained from XPS, secondary ion mass spectrometry (SIMS), and microhardness measurements to further investigate the phase formation and changes in the mechanical properties resulting from thermal treatment.

II. EXPERIMENT

A. Materials and methods

In this study the substrate materials were BN disks. The disks were 6 mm in diameter and 3 mm in height. The chemical composition of the *c*-BN was found by XPS to be C-0.04, Fe-0.002, Mg-0.004, Al-0.002, Si-0.02, and Ca-0.05 with the balance being BN with 1:1 at. % and oxides.

Prior to the Ti/TiN deposition, the chamber was evacuated and the BN substrates were ionically cleaned and heated in the range of 200–650 °C. Ti and TiN films were grown by the arc-plasma vapor deposition method: evaporation of pure Ti into the argon plasma (Ti coating) and reactive N_2 gas (99.99 purity) (TiN coating) at a chamber pressure of 0.001 and 0.01 Pa, respectively. Following the coating deposition, a few of the coated specimens were subjected to postdeposi-

tion annealing in a quartz tube at 1000 and 1400 °C for 2 h in a vacuum furnace.

B. Material characterization methods

1. X-ray photoelectron spectroscopy

The surface chemistry and composition of the deposited layer and the resulting interfaces were studied using a Hewlett-Packard (HP) 5950A x-ray photoelectron spectrometer with an Al $K\alpha$ (1476 eV) anode. General calibration produced a binding energy scale specified by Au ($4f_{7/2}$) = 83.98 ± 0.05 at a linewidth of < 1.0 eV. The charging shifts produced by the insulating samples were removed by a combination of charge neutralizer adjustments and fixing the C ($1s$) binding energy of the hydrocarbon part of the adventitious carbon line at 284.6 eV.¹⁹ Surface oxides were removed by Ar ion sputter etching at 2 keV. Curve fitting of the data was performed by Shirley background subtraction, using a nonlinear least square curve fitting method with a Gaussian/Lorentzian function.²⁰ The photoelectron peaks for Ti ($2p$), B ($1s$), O ($1s$), and N ($1s$) of the deposited layers (Ti/TiN on BN) were examined to characterize the chemical interactions in the B-N-Ti systems.

2. Near edge x-ray absorption spectroscopy

Soft x-ray absorption spectroscopy offers a unique opportunity to directly measure the site-selective energy distribution of the unoccupied “*d*” states of these compounds. X-ray absorption and emission are generally considered to be independent of the excitation process producing a core hole. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy²¹ has been used to study the bonding characteristics of the surfaces of various nitrides.²² NEXAFS measurements were carried out at beamline 6.3.2 [equipped with a Hettrick–Underwood type varied line space (VLS) grating monochromator],^{23,24} at the Advanced Light Source of Lawrence Berkeley National Laboratory in the range of 50–1000 eV. The resolving power of the monochromator, $E/\delta E$, at the $L_{2,3}$ edge of S is about 1700, and at the transition metal $L_{2,3}$ edges of Mn through Ni it is between 1000 and 1500. This energy resolution was sufficient to distinguish the fine changes in the spectra as a function of transition metal content. The B $1s$ (K edge), N $1s$ (K edge) and Ti $2p$ (L edge) photoabsorption spectra of the selected thin films were employed and the standards reported in this article were obtained by step scanning the monochromator and measuring the total electron yield (photoelectrons, Auger, and secondary electrons) from the sample in an ultrahigh vacuum (UHV) chamber. The incoming radiation intensity (I_0) was measured by the photocurrent generated by the gold mesh positioned immediately in front of the sample. In the high energy region no structure in the I_0 was found. In the total electron yield mode, the measured core level photoabsorption spectra provide an immediate depth sensitivity, with an electron escape depth of about 60 Å compared to the 5–30 Å of the photoemission process.

3. Secondary ion mass spectrometry

To analyze the chemical state of the near surface structure of the deposited thin films, an alternating sputtering technique was employed. The elemental and phase distributions of the surface coating were evaluated by a VG secondary ion mass spectrometry (VG 12-2S Ionex MR3020 quadrupole SIMS). The primary ion source was a dual plasmatron oxygen ion source with an accelerating voltage of 6 keV and a current of 10–50 nA. The thickness of the as deposited thin films evaluated by SIMS was approximately 1 μm .

4. Mechanical properties

The Vickers hardness (H_v) of the samples was measured with a Tukon hardness tester (from the laboratory of the Center of Research and Education in Optics and Lasers, University of Central Florida) under a load of 1 kg. The microhardness values are calculated using the following equation:

$$H_v = (2L \sin(\alpha/2)/d^2), \quad (1)$$

where L is the load (in kg), d (mm) is the measured length of the diagonal, and α is the angle of indentation (135°). The penetration depth of the indenter was about 1/10 of the diagonal. For maximum hardness the indenter's depth was chosen at about 1/15 of the films thickness, so that the calculated value was a true measurement of the coating hardness.

III. RESULTS AND DISCUSSIONS

A. X-ray photoelectron spectroscopy

XPS was employed to investigate the chemical states of the Ti–B–N systems at 1000 and 1400 $^\circ\text{C}$ for 2 h, respectively. The XPS spectra of Ti–BN (1000 $^\circ\text{C}$ for 2 h) revealed the expected presence of TiO_2 [$\text{Ti}(2p)_{\text{BE}} \sim 459 \text{ eV}$] on the surface due to preferential air induced oxidation of the Ti. Neither boron (B) or nitrogen (N) was found on the surface. After heat treating the same film to 1400 $^\circ\text{C}$ for 2 h, the XPS [$\text{Ti}(2p)$, $\text{N}(1s)$, $\text{B}(1s)$, $\text{O}(1s)$] spectra exhibited a number of distinct phases, such as TiB_2 [$\text{B}(1s)_{\text{BE}} 187.5 \text{ eV}$], TiN [$\text{Ti}(2p)_{\text{BE}} \sim 455.5 \text{ eV}$; $\text{N}(1s)_{\text{BE}} = 397.7 \text{ eV}$],²⁵ and BN [$\text{B}(1s)_{\text{BE}} \sim 190.4 \text{ eV}$], plus perhaps some oxynitrides,^{26,27} as well as the expected oxides of B and Ti. This suggests that at higher temperatures B and N species have diffused toward the surface and have reacted with Ti, forming TiN and TiB_2 compounds. These species improve the hardness, wear, and corrosion resistance. It also forms B_2O_3 with O_2 [$\text{B}(1s)_{\text{BE}} = 192.4\text{--}193.1 \text{ eV}$]. The presence of a contribution at 399.13 eV in the $\text{N}(1s)$ spectrum suggests that an oxynitride²⁶ is also present in the air-oxidized layer. Also, at 1400 $^\circ\text{C}$ we observe a phase separation in the $\text{TiN}+\text{BN}$ samples forming the nonstoichiometric TiN_x ($\text{N}/\text{Ti} > 1$ and different bonding due to the excess nitrogen [$\text{N}(1s)_{\text{BE}} = 396.2 \text{ eV}$ at 1400 $^\circ\text{C}$]. The fraction of nonstoichiometrically bonded N atoms to Ti may be one of the principal tribological factors for determining film quality.²⁸ The presence of the TiB_2 phase was not found in this system. An increase in surface C–O and C=O

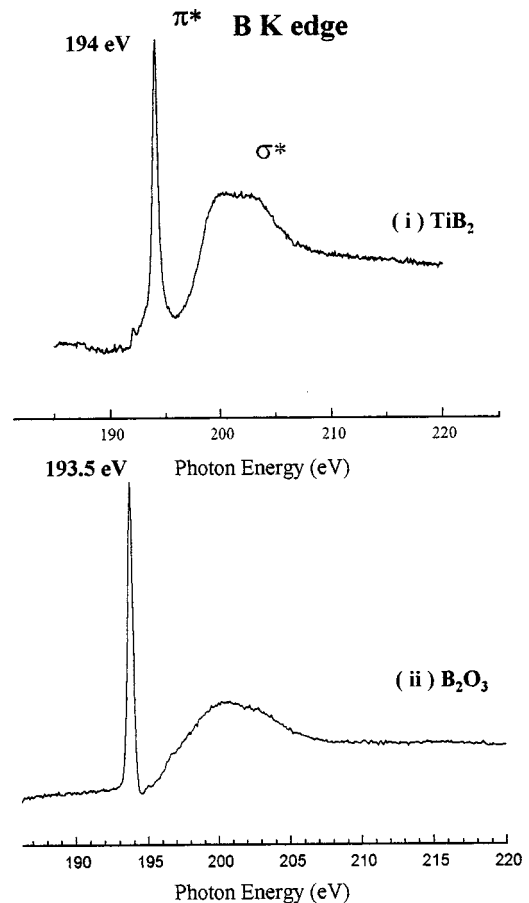


Fig. 2. B K x-ray absorption edge spectra of (i) TiB_2 and (ii) B_2O_3 powder.

type species in the 1400 $^\circ\text{C}$ treated Ti+BN system suggests an increase in surface oxidation compared to the 1000 $^\circ\text{C}$ heat treated Ti+BN sample.

B. Near edge x-ray absorption fine structure spectroscopy

For further confirmation of various phase formations (as detected by XPS) we have measured the boron, titanium, and nitrogen core photoabsorption spectra. The resonances in the NEXAFS measurements²¹ are interpreted as transitions from bound, localized core levels with discrete angular momentum transition to their continuum states.

Figure 2 shows the B K x-ray absorption (NEXAFS) spectra of pure TiB_2 and B_2O_3 powders. These measurements are necessary to understand the complex Ti–B–N system. The absorption spectra of B_2O_3 and TiB_2 exhibit prominent sharp peaks at 193.5 and 194 eV, respectively, and are consistent with that in the literature.²⁹ These peaks are associated with $p\pi^*$ resonance states. In the case of TiB_2 we observe a slight shift in energy for the sharp feature at 194.0 eV in their absorption spectra. In the case of $c\text{-BN}$ spectra (not shown) with sp^3 bonding like diamond, the absorption edge of boron appears to be at 193.9 eV (not a sharp resonance) corresponding to the transition from the $\text{B}(1s)$ core

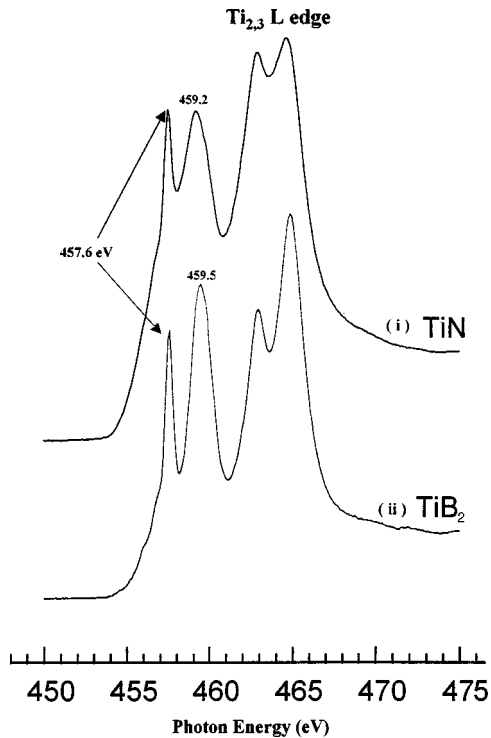


FIG. 3. Ti $L_{2,3}$ x-ray absorption edge spectra of (i) TiN and (ii) TiB_2 powder.

level to a σ^* state in the conduction band. We also measured another sharp peak at 191.8 eV that indicated the π^* peak of the h-BN phases (sp^2 bonding) present in our sample. Thus, our BN substrate indicates the presence of a mixture of sp^2 and sp^3 bonding.

Figure 3 shows the Ti $L_{2,3}$ absorption edge of clean TiN and TiB_2 powders. From these spectra one can observe the unique atomic $3d$ states because they retain some localized character upon forming solids. All these Ti $L_{2,3}$ edges display a two group structure which corresponds to the transitions of $2p_{3/2}-3d$ and $2p_{1/2}-3d$.

Figure 4(i) illustrates the B K absorption edge of a Ti/TiN coated (by PVD) BN substrate heated at 1400 °C for 2 h. No significant feature in the B $1s$ NEXAFS spectra region was found to be present in the TiN/BN system [Fig. 4(ii)]. In the Ti/BN system, prominent π^* features at 194 and 191.7 eV indicate the presence of TiB_2 and BN phases in this composite system. A similar presence of TiB_2 was observed in the corresponding XPS spectra. The σ^* absorption now appears at 199.5 eV. The most stable phase of BN is the hexagonal one, the transition temperature from cubic to hexagonal being about 1820 K.³⁰ Since our annealing temperatures were 1000 and 1400 °C, no changes have taken place in the sp^3 BN phase which is present with the sp^2 BN phase at around 194 eV. (Note the broadening of the peak at 194 eV.) In the 1000 °C treated Ti/TiN coated BN, the presence of BN and TiB_2 was not observed, as also found from the XPS data.

Figure 5 shows the $Ti_{2,3} L$ and N K absorption edges of a heat treated (1400 °C, 2 h) Ti/TiN thin film grown on a BN substrate. In the TiN/BN system, the prominent features at 459.3 and 457.6 eV indicate the formation of TiO_2 (suggest-

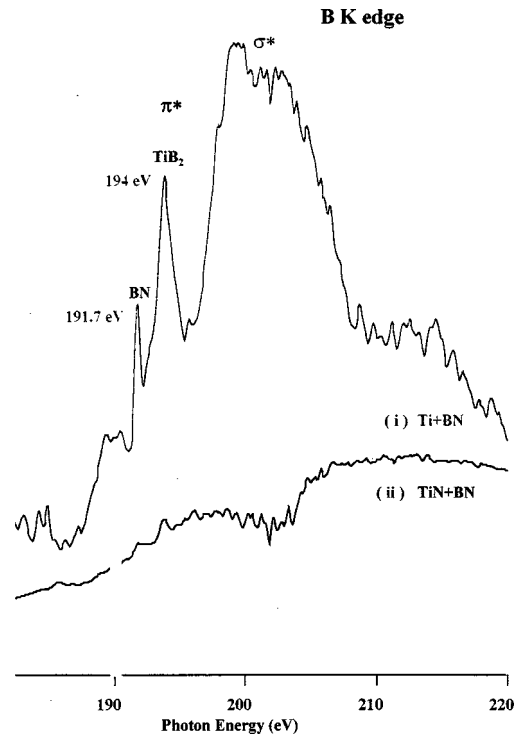


FIG. 4. B K absorption edges of (i) Ti/BN and (ii) TiN/BN annealed at 1400 °C for 2 h.

ing surface oxidation) and TiN phases. The peak structure at 459.5 eV in the curve of Fig. 5(ii) shows the formation of the TiB_2 phase as was also suggested by our B K absorption edge and our previous XPS measurements. At this annealing

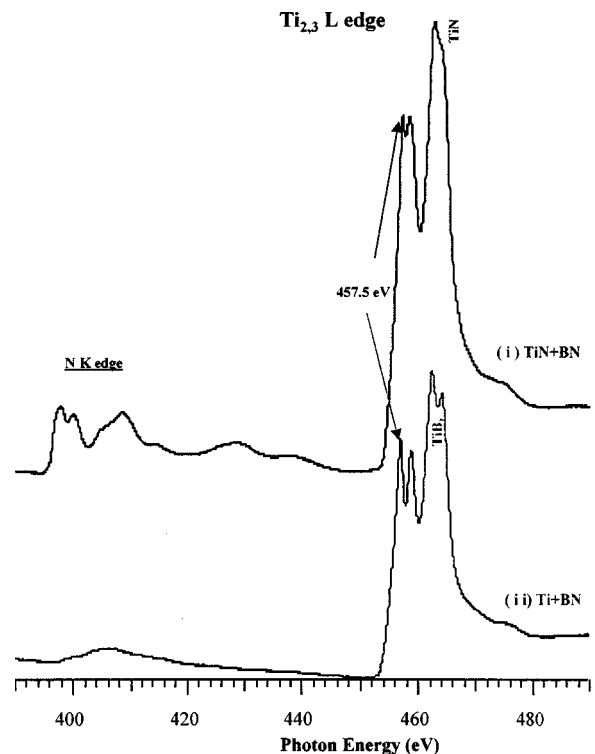


FIG. 5. Ti $L_{2,3}$ and N K absorption edges of (i) TiN/BN and (ii) Ti/BN annealed at 1400 °C for 2 h.

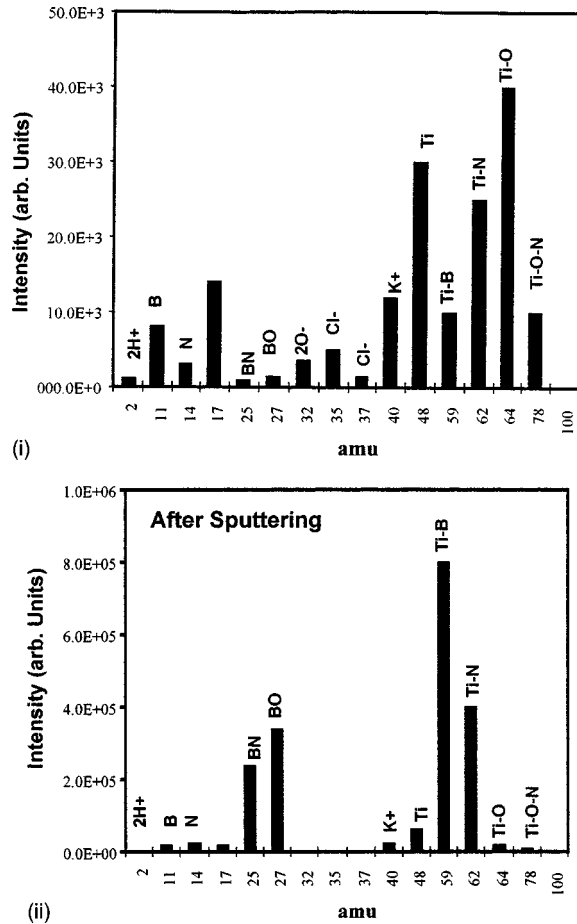


Fig. 6. SIMS spectra of Ti/BN annealed at 1000 °C, (i) control and (ii) after sputtering.

temperature, the corresponding N 1s absorption edge shows the nitrogen enrichment in the TiN films [Fig. 5(i)] compared to Ti films on the BN substrate. Also, several features at the N 1s edge were found in curve (i) but are absent in curve (ii). In curve (i) two new peaks at 397.5 and 399.8 eV are attributed to the formation of stoichiometric and nonstoichiometric TiN. At higher annealing temperatures a phase separation was also observed from our XPS studies. In addition, microcracks were observed in the TiN films annealed at 1400 °C. Thus at higher temperatures B and N have diffused to the outer surface to form borides and nitrides in the Ti/BN system. In the case of 1000 °C treatment no boride was found in the Ti/BN system. The presence of extensive surface oxides was evident from both the NEXAFS and XPS spectra (not shown).

C. Secondary ion mass spectrometry

From our XPS and NEXAFS studies it was evident that 1000 °C treated Ti/BN does not exhibit the presence of borides and nitrides on the deposited thin film surfaces. SIMS, an extremely surface sensitive technique (it probes 5–10 Å of the outermost surface), was performed to examine the phase formation in the Ti/BN system. Figure 6(i) indicates the presence of surface oxides and small amounts of various nitrides and borides on the surface of Ti coated BN that were not detected in our previous measurements. After sputtering for 30 min, Fig. 6(ii) indicates the removal of the outer surface titanium oxides and oxynitride; further, the intensity of the Ti–B type species intensifies. This clearly indicates the formation of titanium borides in the inner layer of the coating; this was also evident from our earlier XPS depth profile results.³¹ We believe that the observed titanium boride formation at intermediate Ti is likely due to the presence of excess elemental boron in the film once all the N atoms are bonded to Ti, forming TiN.

D. Microhardness of the composite films

A Tukon hardness tester measured the microhardness of the deposited thin films to correlate the mechanical properties of the deposited thin films to the corresponding surface chemistry. In general, the thin film hardness is affected by the mechanical properties of the underlying substrate. Both BN and Ti have a lower hardness than TiB₂ and TiN. It should be noted that the Ti/BN system achieves higher hardness (H_v 3500) after annealing at 1400 rather than at 1000 °C (see Table I). An increase in temperature promotes the nucleation and growth of hardness and wear resistant phases like those in TiB₂ and TiN. This seems to appear in the form of nanostructures. This is consistent with our earlier XPS, NEXAFS, and SIMS data. Of course, we do not exclude the presence of mixed Ti–B–N phases of various stoichiometries as is evident from our earlier XPS studies.¹⁸ The hardness values in the TiN/BN system treated at 1000 and 1400 °C are considerably lower than that of the 1400 °C treated Ti/BN. In this system, only TiN was found to be present and the hardness values (Table I) are comparable to pure TiN (H_v 2000). TiN/BN annealed at 1400 °C exhibits a lower hardness value of H_v 1500 compared to the one annealed at 1000 °C. The decrease in hardness at higher tem-

TABLE I. Microhardness measurements of Ti–B–N systems.

Sample	Ti+BN		TiN+BN		Individual substrate			
	Annealed at 1000 °C	Annealed at 1400 °C	Annealed at 1000 °C	Annealed at 1400 °C	Ti	BN	TiN	TiB ₂
Hardness H_v	750	4200	1975	1500	650	—	2050	4010

perature in the TiN/BN system can be understood as due to the presence of nonstoichiometric TiN_x along with stoichiometric TiN (observed from XPS measurements). The film annealed at 1400 °C showed microcracks due to internal stress during phase separation. This suggests that the coatings with the best tribological properties contained the smallest fraction of excess nitrogen bonds with titanium.^{32,33} Also, the films with maximum hardness contain a minimum of TiN_x and oxynitrides as is evident from the XPS studies. This provides useful information for surface coating and modification of cutting tools.

IV. CONCLUSION

Physical and chemical properties of Ti/TiN films on BN substrates deposited by PVD have been studied. Distinct correlations between surface chemistry and mechanical properties (microhardness) of these thin films were observed. Higher annealing temperature treatment of Ti/BN revealed (by XPS) the formation of a TiB_2 phase and a phase separation of TiN in the TiN/BN system. The sensitivity of NEXAFS spectroscopy is used to better understand the chemistry and morphological changes occurring during the thermal treatment of these nitride surfaces. NEXAFS measurements provide a clear spectroscopic signature of TiB_2 and TiN formation and the presence of sp^2 and sp^3 phases in the BN substrate. An increase in the postdeposition annealed temperature increases the hardness of Ti+BN to a maximum of H_v 4200. But the hardness in TiN/BN under the same annealing conditions was found to decrease due to the formation of nonstoichiometric TiN.

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