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Effect of Temperature on Ti and TiN Films Deposited on BN Substrate

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Abstract

Nitrides (such as BN, TiN) are widely used in various industrial applications because of their extreme wear and corrosion resistance, thermal and electronic properties. In the present case structural and chemical features formed during plasma vapor deposition (PVD) 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. XPS and SIMS measurements complement our NEXAFS data. Phase formation and chemical bonding between the coating and the substrate was shown to be the determining factor for the microhardness.

1. 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. The incorporation of a transition metal (Ti) in the BN system introduces metallic bonding which may increase the probability of better adhesion between the coating and the substrate enhancing the wear properties of these metal nitrides. The potential applications of these nitrides vary from high temperature - 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 and chemical vapor deposition (PVD and CVD) techniques for the processing of Ti-B-N composite coatings.\(^{(5-12)}\) The Ti-B-N phase diagrams (Figure 1) gives the composition for a particular stoichiometry at a thermodynamic equilibrium.\(^{(13)}\) However coatings deposited by PVD technique are considered to be in a non-equilibrium 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, TiNx, TiB\(_2\), BN, and TiBxNy.\(^{(13)}\) These multiphase compounds provide improved hardness, wear resistance and toughness as compared to that of the single-phase materials. Several spectroscopic techniques, such as, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (XTEM) combine with electron energy loss spectroscopy (EELS) have been used to characterize the surfaces and interfaces of the 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 occurs at the interfaces,\(^{(17)}\) but the 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 the TiN coated cutting tools subjected to harsh and aggressive tribological environments normally reach 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 sensivity of the core level photoabsorption spectroscopy to identify
the presence and formation of various Ti and B containing phases in connection to TiN film growth on BN substrates and to address some questions concerning bonding structure of the ternary Ti-B-N systems. These phases are obtained by different annealing treatments of Ti/TiN coated BN thin films. In addition, supporting data has been obtained from X-ray photoelectron spectroscopy (XPS), Secondary ion mass spectrometry (SIMS) and microhardness measurements to investigate further the phase formation and changes in the mechanical properties due to the thermal treatment.

2. Experimental

2.1 Materials and Methods

In this study the substrate materials were BN discs. The resulting 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 of BN with 1:1 atomic% along with 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 arc-plasma vapor deposition method: evaporation of pure Ti into the argon plasma (Ti coating) and reactive N₂ gas (99.99 purity) (TiN coating) at a chamber pressure of 0.001 and 0.01 Pa respectively. Following coating deposition, a few of the coated specimens were subjected to postdeposition annealing in a quartz tube at 1000°C and 1400°C for 2 hours in a vacuum furnace.

2.3 Material characterization methods

2.3.1 X-ray photoelectron spectroscopy (XPS)

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 Kα (1476 eV) anode. General calibration produced a binding energy scale specified by Au
(4f7/2) = 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 a 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 a Shirley background subtraction, using a non-linear least square curve fitting
method with a Guassian/Lowrentzian function.\(^{(20)}\) The photoelectron peaks for Ti (2p), B (1s), O
(1s), N (1s) of the deposited layers (Ti/TiN on BN) were examined to characterize the chemical
interactions in the B-N-Ti systems.

2.3.2 Near edge x-ray absorption spectroscopy (NEXAFS)

The soft X-ray absorption spectroscopy offers a unique opportunity to measure directly
the site-selective energy distribution of the unoccupied d states of these compounds. X-ray
absorption and emission is generally being considered to be independent of the excitation
process producing a core hole. Near edge x-ray absorption fine structure spectroscopy\(^{(21)}\) 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 grating (VLS) 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/ΔE, at the L_{2,3} edge of S is about 1700, and at the transition metal L_{2,3} edges
of Mn through Ni are 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 paper were obtained by step scanning the
monochromator and measuring the total electron yield (photoelectrons, auger and secondary electrons) from the sample in an UHV chamber. The incoming radiation intensity \( I_0 \) was measured by the photocurrent generated in the gold mesh positioned immediately before 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 provides an immediate depth sensitivity, with an electron escape depth of about 60 Å compared to the 5-30 Å of the photoemission process.

2.3.3 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 distribution of the of the surface coating were evaluated by a VG secondary ion mass spectrometry (VG 12-2S Ionex MR3020 Quadropole 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 micron.

2.3.4 Mechanical Properties

The Vickers hardness \( (H_v) \) of the samples was measured with a Tukon hardness tester (Dr. A. Kar’s laboratory at CREOL, UCF) under a load of 1kg. The microhardness values are calculated using the following equation:

\[
H_v = \frac{2L \sin(\alpha/2)}{d^2}
\]

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

3.1 X-ray photoelectron spectroscopy (XPS)

XPS was employed to investigate the chemical states of the Ti-B-N systems at 1000°C and 1400°C for 2 hours (hrs) respectively. The XPS spectra of Ti-BN (1000°C for 2 hrs) revealed the expected presence of TiO₂ (Ti (2p) B.E. ~ 459 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°C for 2 hrs, the XPS (Ti (2p), N (1s), B (1s), O (1s)) spectra exhibited a number of distinct phases, such as, TiB₂ (B (1s) B.E. 187.5 eV), TiN (Ti (2p) B.E. ~ 455.5 eV: N (1s) B.E. = 397.7 eV), BN (B (1s) B.E. ~ 190.4 eV), plus perhaps some oxynitrides, as well as the expected oxides of B and Ti. This suggests that at higher temperatures B and N species have diffused towards the surface and reacted with Ti, forming TiN and TiB₂ compounds. These species improve the hardness, wear and corrosion resistance, and also with O₂ to produce B₂O₃ (B (1s) B.E. = 192.4-193.1 eV). The presence of a contribution at 399.13 eV in the N (1s) spectrum suggests that an oxynitride is also present in the air-oxidized layer. Also, at 1400°C we observe a phase separation in the TiN+BN samples forming non-stoichiometric TiNx (N/Ti >1 and different bonding due to the excess nitrogen) (N (1s) B.E. = 396.2 eV at 1400°C). The fraction of non-stoichiometrically bonded N atoms to Ti may be one of the principal tribological factors for determining film quality. The presence of TiB₂ phase was not found in this system. An increase in surface C-O, C=O type species in the 1400°C treated Ti+BN system, suggested an increase in surface oxidation compared to the case of 1000°C heat treated Ti+BN sample.
3.2 Near edge x-ray absorption fine edge 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 $^{(21)}$ 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$_2$O$_3$ powders. These measurements are necessary to understand the complex Ti-B-N system. The absorption spectra of B$_2$O$_3$ and TiB$_2$ exhibit prominent sharp peaks at 193.5 eV and 194 eV respectively and are consistent with the existing literature. $^{(29)}$ These peaks are associated with $\pi^*$ 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 c-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 B (1s) core level to a $\sigma^*$ state in the conduction band.

We also measured another sharp peak at 191.8 eV indicating the $\pi^*$ 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$_{2,3}$ L absorption edge of clean TiN and TiB$_2$ powders. From these spectra one can observe the unique atomic 3d states in the sense that they retain some localized character upon forming solids. All these Ti L$_{2,3}$ edges display two groups 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 Ti/TiN coated BN substrate (by PVD) heated at 1400°C for 2 hours. No significant feature in the B 1s NEXAFS spectra region was found to be present in the TiN/BN system (Figure 4(ii)). In the case of Ti/BN system, prominent
features at 194 eV and 191.7 eV indicating the presence of TiB₂ and BN phases in this composite system. Similar presence of TiB₂ 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 1820K. Since our annealing temperature was 1000°C and 1400°C, no changes have taken place in the sp³ BN phase which is present with the sp² BN phase at around 194 eV. (Note the broadening of the peak at 194 eV). In the case of 1000°C treated Ti/TiN coated BN, the presence of BN and TiB₂ was not observed, as also found with the XPS data.

Figure 5 shows the Ti₂,₃ L and N K absorption edge of a heat treated (1400°C, 2 hours) Ti/TiN thin film grown on a BN substrate. In the case of the TiN/BN system, the prominent features at 459.3 and 457.6 eV indicate the formation of TiO₂ (suggesting a surface oxidation) and TiN phases. The peak structure at 459.5 eV in curve 5(ii) shows the formation of TiB₂ phase as also suggested in our B K absorption edge and our previous XPS measurement. At this annealing temperature, the corresponding N 1s absorption edge shows the nitrogen enrichment in TiN films (i) as compared to Ti films on BN substrate. Also several features at N 1s edge was found in curve (i) but are absent in (ii). In (i) two new peaks at 397.5 eV and 399.8 eV are attributed to the formation of stoichiometric and non stoichiometric TiN. At higher annealing temperatures a phase separation was also observed from our XPS studies. Micro cracks were also observed in the TiN films annealed at 1400°C. Thus at higher temperatures B and N has 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 on the Ti/BN system. The presence of extensive surface oxides was evident from both NEXAFS and XPS spectra (not shown).
3.3 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 minutes, Figure 6 (ii) indicates the removal of 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 that was also evident from our earlier XPS depth profile results. We believe that the observed titanium boride formation at intermediate Ti is likely to be due to the presence of excess elemental boron in the film, once all N atoms are bonded to Ti, forming TiN.

3.4 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 achieve higher hardness (Hᵥ 3500) after annealing at 1400°C as compared to 1000°C (see Table 1). Increase in temperature promotes the nucleation and growth of hard and wears resistant phases like TiB₂ and TiN. This seems to appear in the form of nanostructures. This is consistent with our earlier XPS, NEXAFS and SIMS data simultaneously. Of course, we do not exclude the presence of mixed Ti-B-N phases of various stoichiometries as
evident from our earlier XPS studies.\(^{(18)}\) The hardness values in TiN/BN system treated at 1000°C 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 1) are comparable to the pure TiN (H\(_v\) 2000). TiN/BN annealed at 1400°C exhibits a lower hardness value of H\(_v\) 1500 as compared to the one annealed at 1000°C. Decrease in hardness at higher temperature in TiN/BN system could be understood because of the presence of nonstoichiometric TiN\(_x\) along with stoichiometric TiN (observed from XPS measurements). The film annealed at 1400°C show microcracks due to the internal stress during the 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 of maximum hardness contain a minimum of TiN\(_x\) and oxynitrides as evident from XPS studies. This provides useful information for surface coating and modification of cutting tools.

4. Conclusion

Physical and chemical properties of Ti/TiN films on BN substrates, deposited by PVD, have been studied. Distinct correlations between surface chemistry and microhardness of these thin films were observed. Higher annealing temperature treatment of Ti/BN revealed the formation of a TiB\(_2\) phase and a phase separation of TiN in the TiN/BN system (by XPS). The sensitivity of NEXAFS 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. Increase in post deposition 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 non-stoichiometric TiN.
Acknowledgments

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References

31. S. Seal, T. L. Barr, E. Benko, (accepted MRS proceedings'97)
Table 1. Microhardness measurements of Ti-B-N systems.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti+BN</th>
<th>TiN+BN</th>
<th>Individual substrate</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1000°C</td>
<td>1400°C</td>
<td>Ti</td>
</tr>
<tr>
<td>Hardness</td>
<td>750</td>
<td>4200</td>
<td>1975</td>
</tr>
<tr>
<td>Hv</td>
<td></td>
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</table>
Figures

1. Phase diagram of Ti-B-N (Ref. 13). Numbers circled are 1: TiB₂+TiN+BN, 2: TiB₂+B+BN, 3: TiN₁₋ₓ+TiB₂, 4: TiB+TiB₂+TiN₁₋ₓ.
2. The B K x-ray absorption edge spectra of (i) TiB₂ and (ii) B₂O₃ powder.
3. The Ti L₂,3 x-ray absorption edge spectra of (i) TiN and (ii) TiB₂ powder.
4. The B K absorption edge of (i) Ti/BN, (ii) TiN/BN annealed at 1400°C for 2 hours.
5. The Ti L₂,3 and N K absorption edge of (i) TiN/BN and (ii) Ti/BN annealed at 1400°C for 2 hours.
6. The SIMS spectra of Ti/BN annealed at 1000°C, (i) control, (ii) after sputtering.
Figure 2

(i) TiB$_2$

(ii) B$_2$O$_3$
Figure 3

Ti$_{2,3}$ L edge

(i) TiN

(ii) TiB$_2$

Photon Energy (eV)
Photon Energy (eV)

190 191.7 eV 194 eV

BN

TiB₂

\( \pi^* \)

\( \sigma^* \)

(i) Ti+BN

(ii) TiN+BN

B K edge

Figure 4
Ti$_{2.3}$ L edge

NK edge

457.5 eV

(i) TiN+BN

(ii) Ti+BN

Photon Energy (eV)