



ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

CONF-970302--19

An X-Ray Photoelectron
Spectroscopic Study of
the B-N-Ti System

Sudipta Seal, Tery L. Barr,
Natalie Sobczak, Ewa Benko,
and J. Morgiel

Accelerator and Fusion
Research Division

RECEIVED

JUL 31 1997

OSTI

March 1997
Presented at the
*Materials Research
Society Spring Meeting*,
San Francisco, CA,
March 31–April 4, 1997,
and to be published in
the Proceedings

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF THE B-N-TI SYSTEM*

Sudipta Seal¹, Tery L. Barr², Natalie Sobczak³, Ewa Benko⁴, J. Morgiel⁵

¹Advanced Light Source, Accelerator & Fusion Research Division, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

²Materials Engineering and Laboratory for Surface Studies, University of Wisconsin, EMS 574, 3200 N. Cramer Street, Milwaukee, WI 53211

³Foundry Research Institute, Cracow, 30-418, Poland

⁴Institute of Metal Cutting, Cracow 30-011, Poland

⁵Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Cracow, Poland

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098, and by the Polish American Sklodowska-Curie Joint Fund II in cooperation with the Ministry of Industry (Poland) and Office of International Affairs, National Institute of Standards and Technology (USA) under project No. MP/NIST-96-261.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

| | |
|--------------------------|----------------------|
| Light Source Note: | 29/11/96 17:47 |
| Author(s) initials: | <i>Sudipta Seal</i> |
| Group Leader's initials: | <i>J. M. Morgiel</i> |
| Date: | 10/12/97 |

An X-ray Photoelectron Spectroscopic Study of B-N-Ti Systems

Sudipta Seal¹, Tery L. Barr², Natalie Sobczak³, Ewa Benko⁴, J. M. Morgiel⁵
¹MS 7-222, Advanced Light Source, LBL, UC-Berkeley, Berkeley, CA 94720, USA,
 sudipta@csa1.lbl.gov

²Materials Eng. and Laboratory for Surface Studies, University of Wisconsin, EMS 574, 3200 N. Cramer St., Milwaukee, WI 53211, USA, terybarr@alpha2.csd.uwm.edu

³Foundry Research Institute, Cracow, 30-418, Poland, natalie@czapla.IOd.krakow.pl

⁴Institute of Metal Cutting, Cracow 30-011, Poland, Ewa.Benko@atena.ios.krakow.pl

⁵Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Cracow, Poland, nmmorgie@al.imim-pan.krakow.pl

ABSTRACT

Composite nitrides (such as BN, TiN) are widely used in various industrial applications because of their extreme wear and corrosion resistance, thermal and electrical properties. In order to obtain composite materials with these optimal properties, it is important to elucidate whether any chemical reactions occur at nitride/metal interfaces, e.g., those involving BN-Ti/TiN. Materials of interest include the deposition by PVD of Ti and TiN on BN substrates. Some of these systems were then subjected to varying degrees of physical and thermal alteration. Detailed X-ray photoelectron spectroscopy (XPS) has therefore been rendered of these interfaces using cross-sectional display and sputter etching. Resulting structural and morphological features have been investigated with transmission electron microscopy (TEM) and X-ray diffraction (XRD). Diffusion of the nitridation, oxynitride formation and interfacial growth are of general interest.

INTRODUCTION

Nitrides of various elements play a major role in today's industry, science and technology for their interesting and useful resilient properties. Cubic boron nitride (c-BN) which, similar to diamond⁽¹⁾ is thermodynamically stable under high pressure and high temperature, has unique characteristics, such as, high hardness (>50 Gpa), strength, chemical stability, wear resistance and chemical inertness. Thus the c-BN is expected to be a promising material which can have a wide range of usage in cutting tools and electronic device industries. Recent studies has been focused into manufacturing thin films of ternary compounds to improve the mechanical properties of binary coatings. In an attempt to improve the film/substrate adhesion and other mechanical properties, research is continuing into BN based transition metal coatings, including Ti-B-N. The inclusion of a transition metal in the coating introduces metallic bonding which may increase the probability of better adhesion between the coating and the substrate.⁽²⁾ Also TiN is widely accepted in industry on its own right as a surface coating because of its high hardness, good wear and corrosion resistance.⁽²⁻⁵⁾ The synthesis of Ti-B-N coatings has recently attracted considerable attention from many researchers who have adopted various chemical and plasma vapor deposition (CVD and PVD) techniques for preparing the coating.⁽⁶⁻¹³⁾ The phase diagram for Ti-B-N gives the composition for a particular stoichiometry at a thermodynamic equilibrium.⁽¹⁴⁾ However coatings deposited by PVD technique are considered to be in a non-equilibrium state due to the high quenching rates occurring during deposition.⁽¹⁵⁾

Some of the most important properties of these coatings occurs due to the presence of the resulting binary and ternary phases TiN, TiN_x, TiB₂, BN, TiB_xN_y.⁽¹⁴⁾ These multiphase systems are often analogous to bulk composite materials, i.e., generally showing better hardness and toughness properties than single phase materials. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS) and cross-sectional transmission electron microscopy (XTEM) methods have been used to characterize the interfaces.⁽¹⁴⁻¹⁷⁾ From these investigations, it appears that the nature of any adhesion is strongly related to the extent of any physicochemical interactions, that occurs at the interfaces,⁽²¹⁻²²⁾ but the information is often conflicting or incomplete from the point of view of characterization of both the spectra and the material composition.

The intention of this work was to explore the types of chemical interactions found in these B-N-Ti systems and further explore any changes in features during thermal treatment. Detailed

XPS has been rendered of these surfaces and interfaces using both sputtering and cross-sectional display to clarify the origin of the different phase components that comprise the Ti(2p), N(1s), B(1s), O(1s) levels in B-N-Ti systems. Also the structural and microstructural features of the BN-TiN based material were examined with an analytical transmission microscope and a x-ray diffractometer.

EXPERIMENTAL

In this study the substrate materials were cubic BN, prepared from h-BN by pressing the as received powder into preshaped 6 mm diameter and 2 mm thick disks and heating to a temperature of 2800°K, at a pressure of 9 GPa. The BN disks were then ion plated with Ti/TiN in a NNW6.6 coating apparatus with 3 cathodes (located in the Institute of Metal Cutting, Poland) using the arc PVD method.⁽²⁰⁾ Following ion 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 high vacuum furnace to identify surface modifications in the specimens.

Surface analytical spectra were generally performed on a Hewlett-Packard (HP) ESCA 5950A spectrometer with a high-resolution X-ray monochromator, using Al K α (1486 eV) radiation, with the analyser operating in the constant analyzer pass energy mode. The spectrometer was calibrated using 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 electron flood gun adjustments and fixing the C(1s) binding energy of the hydrocarbon part of the adventitious carbon line at 284.6 eV.⁽²⁰⁾ We have measured the Ti(2p), B(1s), O(1s), N(1s) of the deposited layers and the interfaces (Ti/TiN on BN) to examine the chemical interactions between BN and Ti/TiN. For calibration XPS was also carried out on standard (i.e., pure and clean) samples of Ti, TiN, BN and TiB₂. The samples were also sputtered with 2.5 KeV argon ions to determine the chemical state of the subsurface and interfacial features of the deposited film as a function of depth. Curve fitting program of the data was performed after a Shirley background subtraction⁽²⁴⁾, using a 2 point box curve fitting program with a Guassian/Lowrentzian product function.

Additionally, x-ray diffraction studies using Philips PW 1710 X-ray diffractometer) were carried out on these samples to determine the film crystallinity and structure. Microstructural observations and chemical microanalysis were also performed in a Philips CM20 TWIN (200 kV) transmission electron microscope equipped with a Link Exl 1 energy dispersive spectroscopy system.⁽²⁵⁾

RESULTS AND DISCUSSION

TEM observations of thin films have shown that the matrix of the material is mainly composed of tightly packed TiN and BN grains (Figure 1). At the interface of BN and TiN, a thin layer of columnar grain structure has been observed. Selected area electron diffraction pattern and X-ray microanalysis confirmed this phase as a TiB₂ crystal lattice and exclude other boride or nitride phases.⁽²⁵⁾

The chemical state data obtained from XPS analysis of Ti-B-N films enables information regarding the phase composition of the material. XPS was employed to investigate the changes in chemical states in Ti(2p), N(1s), B(1s), O(1s) in Ti-B-N systems at 1000°C and 1400°C for 2 hours respectively. The Ti(2p) XPS spectra (not shown) of Ti-BN (1000°C) revealed the expected presence of TiO₂ on the surface due to air induced surface oxidation of the Ti. Neither boron (B) or nitrogen (N) was found on the surface. When heated to 1400°C for 2 hrs, distinct changes in the XPS (Ti(2p), N(1s), B(1s), O(1s)) spectra exhibits the formation of various phases such as, TiB₂, TiB_xN_y, TiN, BN, some oxynitrides,^(26,27) as well as the oxides of B and Ti (Table 1, Figure 2a and 3).

In conjunction, XRD studies also confirms the material crystallinity and formation of these phases occurred during the growth process.⁽²⁰⁾ This suggests that at higher temperatures B and N species have diffused towards the surface and reacted with Ti, forming TiN and TiB₂ compounds, and also with O₂ producing B₂O₃ (Figure 3). The B(1s) peak separation between TiB₂ and BN is sufficient large enough to identify the presence of these chemical states. XPS N(1s) spectrum (not

shown) at 399.13 eV suggests the presence of weakly oxidised oxynitrides in the air oxidized layer. We also observed the presence of moderate amounts of TiO_2 and B-O containing species in the surface layer. The boron oxide peak has a higher binding energy than that of BN due to the more ionic nature of B-O bonds (compared to B-N). Different chemical species forming in the B-N-Ti system during heat treatment have drawn various interpretation in the literature.⁽²⁶⁻²⁹⁾ Ermolieff et al.,^(26,27) suggested an oxidation of suboxides at the interface between the oxide and the nitride, while Ernesberger et al.,⁽²⁹⁾ label oxinitrides as the principal species resulting from TiN oxidation.

Table 1: Binding energies (± 0.2 eV) for representative Ti-B-N deposition systems. Binding energies are referenced to C(1s) = 284.6 eV.

| No | Material | $\text{Ti}(2\text{p})_{3\text{p}}$ (eV) | $\text{N}(1\text{s})$ (eV) | $\text{B}(1\text{s})$ (eV) | $\text{O}(1\text{s})$ (eV) |
|----|---------------------|---|---|---|--|
| | X=1000C Y=1400C | ¹ Ti ⁴⁺ , ² TiN _{x(unsat)} ³ TiN, ⁴ TiB ₂ ⁵ Ti-oxynitrides, | ¹ TiN, ² TiN _{x(unsat)} ³ BN, ⁴ BN _y O _z , ⁵ Ti-oxynitrides | ¹ TiB ₂ , ² BN, ³ TiB _x N _y , ⁴ BN _y O _z , ⁵ BO, ⁶ B ₂ O ₃ | ¹ Ti-O, ² B-O, ³ Si-O, ⁴ Oxynitrides, ⁵ OH/C-O-C |
| 1 | ^x Ti+BN | ¹ 458.97 | Nil | Nil | ¹ 530.3, ³ 532.66 |
| 2 | ^x Ti+BN | ¹ 458.8, ³ 455.5, ⁴ 454.5, \uparrow TiB _x N _y | ¹ 397.25, ³ 398.1, ⁴ 399.13 | ¹ 187.57, ² 190.38, ³ 189.44, ⁴ 191.8, ⁵ 192.4, ⁶ 193.1 | ¹ 530.22, ² 532.8, ⁴ 530.5-531.6 |
| 3 | ^x TiN+BN | ¹ 458.8, ² 456.5 ³ 455.5 | ¹ 397.3, ² 396.8, ⁵ 400.2-398.3 | Nil | ¹ 530.07, ³ 532.8, ⁴ 530.8-531.5 |
| 4 | ^x TiN+BN | ¹ 458.2, ² 456.7 ³ 455.6, ⁵ 457.2 (?) | ¹ 397.2, ² 396.2, ⁵ 398.5 | Nil | ¹ 529.92, ⁴ 530.7-531.8, ⁵ 533.8 |

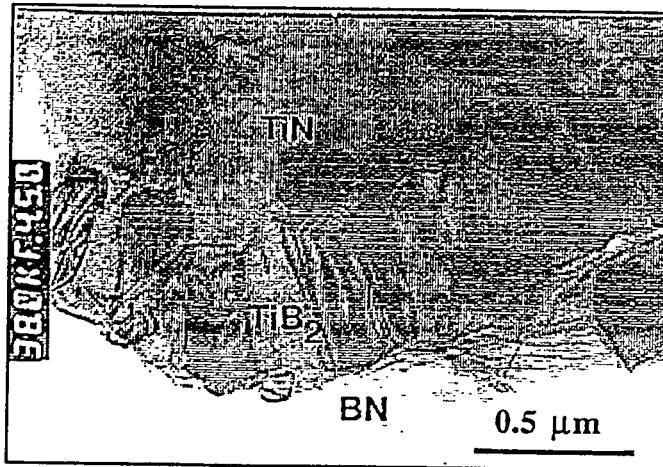


Figure 1: TEM micrograph showing columnar layer of TiB_2 grains between the TiN and BN.

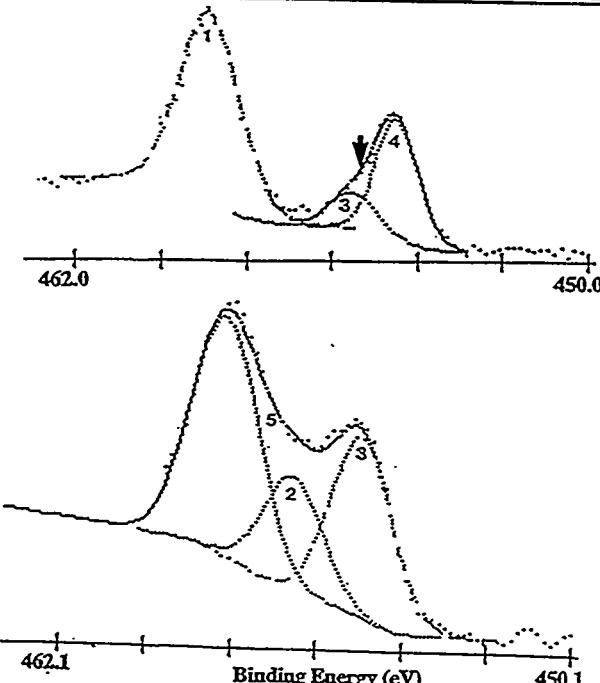


Figure 2. XPS $\text{Ti}(2\text{p})$ spectra: (a) Ti+BN and (b) TiN+BN (treated at 1400°C, 2 hrs). Possible peak identifications: (1) TiO_2 , (2) TiN_x , (3) TiN and (4) TiB_2 , (5) Ti-oxynitride (may be), \uparrow TiB_xN_y , $x=1.8$

The XPS binding energies of 1000°C and 1400°C heat treated BN+TiN systems are also listed in Table 1. From Table 1, from the resulting N(1s) lines, we find two types of chemical species for N atoms in TiN film: (1) one, designated as TiN, with apparently stoichiometric bonds with titanium (Ti atoms surrounded by N atoms: $\text{N}(1\text{s})_{\text{B.E.}} = 397.3-397.2$ eV for 1000°C and

1400°C respectively) and (2) one, designated as TiN_x , with non-stoichiometric N-Ti bonds (i.e., $\text{N}/\text{Ti} > 1$ and different bonding due to the excess nitrogen) ($\text{N}(1s)_{B.E.} = 396.8$ and 396.2 eV for 1000°C and 1400°C respectively). The 0.6 eV downfield BE shift of N(1s) in TiN_x (1400°C) is due to a nitrogen composition difference, 1.8 N atoms (i.e., $\text{TiN}_{1.8}$) in the former as compared to 1.5 N atoms (i.e., $\text{TiN}_{1.5}$) in the latter case. The fraction of N with non-stoichiometric bonds with Ti may be one of the principal factors for determining film quality. It was shown that coatings with the best tribological properties contained the smallest fraction of "excess" nitrogen bonds with titanium.^(30,31) No TiN_x -type compounds were found in the Ti+BN system. Only nitrogen seems to be sensitive to the non-stoichiometry, and therefore, Ti+BN may exhibit better tribological properties than $\text{TiN} + \text{BN}$ due to the absence of TiN_x in the former case. Also, the intensity of N in the 1000°C treated BN+TiN sample is 4 times lower than the one treated at 1400°C. This suggests that the mobility of N atoms is higher at higher temperature to form the titanium nitrides. Also, the probability of surface TiB_2 formation in TiN/BN is minimal and is due to the less availability of free Ti atoms (which are strongly bonded to N atoms in TiN). In all of the coated samples XPS Si(2p) spectra shows a definitive surface presence of Si-O, Si-C and Si_3N_4 which has apparently occurred during the heat treatment of these samples in a quartz tube, indicating migration of Si from the quartz tube to the sample surface.

In order to analyze the chemical state of the subsurface region, Ti coated BN sample was repeatedly sputtered with Ar^+ ions at 2.5 KeV followed by XPS analysis of the resulting surface. After ion etching, the level of carbon (primarily adventitious) concentration decreased dramatically with time (Figure 4), but the O(1s) line remained significant, suggesting a diffusion of oxygen throughout the entire film during heat treatment. The contribution of oxygen containing phases is maximal at the surface and decreases to a small extent with depth. A decrease in the silicon concentration following modest sputtering, suggesting it to be a surface impurity. From the XPS quantification and the binding energy of Ti(2p) (458.9 eV) pertains to that of TiO_2 on the surface of the implanted Ti film. After Ar^+ ion sputtering for 6 minutes (~ 6 Å) the very thin layer of TiO_2 was removed and the Ti(2p) binding energy suggested primarily TiN. The atomic % of Ti(2p) and N(1s) calculated by XPS were listed in Figure 4. During 1 minute of sputtering (~ 10 Å) we found the presence of oxynitrides that disappeared after 50 minutes of sputtering (~ 500 Å), apparently resulting in a phase separation into stoichiometric and non-stoichiometric TiN, plus some interfacial TiO_2 . Earlier, studies have proposed the presence of suboxides at the interface between the oxide and the nitride.⁽²⁸⁾ In our case we find XPS evidence of TiN films oxidized to TiO_2 with a suggested sublayer of Ti-oxynitrides, a similar feature was also reported by other researchers.⁽²⁹⁾ After sputtering off ~ 2300 Å, B was detected (Figure 4). With further sputtering the B and N content increased while the Ti content in the film decreased. This suggests the near completion of any Ti and N reaction. However in this region, a mixture of TiB_2 ($\text{B}(1s)_{B.E.} = 187.57$ eV), TiB_xN_y ($\text{B}(1s)_{B.E.} = 189.44$ eV) and BN ($\text{B}(1s)_{B.E.} = 190.38$ eV) was found to be present, suggesting that with depth the Ti-N reaction is replaced by a reaction between Ti and B. At lower temperature of treatment, the formation of TiB_2 is well underneath the surface, whereas at higher heat treatment temperatures the formation of the boride phase is most likely to appear on the surface. The resulting metallic boride provides high hardness and resistance to corrosion. From the XPS analysis we found that the inner region of the coating was primarily TiN and TiN_x ($x > 1$), while the region near the substrate (BN) /coating (Ti) interface consists of a mixture of TiB_xN_y , TiB_2 layer along with boron oxide.

As a result of ion bombardment, the line shape and FWHM are changed in all of the Ti(2p) spectra. These changes are caused by the appearance of additional chemical states, which, based on analogy with previous studies,⁽³⁰⁾ were characterized as Ti^{+3} , Ti^{+2} and is perhaps due to sputter induced reduction reactions. Deeper in the film (> 8000 Å), the TiB_2 phase disappears, while the relative XPS quantification of the BN phase increases. In addition the relative amount of TiN_x (or TiN) decreases with increasing depth of sputtering.

CONCLUSION

XRD revealed the presence of crystalline TiN and TiB_2 phases in the Ti-B-N systems. TEM observation exhibited a compact structure in the TiN+BN systems showing the formation of TiB_2 at the BN/TiN interface. XPS analysis of 1000°C treated Ti+BN showed no TiN on the surface, but the formation of TiN and TiB_2 was evident during the 1400°C treatment, suggesting

the migration of boron to the surface at higher temperatures. Thus the thermal treatment do play an important role in the chemical interaction of Ti-B-N systems. Also XPS data indicated the formation of both stoichiometric TiN and nonstoichiometric TiN_x and oxynitrides on the surfaces of Ti/TiN coated BN substrates. XPS data of sputtered Ti+BN systems has enabled the clear identification of TiN and TiB_2 phases in the inner layer of the coating/substrate interfaces.

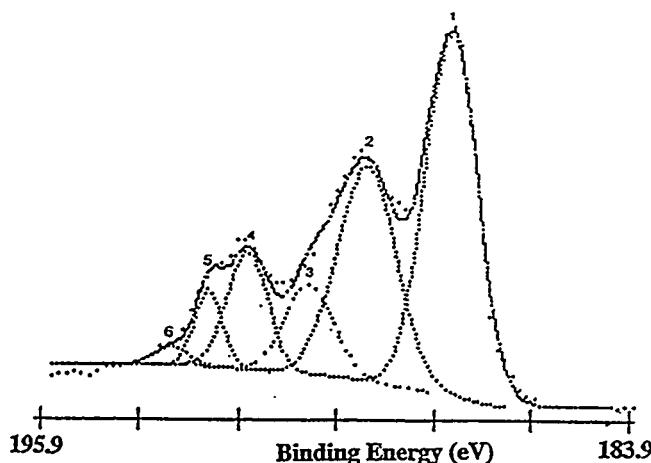


Figure 3: B(1s) spectra of Ti+BN treated at 1400°C, 2 hrs. Possible peak identifications: (1) TiB_2 , (2) TiB_xN_y , (3) BN, (4) BN_yO_z , (5) B-O and (6) B_2O_3 .

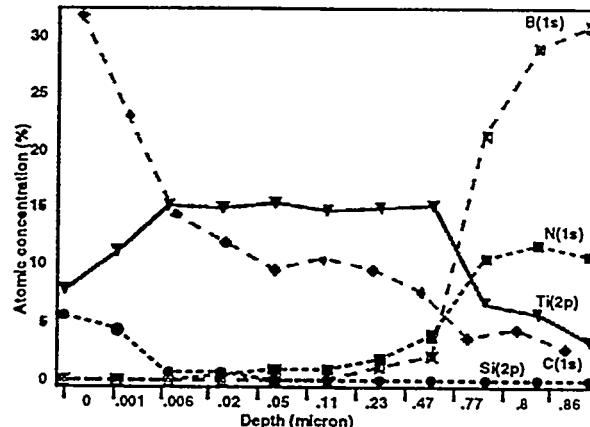


Figure 4: Approximate XPS sputter depth profile of Ti thin film deposited on BN substrate, heated at 1000°C for 2 hrs.

ACKNOWLEDGMENTS

This publication is based on the work sponsored by the Polish American Sklodowska-Curie Joint Fund II in cooperation with Ministry of Industry (Poland) and Office of International Affairs, National Institute of Standards and Technology (USA) under project N0. MP/NIST-96-261.

REFERENCES

1. F. P. Bundy and R. H. Wentorf, Jr., *J. Chem. Phys.* **38**, 1144 (1963).
2. Y. I. Chen and J. G. Duh, *Surf. Coat Technol.* **48**, 163 (1991).
3. J. G. Duh and J. C. Doong, *Surf. Coat Technol.* **56**, 257 (1993).
4. V. R. Parameswaran, J. P. Immarigeon and D. Nagy, *Surf. Coat Technol.* **52**, 251 (1992).
5. F. Hohl, H. R. Stock and P. Mayr, *Surf. Coat Technol.* **54/55**, 160 (1992).
6. J. L. Peytvi, A. Lebugle, G. Montel and H. Pastor, *High Temperatures-High Pressures* **10**, 341 (1978).
7. H. Karner, J. Laimer, H. Stori and P. Rodhammer, 12th Plansee Seminar, 1989, Vol. 3, Tirol, Austria, 8-12 May (1989).
8. J. Aromma, H. Ronkainen, A. Mahiout, S. P. Hannula, A. Leyland, A. Matthews, B. Matthews and E. Broszeit, *Mater. Sci. Eng. A* **140**, 722, (1991).
9. C. Mitterer, M. Reuter and P. Rodhammer, *Surf. Coat. Technol.* **41**, 351, (1990).
10. W. Herr, B. Matthews, E. Broszeit and K. H. Kloss, *Mater. Sci. Eng. A* **140**, 616 (1991).
11. O. Knmotek, R. Breidenbach, F. Jungblut and F. Loffler, *Surf. Coatings Technol.* **43/44**, 107 (1990).
12. G. Dearnley and A. T. Peacock, UK patent GB 2.197.346, A and B (1988).
13. T. Friesen, J. Haupt, W. Gissler, A. Barna and P. B. Barna, *Vacuum*, **43**, 657 (1992).

14. H. Nonotny, F. Benesovsky, C. Brukl and O. Schob, *Mh. Chem.* **92**, 403 (1961).

15. H. Holleck, *J. Vac. Sci. Technol. A* **4**, 2661 (1986).

16. A. Erdemir and C. C. Cheng, *Ultramicrosc.* **29**, 266 (1989).

17. A. Erdemir and C. C. Cheng, *J. Vac. Sci. Technol. A7*, 2486 (1989).

18. A. Erdemir and C. C. Cheng, *Surf. Coat. Technol.* **41**, 285 (1990).

19. C. C. Cheng, A. Erdemir and G. R. Fenske, *Surf. Coat. Technol.* **39/40**, 365 (1989).

20. S. Seal, T. L. Barr, N. Sobczak and E. Benko, *JVST*, (to be published).

21. U. Helmersson, B. O. Johansson, J. E. Sundgren, H. T. G. Hentzell and P. Billgren, *J. Vac. Sci. Technol. A3*, 308 (1985).

22. D. S. Rickerby and R. B. Newbery, in *Proceedings of IPAT 87* (CEP Consultants, Brighton, Edinburgh, UK, 1987), 224 (1987).

23. T. L. Barr and S. Seal, *J. Vac. Sci. Tech. A13*, 1239 (1995).

24. T. L. Barr, *Modern ESCA: The Principles and Practice of X-Ray Photoelectron Spectroscopy*, CRC Press, Boca Raton, (1994).

25. J. Morgiel, E. Benko, *Materials Letters* **25**, 49 (1995).

26. J. Halbritter, H. Leiste, H. J. Mathes and P. Walk, *J. Anal. Chem.* **341**, 320 (1991).

27. K. S. Robinson and P. M. A. Sherwood, *Surf. Interface. Anal.* **6**, 261 (1984).

28. A. Ermolieff, M. Girard, C. Raow, C. Bertrand and T. M. Duci, *Appl. Sur. Sci.* **21**, 65 (1985).

29. C. Ernsberger, J. Nickerson, A. E. Miller and J. Moulder, *J. Vac. Sci. Technol. A3*, 2415 (1985).

30. J. S. Colligon, H. Kheyrandish, L. N. Lesnervsky, A. Naumkin, A. Rogozin, I. I. Shkarban, L. Vasilyev and V. E. Yurasova, *Surf. Coat. Technol.* **70**, 9 (1994).

31. R. D. Arnell, J. S. Colligen, K. F. Minnebaev, V. E. Yurasova, *Vacuum*, **47**, 425 (1996).

32. A. R. Gonzalez-Elipe, G. Munnera, J. P. Espinos and J. M. Sanz, *Surface. Sci.* **220**, 368 (1989).