Ti-B-N and Ti-B-O Scratch Resistant Weakly Conductive Transparent Coatings for Aerospace Applications

M. Ersoy and P.D. Hambourger, Cleveland State University, Cleveland, OH

ABSTRACT

Lunar dust is extremely hard and abrasive. It is considered a serious threat to transparent surfaces such as photovoltaic panels, lenses and spacesuit faceplates used for robotic or human lunar exploration. Static electric charge causes the dust to stick to such surfaces. Abrasion resistant coatings with weak electrical conductivity are needed to meet this challenge. They may also have terrestrial applications, for example in desert environments. Tailorable conductivity is useful since the requirements for proper charge bleed off depend on the application. Due to the harsh environment, it is unlikely that conventional transparent semiconductors such as ITO will be suitable.

Titanium nitriboride (Ti-B-N) and titanium oxyboride (Ti-B-O) are candidates; however, previous reports do not fully explore the tradeoff between transparency and conductivity. This paper presents data that fill some of the gaps.

INTRODUCTION

Titanium diboride (TiB_2) is an opaque, highly-conductive material. Addition of nitrogen (N) or oxygen (O) increases transparency and resistivity [1-4]. At high N (O) content, Ti-B-N is a nanocomposite of titanium nitride and amorphous boron nitride, while Ti-B-O is an amorphous solid solution of titanium and boron oxides [3]. At high N (O) content, the films have high visible-light transmittance (~0.8), with a cutoff in the near-ultraviolet similar to wide-bandgap materials, and are nonconductive [1].

Previous workers mapped the resistivity of Ti-B-N and Ti-B-O [3, 4] over a rather wide range of N (O) concentrations and showed that it can indeed be tailored over many orders of magnitude. The visible transmittance of weakly-conductive Ti-B-O has also been measured and correlated with resistivity [4]. However, the observed transmittances were < 0.25 in 100 nm thick films, possibly due to insufficient oxygen content.

In this work, Ti-B-N and Ti-B-O films with a wide range of N (O) content were prepared by magnetron sputtering. Most substrates were polycarbonate, which is typically used in spacesuit faceplates. We obtained sheet resistances spanning a wide range of $10^3 – 10^{11}$ ohms per square (corresponding to bulk resistivities of $10^{-2} – 10^6$ ohm cm). Visible transmittance data are also presented.

EXPERIMENT

Films ~80 nm thick were deposited by rf (13.56 MHz) magnetron sputtering from 5.1 cm diameter sources with target-to-sample distance of ~10 cm. Different methods were used for Ti-B-N and Ti-B-O.

Ti-B-N was deposited from two simultaneously-operating sources, one with a titanium target, and the other with a boron nitride (BN) target. The atmosphere was pure argon at ~7 mTorr pressure. The BN/Ti ratio was varied by rf power adjustments. This ratio was estimated by separate sputtering rate measurements on each source. It should be noted that previous workers [1-4] used a single TiB_2 target and admitted controlled amounts of nitrogen to the chamber.

Ti-B-O was deposited by the usual reactive sputtering method [1-4], using a single TiB_2 target and two mass flow controllers, one feeding pure argon, the other a 10% oxygen/90% argon mixture. Total pressure in the chamber was kept at ~7 mTorr. The partial pressure of oxygen (PO_2) was estimated from the readings of the mass flow controllers and total pressure gauge (Pirani).

In both methods, the background pressure in the chamber with gas flows turned off and pump throttle valve set as for deposition was ~2-3x10^{-5} Torr.

Sample thickness was determined by a single quartz crystal microbalance (QCM) located near the sample. The QCM was calibrated by optical interference measurements on a titanium dioxide (TiO_2) film.

All Ti-B-N samples and many Ti-B-O samples were deposited on commercial-grade polycarbonate. Some Ti-B-O samples were deposited on borosilicate glass cut from microscope slides.

Sheet resistance measurements were made at room temperature in ambient atmosphere by the four-inline-probe method. Guarded cabling and high input resistance DC electrometers minimized errors due to the high resistance of some samples.

The largest measureable sheet resistance was ~10^{12} ohms per square with polycarbonate substrates and ~$5x10^{10}$ ohms/square with glass substrates due to slight conduction of the glass. Optical transmittance measurements were made over the wavelength range 200-900 nm using a broadband UV-visible light source and a fiber-optic grating spectrometer. Except where noted, data were not corrected for substrate absorption.

RESULTS

Resistivity

Ti-B-N sheet resistance is plotted vs B/Ti atomic ratio in Figure 1. Since the target is the only source of nitrogen, increased B/Ti ratio also implies increased nitrogen content. Thus the behavior shown here is consistent with the effect of nitrogen gas in previous experiments [1-4].

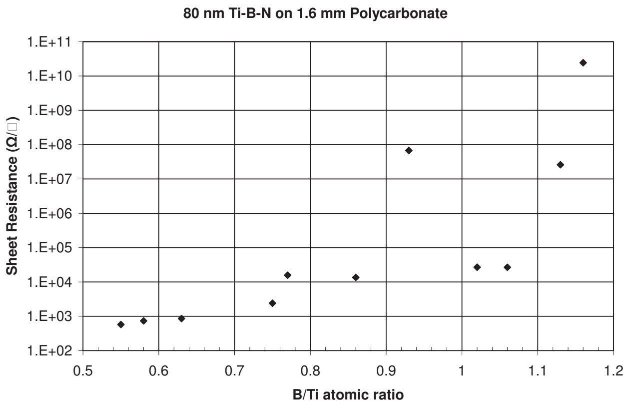

Figure 1: Sheet resistance of Ti-B-N films vs B/Ti atomic ratio (also ~ the N/Ti ratio).

Ti-B-O sheet resistance is plotted vs oxygen partial pressure in Figure 2. Despite the strong dependence on PO_2, it was relatively easy to tune the resistance over a wide range by adjusting the mass flow controllers. The systematic dependence on substrate material at high PO_2 is most likely due to the slight conductivity of the glass substrates. However, the apparent drop-off in sheet resistance at PO_2 > 0.18 mTorr is of unknown origin. It may be related to the influence of PO_2 on titanium/boron ratio noted by previous workers [3, 4].

Transparency

Optical transmittance of Ti-B-N films on polycarbonate is plotted vs wavelength in Figure 3. Relatively high transmittance is achieved, but only in films with very high sheet resistivity. The high cutoff wavelength of polycarbonate (~420 nm) prevents evaluation of the films' behavior below that wavelength.

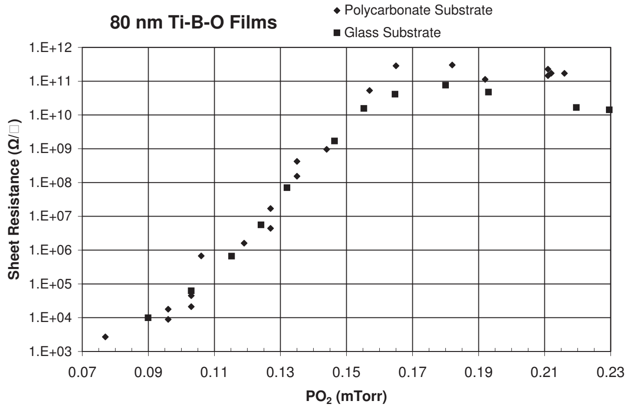

Figure 2: Sheet resistance of Ti-B-O films vs partial pressure of oxygen during deposition.

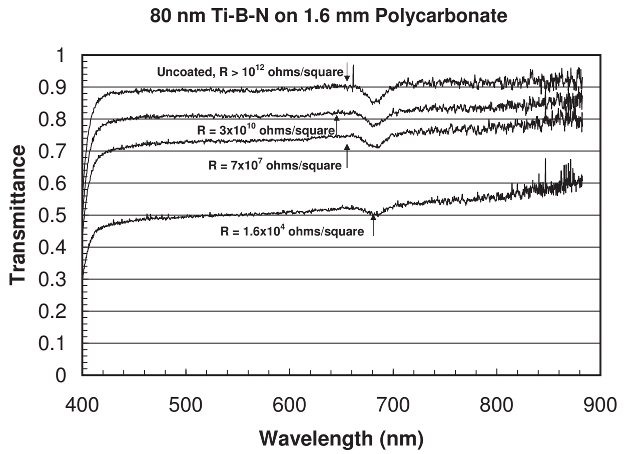

Figure 3: Optical transmittance of Ti-B-N coatings on polycarbonate. Sheet resistance (R) of each film is shown.

Transmittance data for Ti-B-O films on polycarbonate are shown in Figure 4. Results are similar to those of Ti-B-N, but the transmittance of Ti-B-O appears to be slightly smaller than that of Ti-B-N with similar sheet resistance.

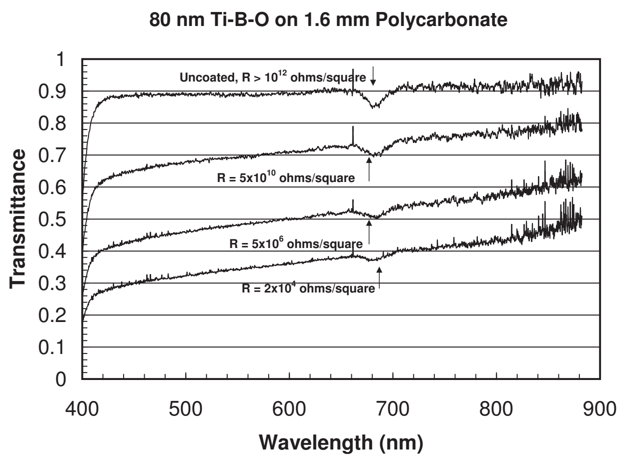

Figure 4: Optical transmittance of Ti-B-O coatings on polycarbonate.

For comparison, transmittance data are shown in Figure 5 for titanium-rich titanium dioxide ($Ti_{1+x}O_2$), which is another candidate for lunar exploration use [5]. Figures 4 and 5 show that Ti-B-N offers somewhat higher transmittance than $Ti_{1+x}O_2$ with similar sheet resistance. This arises, at least in part, from the smaller reflectivity of Ti-B-N, which has a lower index of refraction than TiO_2 [1].

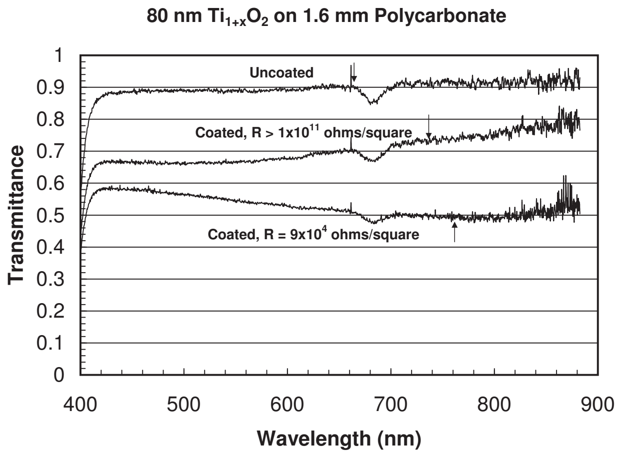

Figure 5: Optical transmittance of titanium-rich TiO_2 coatings on polycarbonate.

Adhesion

Ti-B-N and Ti-B-O films with high transparency tended to spall and separate from the substrate. The problem was much more severe with polycarbonate than with glass substrates. This may be related to the dramatic reduction in hardness at high N (O) concentrations noted by previous workers [3, 4] and could be a limiting factor in the use of these materials. Experiments with a silicon dioxide adhesion layer were unsuccessful.

CONCLUSIONS

We have prepared titanium nitriboride and oxyboride films with a wider range of transparency and electrical conductivity than previously available. Some of the samples have sufficient transparency for application to windows and faceplates for lunar exploration, provided their conductivity is sufficient for elimination of electrostatic charge. However, spalling of high-transparency samples may be a problem unless a suitable adhesion layer can be found.

Further experiments are planned to vary independently the concentration of titanium, boron and nitrogen/oxygen and study its effects on electrical, optical and mechanical properties of the films.

ACKNOWLEDGMENTS

We thank Dr. Juan H. Agui for many helpful discussions. Financial support from NASA Glenn Research Center Purchase Order NNC07CV16P and the Cleveland State University Summer Undergraduate Research Program is gratefully acknowledged.

REFERENCES

1. P.M. Martin, D.C. Stewart, W.D. Bennett, E. Savrun, M.M. Opeka, and L.F. Johnson, "Optical Properties of Magnetron Sputtered Boride, Oxiboride, and Nitriboride Coatings," *40th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, pp. 187-191, 1997.

2. Peter M. Martin, "Promising Thin Film Boride Materials," *Vacuum Technology & Coating*, p. 36, February 2007.

3. J.F. Pierson, V. Chapusot, A. Billard, M. Alnot, and Ph. Bauer, "Characterisation of reactively sputtered Ti-B-N and Ti-B-O coatings," *Surface and Coatings Technology*, 151-152, 526, 2002.

4. J.F. Pierson, M. Alnot, Y. Fagot-Revurat, and J. Jolly, "Influence of the oxygen flow rate on the properties of reactively sputtered Ti-B-O films," *Surface and Coatings Technology*, 174-175, 1145, 2003.

5. Juan H. Agui, Paul Hambourger, Jordan Wirfs-Brock, John M. Griffin, Jason T. Hindall, and Ashraf Morgan, "Durable Coating Technology for Lunar Dust Protection and Mitigation," SAE Paper # 2006-01-2205, Society of Automotive Engineers, July 2006.