Proceedings of the International Congress on Advances in Applied Physics and Materials Science, Antalya 2011

Effect of the Plasma Deposition Parameters on the Properties of Ti/TiC Multilayers for Hard Coatings Applications

N. Saoula[a,*], K. Henda[a], R. Kesri[b], S. Shrivastava[c], R.M. Erasmus[c] and J.D. Comins[c]

[a]Plasma Discharges Group, DMIL, CDTA, P.O. Box 17, Baba hassen, Algiers, Algeria

[b]LECTCM, USTHB, P.O. Box 32, El Alia, BabEzzouar, Algiers, Algeria

[c]Department of Physics, University of the Witwatersrand, Johannesburg, Wits2050, South Africa

Titanium carbide (TiC) hard coatings have been obtained on steel and silicon substrates by rf magnetron sputtering process. Two layer coatings have been deposited in order to improve adhesion on steel. The lower layer was titanium metal and the upper TiC layer was obtained by reactive sputtering of the titanium target in Ar and methane gas mixture. The study confirmed that the TiC layer composition depends on the reactive sputtering gas composition and substrate bias voltage. Film microhardness was measured by microindentation. Measurement results showed that the hardness coating depends on the microstructure of our coatings and the polarization of bias substrate is an important parameter to control the microstructure.

PACS: 81.15.Cd, 68.35.Ct, 68.55.–a, 68.37.Ps

1. Introduction

Transition metal carbides, such as TiC, characterized by short bonds, high hardness, high strength and high thermal and chemical stability, are widely used as wear-resistant materials in, for example, carbide cutting tools [1–4].

Titanium carbide (TiC) thin films have been classically used as protective hard coatings due to the good mechanical properties: high hardness, corrosion resistance, and low wear properties, that sustained up to 400 °C. Recently, this material has increased its technological interest because of its use as composite coatings TiC–C [5–7].

For the deposition of titanium carbide, several processes are used: chemical vapour deposition (CVD), plasma assisted chemical vapour deposition and physical vapour deposition (PVD). Different physical vapour deposition processes for TiC at low temperatures have been used through the years [8–10].

Sputtering deposition is a PVD process that is increasingly used in industrial hard coating deposition because it is a low temperature process and it uses unpolluting products. In the present work, rf magnetron sputtering process has been used to obtain Ti/TiC bilayer coatings on substrates. The sputtering was carried out from a pure titanium metal target and using pure Ar or Ar/CH_4 mixture as sputtering gas. The Ti intermediate layer was deposited in order to improve the adhesion of the TiC film to the substrates. In previous work [11, 12] we were interested in the optimisation of the deposition conditions in order to obtain good quality layers and good adhesion. It was found that the bilayers were more adhesive to the alloy than the monolithic films [11, 13]. We found that Ti interlayers have played important role during the growing of the outer layer grains, in fact the titanium grains serve as nuclei. The roughness of Ti films depends on substrate bias voltage. When reaching a high substrate bias voltage, the adhesion of the film seems poor.

However, substrate bias voltage corresponding to −25 and −50 V gives more adherent films. So for this work, the Ti layer is deposited on the steel substrate by sputtering the Ti target with pure Ar gas under fixed parameters (power: 100 W, argon pressure: 10^{-2} mbar). After the prefixed deposition time of 20 min, the Ar gas is substituted by an Ar/CH_4 mixture without any intermediate step [14].

The coatings have been analyzed in their composition in order to determine the gas mixture proportion and the reactive sputtering parameters that allow the obtention of the optimal TiC film. The bilayer coatings have been characterized in their hardness.

2. Experimental details

The deposition system used was a rf magnetron sputtering working at a rather high sputtering gas pressure and at a high current density (Table). The sputtering cathode was thick pure titanium target and was continuously water cooled. The substrates were located at distance of 5 cm. The sputtering gases were Ar or Ar/CH_4 mixture in the case of reactive sputtering. The total chamber pressure and the relative gas fluxes were controlled by separate mass flow controllers. Coatings

* corresponding author; e-mail: nsaoula@cdta.dz

were deposited onto substrates, which were previously polished and ultrasonically cleaned in alcohol and acetone. The target and the substrates were separately pre-sputtered in Ar plasma during 10 min before deposition. In all the runs, the substrate was not heated. Films' morphology was studied by atomic force microscopy (AFM).

TABLE

Sputtering conditions for the deposition of Ti/TiC coatings.

target	pure Ti metal
target–substrate distance	5 cm
sputtering gas	Ar
reactive sputtering gas	CH_4
substrate temperature	not heated
sputtering gas pressure	20 mTorr
sputtering parameters	50–150 W
substrate bias	$0 \div -100$ V

3. Results and discussion

The coatings are uniform and have very low average and roughness values which were found to be in the range of 20–120 nm. The pure Ti deposition process presents the highest deposition rate (96 nm/min). Figure 1 shows the deposition rate as function of the gas composition (%CH_4) and power of the deposition. The deposition rate decreases when the amounts of CH_4 in gas mixture increase. When the entire target surface is covered with the compound material, the target is said to be poisoned. It is possible to reactively sputter compound materials from a poisoned target, but the rate of deposition is usually very low compared to the elemental deposition rate for the same amount of power delivered to the target. Obviously, the extent of reduction of deposition rate also depends on the sputtering yield. Several works present their results in similar effects that use reactive gas (N_2, CH_4, or C_2H_2) [15–18]. Moreover, increase of the RF power applied to the titanium target causes an increase in deposition rate. When the applied power is higher, the incident ions increase on the target resulting in a decrease of sputtering yield, heating of the target caused by increase of the self-polarization of the target.

The deposition rate of the coating was also measured as a function of substrate bias as shown in Fig. 2. The deposition rate decreases significantly with the application of bias to substrate. At low bias voltages (−25 V), the deposition rate was approximately 10 nm/min. At a bias of −100 V, the deposition rate dropped by 50%. The polarization of the substrate is an important parameter for the quality of hard coatings. Indeed, the polarization has a strong influence on the morphology of the coating (densification), but also on the mechanical properties (internal stress, hardness etc.). Thus, for the development of our coating of TiC, it is necessary to determine the

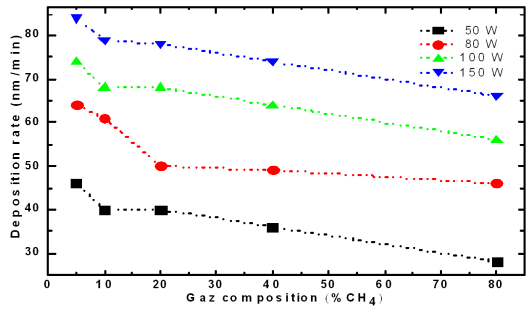

Fig. 1. Deposition rate versus gas composition (%CH_4).

optimal bias applied at the substrate holder. For this series of experiments the processing parameters are presented in Table. The evolution of the hardness of TiC as a function of substrate bias is shown in Fig. 3.

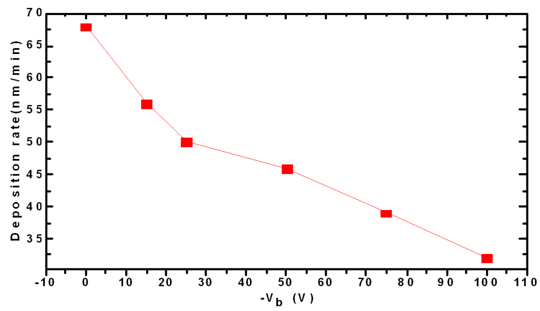

Fig. 2. Deposition rate versus bias substrate.

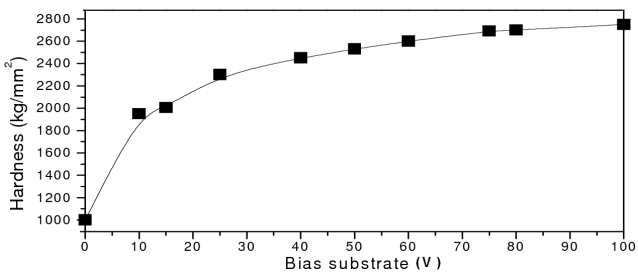

Fig. 3. Variation of hardness as a function of substrate bias TiC.

There is an increase of hardness with bias voltage, which observation is in agreement with the work of Kondo et al. [17]. When bias is applied to the substrate, the number of ionized particles on the substrate increases and therefore causes increase of the number of collisions at the substrate by ions of argon and methane [20]. This new organization is accompanied by an increase in the densification of the layer.

Figure 4 shows AFM images of layers of titanium carbide produced without bias (a) and with substrate bias (b) (−80 V). The increase in hardness is caused by the decrease of grain size with the bias voltage.

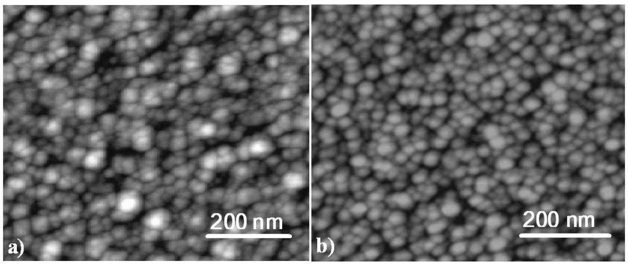

Fig. 4. AFM images of layers of titanium carbide produced without bias (a) and with substrate bias (b) (−80 V).

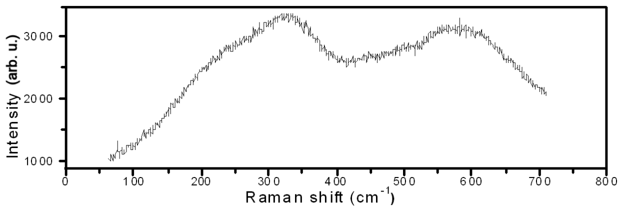

Fig. 5. Typical Raman spectra of titanium carbide.

Figure 5 shows the typical Raman spectra of the TiC thin film deposited at −80 V. Two major doublets ranging from 300 to 390 cm^{-1} and 560–620 cm^{-1} have been identified corresponding to the acoustic modes and optical modes spectral characteristics of titanium compounds. We notice that the band around 1100 to 1700 cm^{-1} characteristic of the carbon phase hydrogenated has not been revealed.

4. Conclusion

In summary, a magnetron sputtering has been used to deposit TiC layers at room temperature and low pressure. The deposition rate decreases when the amounts of CH_4 in gas mixture increase. The deposition rate is low, once in the poisoned state, the process is very stable.

The mechanical properties were found to depend on the roughness layer. The application of a sufficient negative bias voltage V_b on the substrates during reactive rf magnetron sputtering of titanium greatly improves the hardness of the films and the nature of the coating.

In the case of high substrate bias, smoother and denser films are produced. The increase of substrate bias changes the preferred orientation of the films and their hardness.

References

[1] A. Mani, P. Aubert, F. Mercier, H. Khodja, C. Berthierd, P. Houdy, *Surf. Coat. Technol.* **194**, 190 (2005).

[2] D. Nilsson, F. Svahn, U. Wiklund, S. Högmark, *Wear* **254**, 1084 (2003).

[3] W. Wu, J. Ting, *Thin Solid Films* **420**, 166 (2002).

[4] D. Martinez-Martinez, C. Lopez-Cartes, A. Justo, A. Garcia-Luis, M. Brizuela, J.I. Onate, *J. Vac. Sci. Technol. A* **23**, 1732 (2005).

[5] A.A. El Mel, E. Gautron, C.H. Choi, B. Angleraud, A. Granier, P.Y. Tessier, *Nanotechnology* **21**, 5603 (2010).

[6] L.I. Svistun, T.M. Pavlygo, D.V. Dmitrenko, *Russian Metallurgy (Metally)* **2009**, 237 (2009).

[7] M. Antonov, I. Hussainova, J. Pirso, K. Juhani, M. Viljus, *Estonian J. Eng.* **16**, 264 (2010).

[8] L.E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York 1971.

[9] S.T. Oyama, *The Chemistry of Transition Metal Carbide and Nitrides*, Blackie Academic and Professional, London 1996.

[10] H.O. Pierson, *Mater. Manuf. Proc.* **8**, 519 (1993).

[11] N. Saoula, K. Henda, R. Kesri, *AIP Conf. Proc.* **1047**, 256 (2008).

[12] N. Saoula, K. Henda, R. Kesri, *Mater. Sci. Forum* **609**, 117 (2009).

[13] T. Sonoda, S. Kotake, A. Watazu, K. Katou, T. Asahina, *Sil. Ind. Special Issue* **69**, 173 2005.

[14] N. Saoula, K. Henda, R. Kesri, *Adv. Mater. Res.* **227**, 156 (2011).

[15] G. Lemperiere, J.M. Poitevin, *Thin Solid Films* **111**, 339 (1984).

[16] L.J. Meng, M.P. Dos Santos, *Surf. Coat. Technol.* **90**, 64 (1997).

[17] L.F. Senna, C.A. Achete, T. Hirsh, F.L. Freire Jr, *Surf. Coat. Technol.* **94-95**, 390 (1997).

[18] T.W. Kang, C.Y. Hong, C.K. Chung, T.W. Kim, *Thin Solid Films* **342**, 184 (1999).