PVD protective multilayer coatings for tribological applications

Nowadays protective coatings are identified as a fundamental key to guarantee strong mechanical resistance, high hardness and high wear resistance for the coated components. As a consequence, continuous research is conducted to find innovative coating solutions with improved performances. To this aim, we report about the sputtering deposition of different multilayer structures made of zirconium and titanium nitrides layers (ZrN/TiN) on WC-Co substrates and milling tools, demonstrating an increased tool lifetime of about 30%

Antonella Rizzo, Maria Assunta Signore, Daniele Valerini

Rivestimenti protettivi a multistrato realizzati tramite PVD per applicazioni tribologiche

L'uso di rivestimenti protettivi è oramai considerato una chiave fondamentale per garantire forte resistenza meccanica, elevata durezza e alta resistenza all'usura dei componenti rivestiti. Di conseguenza, la ricerca di soluzioni di rivestimento innovative è in continuo sviluppo per raggiungere prestazioni sempre migliori. A tale scopo, in questo lavoro sono stati depositati, tramite sputtering, diversi rivestimenti multistrato di nitruro di zirconio e di titanio (ZrN/TiN) su substrati e inserti per fresatura in WC-Co, dimostrando un aumento della vita dell'utensile di circa il 30%

The concept of coating is well established nowadays and coatings are widely used for the design of opportune coating/substrate systems so as to improve their behavior in specific applications. Thus the use of coatings has been proven to be very effective for the development of novel thin film materials with tailored properties.

In particular, dealing with protective coatings for mechanical processing (cutting, milling, machining etc.) and aeronautical/aerospace applications (components for turbines to be used in harsh environments, elements exposed to strong frictions needing good antifretting properties etc.), the increasingly demanding technological requirements lead to find coatings which must work in very strict operational conditions (machining of very hard materials, high work speeds, high temperatures, harsh atmosphere etc.). Also, the needs for productivity drive the materials research to the realization and optimization of coating films which are capable of strongly increasing the lifetime of the coated tools. As a consequence, these tribological coatings must satisfy various requirements, like strong mechanical resistance, high hardness, high wear resistance, good thermal stability and strong adhesion to the coated tool.

In addition, the current and future strict environmental regulations (see, e.g., REACH [1], dealing with the Registration, Evaluation, Authorisation and Restriction of Chemical substances) affect the processes of development and improvement of materials technology, inducing the need to substitute many materials and

Antonella Rizzo, Maria Assunta Signore, Daniele Valerini
ENEA, Technical Unit for Brindisi Material Technologies Material Technologies Laboratory

substances presently used in a lot of technological processes. As an example, chromium and cadmium have to be removed from the present coating processes and they must be replaced by environmentally friendly materials and processes, assuring similar or better performances than the current state of the art. In this context, an environmentally sustainable technology is represented by the realization of conversion layers made by thin film coatings and the deposition of primers by physical vapor deposition (PVD) techniques. These techniques are very versatile methods for thin film deposition, thus allowing the tailoring of the film properties and the optimization of coatings according to the desired application.

To the purpose of coating optimization for mechanical applications, both coating material (e.g., nitride, carbide, oxide etc.) and coating structure (single layer, multilayers, gradient composition layer etc.) have to be considered. The first coating materials used for these applications were titanium carbide (TiC) and titanium nitride (TiN), realized by chemical vapor deposition (CVD) techniques[2]. Several other materials, like alumina (Al_2O_3), titanium aluminum nitride (TiAlN), diamond-like carbon (DLC) etc., were then studied and mainly realized by the more versatile PVD techniques. Transition metal nitrides, like titanium nitride (TiN) and zirconium nitride (ZrN), are among the most useful materials used as protective coatings, thanks to their high hardness, wear resistance and thermal stability[3]. The optimization of the coating structure can then improve the mechanical features of the coating, for example through the use of a multilayer structure made of thin layers (100 atomic layers or less) of different materials[4]. In this kind of structures, the atoms near the interfaces between two layers are displaced from their normal lattice positions and their strain energy is proportional to the shear modulus of the material, given by the ratio of shear stress to the shear strain. When a dislocation moves along a material, an energy barrier is encountered at the interface between a layer with a lower shear modulus and a layer with a higher shear modulus. As a consequence, in a multilayer structure the propagation of dislocations and cracks can be strongly reduced, thus increasing the resistance of the structure. Moreover, a proper tailoring of the micro- and nano-structure of the layers can further enhance this feature, since dislocations and cracks can be deflected and split at grain boundaries, with a consequent crack energy dissipation[5].

In the frame of multilayer structures, a very interesting solution for the realization of hard coatings is represented by the use of *superlattices*, formed by the alternation of ultra-thin layers (typically ~ 2-20 nm) of different materials, allowing to obtain coatings with performances exceeding those of the single constituent materials and of single layer coatings. In this kind of coating systems, the combination of features related to the multilayer structure and to the nanoscale dimensions can permit the development of coated components with superior performances[2]. Besides the block of dislocations at the layer interfaces, also periodical strain fields generated in the alternating layers of polycrystalline superlattice structures can help increase the hardness of multilayer coatings[5,6]. As a consequence the superlattice structures can sometimes present, for suitable combinations of different materials and bilayer periods, a strongly enhanced hardness, giving rise to the so-called "superlattice effect"[5].

Together with hardness enhancement, another significant issue to be considered for the realization of a good protective coating is represented by its adhesion to the substrate. Therefore, a buffer layer between substrate and protective coating is often used to improve the coating/substrate adhesion, which is particularly important for components that can reach high operational temperatures like, e.g., milling inserts. Indeed a proper buffer layer can reduce the formation of residual stress related to the different coefficients of thermal expansion of substrate and coating [7], thus improving the adhesion between coating and substrate and increasing the tool lifetime.

PVD techniques represent a very interesting and convenient route to realize and optimize multilayer structures with a reliable control of thin film thickness and microstructure, as demonstrated by the large number of reports about multilayer and superlattice structures grown by PVD methods and composed by combinations of layers of many different materials, like TiN, VN, AlN, NbN, CrN, TaN, ZrN, TiCN, TiAlN, and so on (see, e.g., [5,6] and references therein). In particular, we

conducted several studies about the tailoring of single nitride layer properties (see for example [8,9,10,11]) and about the control of multilayer properties [12,13].
In this paper, we initially provide an overview about the deposition and characterization of ZrN/TiN multilayer structures having different bilayer periods, obtained by tuning the deposition parameters. Then the adhesion properties of two multilayer coatings deposited on WC-Co substrates are studied through scratch tests and compared to single layer coatings. Finally, a practical application of these coatings on WC-Co inserts during milling operations is examined by measurements of flank wear of the inserts. These operational wear tests were conducted in collaboration with local companies working on mechanical tools (BARItools Srl), during the development of research activities inside a regional research project (TITRiS – Innovative Technology for Surface Treatments and Coatings on Tools and Mechanical Components).

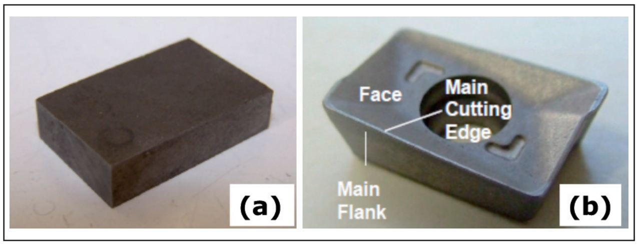

FIGURE 1 (a) Rectangular-shaped WC-Co substrate used for laboratory characterizations. (b) WC-Co milling insert used for tool life tests
Source: ENEA

Experimental details

The deposition process of ZrN and TiN single layers was widely studied and reported in our previous papers (e.g., in [8-11]). Once the process for the single layer coatings was optimized, the realization of ZrN/TiN multilayers was examined. Reactive RF magnetron sputtering in Ar+N_2 atmosphere was used to deposit ZrN/TiN multilayers, adjusting some selected deposition parameters, like rotation speed of the substrate holder in the range 1.2-4.8 rpm (revolutions per minute), nitrogen flux percentage in the range from 4% to 7.5%, and RF power applied to the targets at values of 200 and 250 W. The tuning of the deposition parameters allowed us to obtain bilayer periods from 2 to 13 nm for the ZrN/TiN multilayer coatings, whose deposition and characterization details are extensively discussed in refs [12-13].
For the adhesion and wear tests reported in this work, ZrN/TiN multilayer coatings were deposited by reactive RF magnetron sputtering on two kinds of WC-Co 9.5% substrates (Figures 1(a) and 1(b)): rectangular-shaped substrates (25x20x3 mm^3) for laboratory characterizations (scratch tests) and milling inserts for tool life tests.

The deposition chamber was evacuated down to a base pressure of ~ 6×10^{-5} Pa (~ 4.5×10^{-7} Torr) and, before the deposition of the nitride layers, a 500 nm-thick Zr buffer layer was sputtered onto the substrates in a pure Ar atmosphere at a pressure of 3 Pa (~ 2×10^{-2} Torr) and at Zr target power of 165 W. After the deposition of the Zr buffer layer, the rotation speed of the substrate holder was fixed at 3 rpm and the multilayer structure was obtained through the subsequent transits of the samples under the plasmas generated by the Zr and Ti targets at RF powers of 165 W and 200 W respectively, in Ar+N_2 atmosphere at a pressure of 3 Pa. Two samples were deposited at nitrogen flux percentages of 6% (sample ML1) and 8% (sample ML2). The bilayer period for both multilayers was 6 nm and the total thickness of the coatings (including the buffer layer) was 1.5 μm. Also, for comparison a single ZrN layer was deposited with the same thickness (Zr buffer layer of 500 nm and ZrN layer of 1 μm).
For the evaluation of the coating/substrate adhesion properties, scratch tests were performed by a Rockwell C diamond stylus (radius 300 μm), using a loading rate of 100 N/min and a traverse speed of 10 mm/min. According to the international standards [14], the load on the stylus is gradually increased until failure of the coating/substrate system occurs: the load causing the failure of the coating is indicated as critical load L_C. Failure events are usually detected by the use of microscopic examination, acoustic emission and/or friction force acquired during the test.
In order to evaluate the coating performances for tool life improvement, the coated milling inserts were te-

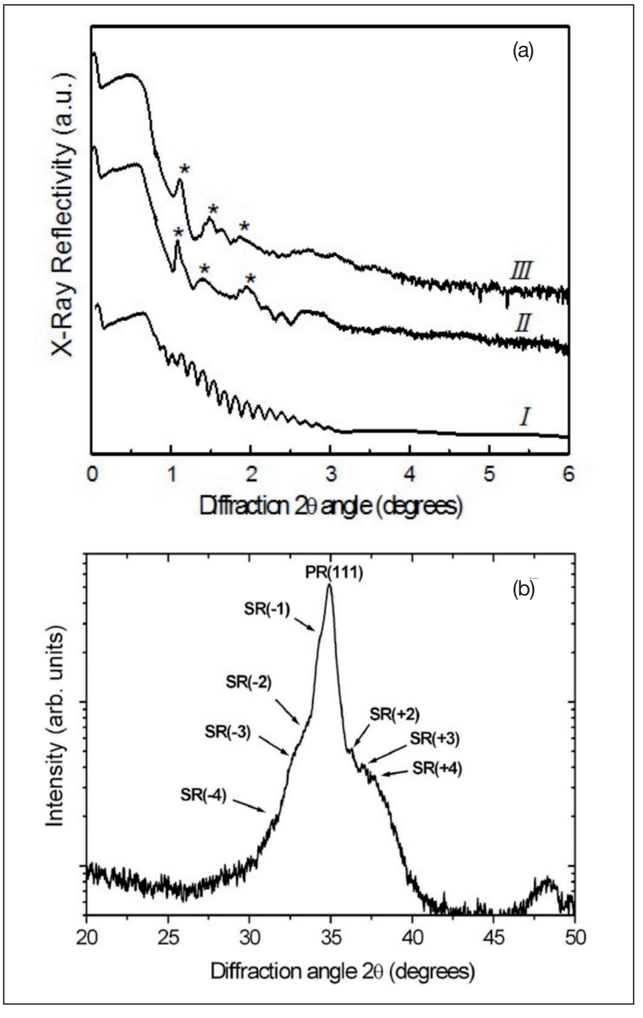

FIGURE 2 (a) XRR spectra of three ZrN/TiN multilayers with bilayer period of about 2 nm (spectrum I), and about 8-11 nm (spectra II and III). (b) XRD spectrum of a multilayer sample with a 13 nm bilayer period
Source: ENEA. (b) extracted from ref. [12]

sted under operational hard machining conditions. According to ISO standard procedures [15], a tool with a diameter of 63 mm and 8 teeth, mounting APKT inserts (WC-Co 9.5%, rake angle 11°), was used. The operational face milling tests were conducted at a cutting speed of 197 m/min, a feed per tooth of 0.2 mm/rev·tooth, a feeding speed of 1600 mm/min, a depth of cut of 2.5 mm, and with no lubrication. Tool life evaluation, in terms of useful working time, was obtained through the measure of the flank wear (VB) as the mean width of the worn flank surface. The worn regions on the tool flank were examined by using a Zoller presetting machine, equipped with two digital cameras (frontal and lateral) and a software for recording digital images and measuring geometric wear parameters.

Results and discussion

An extensive study about the structural and morphological properties of ZrN/TiN multilayers with different bilayer periods was conducted by means of x-ray diffraction (XRD) and reflectivity (XRR), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM)[12,13]. As an example, herein we briefly recall some properties of the obtained multilayers. Figure 2(a) shows the XRR spectra of three multilayers with different bilayer periods. The spectrum of the first sample (sample *I*) did not evidence any presence of satellite peaks, thus indicating the absence of a periodic stacking of the different layers, probably due to the very low thickness of the layers, which does not allow a sharp separation between two subsequent layers. However, the visible fringes in its spectrum indicated a good uniformity of the total thickness. Conversely, the presence of some satellite peaks in the spectra of samples *II* and *III* indicated a periodic stacking of the layers, with a bilayer period which is not perfectly constant over the whole thickness.

Figure 2(b) shows the XRD spectrum of a multilayer sample with a bilayer period of 13 nm. The position of the principal peak (PR) denoted a (111) preferential orientation of the structure, and the occurrence of various positive and negative satellite reflections (SR) confirmed the formation of a superlattice structure. In addition, the angular positions of the principal diffraction peaks and the satellite peaks allowed the evaluation of the bilayer period[6].

The formation of the multilayer structure was also confirmed by microscopy investigations, as observable in Figure 3. The alternation of the different ZrN and TiN layers is evident in the SEM image (Figure 3(a)), which also evidenced the formation of a columnar growth of the structure.

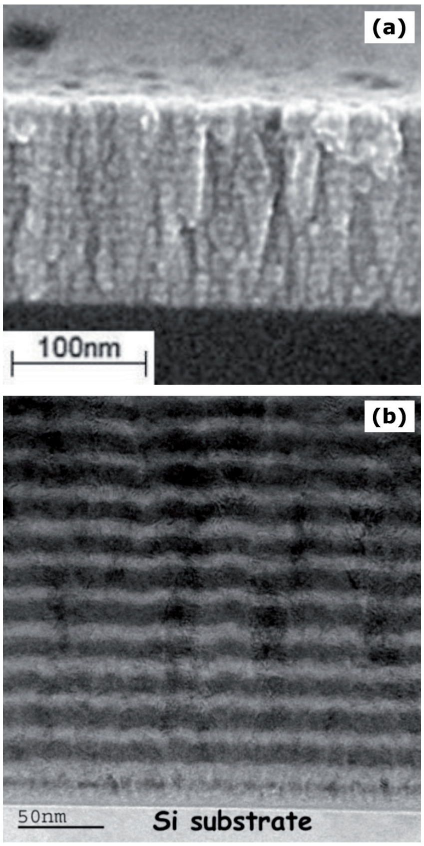

FIGURE 3 (a) Cross-sectional FEG-SEM image of a ZrN/TiN multilayer coating with a bilayer period of 10 nm. (b) Cross-sectional high-resolution TEM image
Source: ENEA. (b) extracted from ref. [13]

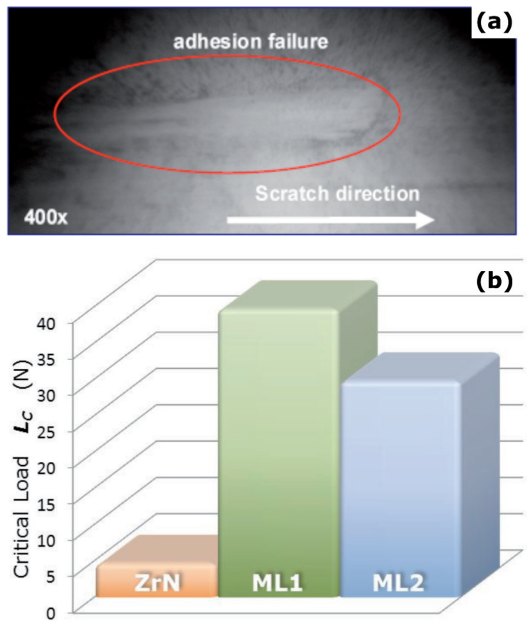

FIGURE 4 (a) Optical microscope image of a scratch track on sample ML1. (b) Comparison of the critical load values for the different coatings
Source: ENEA

The TEM image in Figure 3(b) indicated a dense fine-grained structure of the single layers constituting the multilayer structure. Moreover, from this image it is possible to note that the roughness at the interface with the substrate is very small, then the interface roughness increases as the number of deposited layers increases, due to the known "cumulative roughness" observed in sputtered multilayer structures [17]. In a further addition, also the increasing bilayer period induced an increased surface roughness, as observed by morphological characterization through AFM measurements [12,13]. As an example, the RMS roughness for samples made of 40 stacked bilayers was found to increase from 0.7 nm for a 2 nm period, to 1.3 nm for a 4 nm period, up to 3.1 nm for a 9 nm period[13].

In order to evaluate the usefulness of ZrN/TiN multilayer structures for tribological applications, these kinds of coatings were deposited on WC-Co substrates and their adhesion properties were examined by scratch tests and compared with a single ZrN coating. The scratch depth measured by profilometry at different points along the scratch tracks and the observation of the scratch tracks by optical microscope allowed the determination of the distance where the scratch depth equals the coating thickness. The image of a scratch track observed by optical microscope on sample ML1 is shown in Figure 4(a), indicating a penetration of the stylus inside the coating until the substrate is reached at a length of about 6 mm. Since the normal load cor-

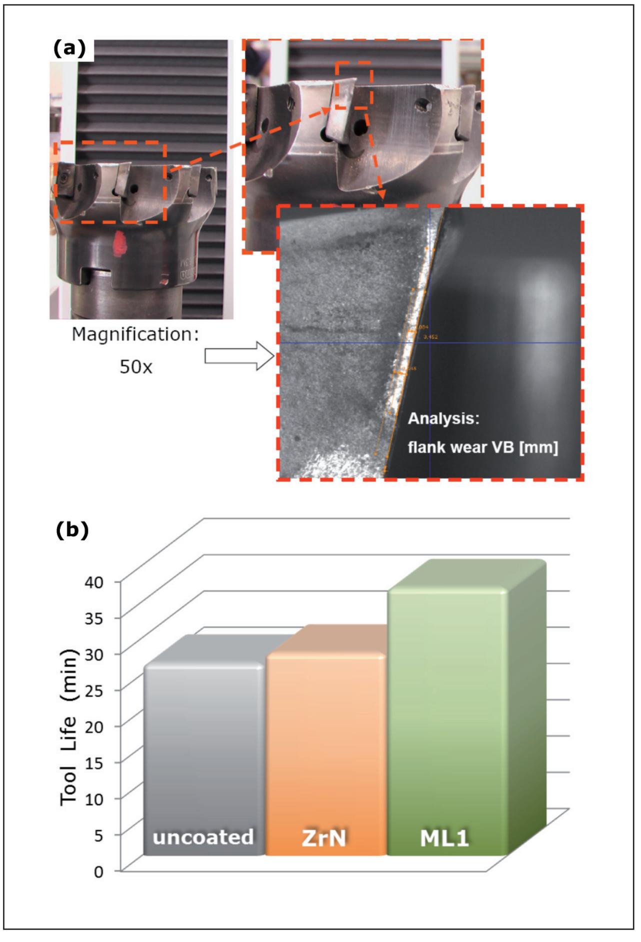

FIGURE 5 (a) Detail of an insert mounted on a milling tool and magnification of the flank wear. (b) Comparison of tool life of uncoated inserts and inserts coated with a single ZrN coating and with a ZrN/TiN superlattice coating (ML1)
Source: ENEA

responding to the different distances along the scratch tracks was known, it was possible to determine the critical load L_C values.

The results reported in Figure 4(b) show that the L_C values of the multilayer coatings are about 6-8 times higher than the single ZrN coating, indicating a stronger adhesion of the multilayer coatings, due to the reduction of residual stress during the deposition process of the different layers and the consequent increase in the coating resistance.

In order to check the functional response of the coatings, the ZrN/TiN superlattice coating with the highest adhesion (ML1) was tested on milling inserts during operational hard machining conditions, as described in the experimental section, and compared with the single ZrN coating and with uncoated milling inserts. As shown in Figure 5(a), the machining tests induced the development of a uniform flank wear beneath the main cutting edge. According to ISO standard procedures[15], the end of the tool life was chosen as the time when a flank wear (VB) of 0.3-0.4 mm was reached, and each VB value was taken as the average value of the flank wear of the eight inserts mounted on the cutting tool.

The results of the flank wear examinations are summarized in Figure 5(b), where it is shown that the single ZrN coating induced a very slight improvement in tool life with respect to the uncoated tool. Conversely, the best results in terms of flank wear and tool life were given by the ZrN/TiN superlattice coating, which promoted a significant increase in tool life of almost 30% with respect to the uncoated tool, as expected due to the blocking effects on the propagation of dislocations at the interfaces between the different layers.

Conclusions

RF magnetron sputtering was used to deposit different kinds of coating for mechanical tools. ZrN single layers and ZrN/TiN multilayers were grown on WC-Co tools in order to verify their adhesion properties and their improvements for lifetime increase of coated tools. Scratch tests, together with profilometry and optical microscopy observations, provided the measurements of the critical load L_C values and indicated that the ZrN/TiN multilayer structure had a stronger adhesion to the substrate than the single ZrN coating. Operational tests under hard machining conditions of milling tools indicated that the multilayer coating induced an increase in tool life up to almost 30% with respect to uncoated or single-layer-coated tools.

These results prove that multilayers can provide a challenging coating design to meet engineering requirements in terms of tool performances and durability improvement for tribological applications.

Sr

Acknowledgments

Part of the activities presented in this paper were funded by the Apulia research project "TITRiS" (Tecnologia Innovativa per Trattamenti e Rivestimenti Superficiali di utensili e componenti meccanici).

Many thanks are due to BARItools Srl and to Eng. G. Quaranta, Eng. G. Palumbo and Prof. L. Tricarico for their support in tribological measurements, and to all colleagues which cooperated in TITRIS research activities and in results published in the cited references.

references

[1] Regulation EC 1907/2006 of the European Parliament and of the Council of 18 December 2006, entered into force on 1 June 2007, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32006R1907:EN:NOT.

[2] W. D. Sproul (1994), "Multilayer, multicomponent, and multiphase physical vapor deposition coatings for enhanced performance", J. Vac. Sci. Technol. A, 12, 1595-1601.

[3] S. T. Oyama (1996), *The Chemistry of Transition Metal Carbides and Nitrides,* Chapman and Hall, London.

[4] J. S. Koehler (1970), *"Attempt to design a strong solid"*, Physical Review B, 2, 547-551.

[5] M. Stueber, H. Holleck, H. Leiste, K. Seemann, S. Ulrich, and C. Ziebert (2009), *"Concepts for the design of advanced nanoscale PVD multilayer protective thin films",* Journal of Alloys and Compounds, 483, 321–333.

[6] P. C. Yashar and W. D. Sproul (1999), *"Nanometer scale multilayered hard coatings"*, Vacuum, 55, 179-190.

[7] A. Zhao, H. Deng, F. Liu, and X. Deng (2012), *"The research about the III-nitride compounds epitaxially grown on Si substrate"*, Advanced Materials Research, 399-401, 935-944.

[8] A. Rizzo, M. A. Signore, D. Valerini, D. Altamura, A. Cappello, and L. Tapfer (2012), *"A study of suppression effect of oxygen contamination by bias voltage in reactively sputtered ZrN films"*, Surface and Coatings Technology, 206, 2711-2718.

[9] M. A. Signore, D. Valerini, L. Tapfer, G. Caretto, and A. Rizzo (2011), *"Zirconium nitride films deposited in (Ar + N2 + H2) sputtering atmosphere: Optical, structural, and electrical properties"*, Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films, 29, 061507.

[10] D. Valerini, M. A. Signore, A. Rizzo, and L. Tapfer (2010), *"Optical function evolution of ion-assisted ZrN films deposited by sputtering"*, Journal of Applied Physics, 108, 083536.

[11] M. A. Signore, A. Rizzo, L. Tapfer, E. Piscopiello, L. Capodieci, and A. Cappello (2010), *"Effect of the substrate temperature on zirconium oxynitride thin films deposited by water vapour-nitrogen radiofrequency magnetron sputtering"*, Thin Solid Films, 518, 1943-1946.

[12] A. Rizzo, M. A. Signore, M. F. De Riccardis, L. Capodieci, D. Dimaio, and T. Nocco (2007), *"Influence of growth rate on the structural and morphological properties of TiN, ZrN and TiN/ZrN multilayers"*, Thin Solid Films, 515, 6665-6671.

[13] A. Rizzo, M. A. Signore, M. Penza, M. A. Tagliente, F. De Riccardis, and E. Serra (2006), *"RF sputtering deposition of alternate TiN/ZrN multilayer hard coatings"*, Thin Solid Films, 515, 500 – 504.

[14] UNI EN 1071-3:2005, Advanced technical ceramics - Methods of test for ceramic coatings - Part 3: Determination of adhesion and other mechanical failure modes by a scratch test.

[15] ISO 8688-1:1989, Tool life testing in milling - Part 1: Face milling.

[16] E. Piscopiello, A. Rizzo, M.A. Signore, L. Tapfer, and M. Vittori Antisari, *"Structural Investigation TiN/ZrN multilayers"*, Proceed. of 8th Multinational Congress on Microscopy (Prague, CZ, 17th-21st June 2007), 297-298.

[17] E. E. Fullerton, J. Pearson, C. H. Sowers, S. D. Bader, X. Z. Wu, and S. K. Sinha (1993), *"Interfacial roughness of sputtered multilayers: Nb/Si"*, Physical Review B, 48, 17432-17444.