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Magnetron reactively sputtered Ti-DLC coatings on HNBR rubber: The influence of substrate bias

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ABSTRACT

In this study, Ti-containing diamond-like carbon (Ti-DLC) coatings have been deposited on HNBR (hydrogenated nitrile butadiene) rubber and also on Si wafer as reference via unbalanced magnetron reactive sputtering from a Ti target in C_2H_2/Ar plasma. The deposition rates of coatings on rubber and Si wafer were about the same. Columnar structures resulting from a rough interface were often observed in the coatings deposited on rubbers. Only at a high bias voltage of ~ 300 V the coating on HNBR rubber became column-free whereas a bias voltage of ~ 100 V could already restrain the columnar structure and thus produced dense and smooth coatings on Si wafer. A segmented morphology of the coatings on HNBR rubber is formed as a result of the large difference in thermal expansion between the coating and HNBR rubber. The crack network that separates the patches plays an important role in maintaining the coating flexibility. The size of the patches reduces with increasing bias voltage and thus the variation of deposition temperature. A high bias voltage enhances the hardness of Ti-coating and the rubber-coating adhesion, and guarantees a good tribological performance. When sliding against $\varnothing 6$ mm 100Cr6 steel ball counterpart, very low coefficients of friction were achieved (< 0.25 for the coated rubber versus > 1.3 for the uncoated). The Ti-DLC coating can be considered as a promising material for the enhancement of tribological performance of rubbers.

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1. Introduction

Coatings on soft substrates such as polymers or rubbers draw much scientific and technological attention. There are mainly three reasons to deposit coatings on components made of polymers or rubbers: decoration, gas barrier and enhancement of its tribological performance. With rigid substrates such as metal, ceramic and Si wafers, a good substrate-coating bonding combined with low residual stress may guarantee a good performance of the coatings. However, for soft polymer or rubber substrates, the flexibility of the coatings also plays an important role because they have to accommodate the large strain of the substrates under applied loads. Metallic coatings such as Mg, Cu, Al, Ag, Ti, Cr, Zr, Mo, W have been deposited on polymer [1] and rubber [2,3] substrates. It is found that the formation of metal atoms complexes with the oxygen at the interface promotes a subsequent increase in the adhesion. In general, metallic coatings enhance the hydrophobicity, the wear resistance and decrease the coefficient of friction (CoF) of polymers and rubbers. Aside from metals, diamond-like carbon (DLC) shows a great potential for coatings on polymers and rubbers in both aspects:

gas barrier and wear protection [4–7]. However, results are scarcely reported on DLC and DLC-based coatings deposited on rubber substrates. Also, studies on the morphology, coating structure and tribological properties are scanty available. Nakahigashi et al. [8] used RF plasma CVD with CH_4 to deposit DLC coatings on CR (chloroprene), NBR (nitrile butadiene), EPT (ethylene-propylene terpolymer), urethane, and silicone rubbers. The CoF of coated rubbers was reported to be 0.7–1.2. Such values are still very high for applications. Using the same deposition method, Aoki and Ohtake [9] have successfully lowered the CoF of DLC-coated rubbers to the range of < 0.4 . However, at the normal load of 3 N or higher, the coated rubber was damaged. Yoshida et al. [10] deposited DLC on silicon rubber by femtosecond-pulsed laser ablation of frozen $C_5H_{11}OH$ target. The friction of coated rubber was evaluated via the “angle of friction”. A 30% reduction in friction angle was reported with DLC-coated rubber compared to uncoated one. Filtered cathodic-arc deposition in the presence of CH_4 , C_2H_2 and C_2H_4 was also employed to deposit DLC on EPDM (ethylene-propylene), FKM (fluorocarbon) and silicone rubbers by Takikawa et al. [11]. The coatings were reported to have a good adhesion to the rubber substrates and did not peel-off when the substrates were bent and stretched by hand. However, no quantitative evaluation of the adhesion and tribological performance was published. In their early work published in Japanese [12,13], hydrogen-free DLC-coated

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rubbers reached a CoF of 0.16–0.39 and hydrogenated DLC coated rubbers with a CoF of 0.15–0.23, in reciprocating tribotests against $\varnothing 10$ mm SUS304 steel ball under 2 N normal load. Recently, we have deposited W-DLC coatings via reactive sputtering on FKM, HNBR and ACM (acrylate) rubbers [14,15]. Low friction of less than 0.25 was achieved with coated HNBR and ACM when sliding against $\varnothing 6$ mm 100Cr6 steel ball as the counterpart. The coatings on HNBR and ACM were still functional even at high normal load of 5 N. The network of close cracks between the coating patches supported the flexibility of the coatings. It is also expected that these close cracks may work as channels, e.g. in holding the oil in oil-lubricated conditions. However, coated FKM was damaged due to poor adhesion and the Cr interlayer contributed in a negative sense to the adhesion of the coating on the substrate.

In this work, Ti-DLC coatings were deposited on HNBR (hydrogenated nitrile butadiene) rubber via unbalanced magnetron reactive sputtering from a Ti target in C_2H_2/Ar plasma under different bias voltages for the purpose of improving the tribological performance of the rubber, in particular, to study the effect of the substrate bias on the morphology and microstructure of the coatings, interfacial adhesion and tribological properties of the coated rubber. A comparison between coatings on rubber and Si substrate was also made.

2. Experimental

HNBR rubber sheets of 2 mm thickness and Si(100) wafer of 525 μm thickness were used as substrate. The properties of the rubber are shown in Table 1. The Si wafers doped with boron exhibit a nominal resistivity of 1–10 $\Omega\cdot cm$. Ti-DLC coatings were deposited via unbalanced reactive magnetron sputtering from a Ti (99.7%) target in Ar/C_2H_2 plasma with a Teer UDP400/4 closed-field unbalanced magnetron sputtering system. Under current control mode, a DC current of 1.5 A was used to sputter the Ti target of size 130×250 mm². The gas flow rate ($Ar/C_2H_2 = 15$ sccm/10 sccm) was controlled and the process pressure of 3×10^{-3} mbar was kept constant during the deposition. The substrate was rotated at a speed of 5 rpm during the deposition. For measurement of the highest temperature in the deposition process, a coil-shape thermometer was fixed near the substrate holder. Pulsed DC bias voltages at frequency of 250 kHz and pulse-off width of 500 ns were applied on the substrates during deposition. The coatings are coded with the bias voltage followed by a dash and substrate, e.g. 100 V-HNBR and 100 V-Si, meaning that the coatings are deposited at –100 V bias on HNBR rubber and Si wafer, respectively.

Cross sections of the coated rubbers were made by fracturing after cooling in liquid nitrogen for ten minutes. The surface morphology, the cross section and wear track of uncoated and coated rubber and Si wafer were characterized with scanning electron microscope (Philips FEG-XL30). The hardness of coatings on Si was determined by nanoindenter (XP) with a Berkovich diamond indenter. The indentation depths were set not to exceed 10% of the coating thickness to insure no interference from the substrate. The coated rubber sheets and Si wafers were glued onto $\varnothing 30$ mm polished M2 steel discs for tribotests. The tests were performed at room temperature (20 $^{\circ}C$) on a CSM high temperature tribometer with ball-on-disc configuration.

Table 1
Properties of HNBR rubber

Color	Specific gravity	Electrical resistivity ($\Omega\cdot cm$)	Max. continuous work temp. ($^{\circ}C$)	Max. intermittent work temp. ($^{\circ}C$)	Coefficient of thermal expansion ($\times 10^{-6} K^{-1}$)	Modulus ^a (MPa)	R _a (nm)
Black	1.0	2×10^{11}	125	150	230	15.2	156

^a See [14] for the details of modulus of rubbers.

Table 2

Maximum deposition temperature and deposition rate of Ti-DLC coatings deposited on HNBR rubber under different bias voltage

Coating code	Bias voltage (V)	Max. deposition temperature ($^{\circ}C$)	Temperature variation ($^{\circ}C$)	Deposition rate (nm/min)
50V-HNBR	–50	60	2	15.5
100V-HNBR	–100	73	4	12.2
200V-HNBR	–200	95	8	9.1
300V-HNBR	–300	112	14	7.1

The counterpart was $\varnothing 6$ mm commercial 100Cr6 steel balls of hardness HRC 60–62. The normal load was 1 N and 3 N. A constant sliding velocity of 10 cm/s was chosen and the diameter of the wear track was in the range of $\varnothing 18$ –22 mm. All the tribotest were carried out at a constant humidity of $35 \pm 1\%$ kept with a humidity regulator.

3. Results and discussion

Table 2 lists the deposition rate of the coatings on HNBR rubber, as well as the maximum deposition temperature and the temperature variation during the process. The maximum temperature did not exceed the working temperature of HNBR rubber (125 $^{\circ}C$, Table 1) therefore no damage would be expected on rubber after deposition process. The deposition rate reaches the highest under –50 V bias (15.5 nm/min) and decreases with increasing bias voltage. At –300 V bias, the deposition rate (7.1 nm/min) is only half of the rate obtained at –50 V bias. This is attributed to the higher rate of re-sputtering of deposited material and densification of the coating at higher bias voltages. The Ti content in Ti-DLC coatings is about 19 at.% measured by energy-dispersive X-ray spectroscopy (EDS). The oxygen contamination is less than 1 at.% for all samples. The bias voltage does not considerably influence the coating composition.

Fig. 1 shows the fracture cross section of the coatings deposited on HNBR rubbers under different bias voltages. The coatings on rubber have a thickness of 1–1.5 μm , depending on the deposition time. At bias voltages of –50, –100 and –200 V, the coatings exhibit a coarse columnar structure. The columnar structure of W-DLC coatings (with or without a Cr interlayer) on various types of rubber (HNBR, FKM, ACM) was also seen in our previous work [14]. Such a columnar structure can only be restrained when high bias voltage of –300 V is applied on rubber substrate. However, for the coating on Si wafer, a bias voltage of –100 V is high enough to prevent column formation, leading to a dense, columnar-free and almost featureless structure (Fig. 2). It has been proved that the columnar growth is related to the interface structure of the growing coating, which is controlled by the intensity of concurrent ion impingement (flux and energy distribution of impinging ions) [16]. In the case of DC magnetron sputtering where the flux of impinging Ar^+ ions is low, an increase in the ion energy by increasing the bias voltage may enhance the mobility of the condensed species to break the network of grooves being the origin of the column boundaries. The difference in the structure of the coatings deposited on Si and rubber substrates at the same bias voltage is mainly attributed to the difference in the surface morphology and roughness of HNBR rubber and Si wafer. HNBR rubber has a powdery morphology [15] with a roughness of 156 nm whereas Si wafer has mirror-like morphology with a roughness of ~ 0.2 nm. Interface shadowing initiated from a rough surface make the columnar structure easier to develop on HNBR rubber. Also, the cross section reveals that under the same deposition condition, the difference in the deposition rate of coatings on HNBR and Si is negligible. The thickness of Ti-DLC coating on HNBR is about 1.10 μm (Fig. 1b) and that of the coating on Si from the same deposition batch is about 1.03 μm (Fig. 2). Such a minor difference is within the error of observation due to the rough interface of rubber substrates. This observation is different from the literature on the deposition rates of

Fig. 1. SEM micrographs showing the fracture cross section of Ti-DLC coatings deposited on HNBR rubber at different bias voltages: (a) –50 V, (b) –100 V, (c) –200 V, (d) –300 V.

DLC coatings deposited on rubber and Si substrates via T-shape filtered-arc [11,17]. It was reported that the deposition rate of coatings on EPDM and silicone rubber is more than 2 times higher than that on Si wafer. However, the authors stated that they had not any practical explanation on such a difference based on experimental or theoretical evidence.

The surface morphologies of coatings deposited under –50, –100, –200 and –300 V bias on HNBR rubber are shown in Fig. 3. Crack networks are observed on all the coatings. These crack networks separate the coatings into micrometer-scale domains (patches) and the size of the patches reduces from 70 μm to 10 μm with increasing bias voltage from 50 V to 300 V. Some delamination bands are seen on the coating deposited at –50 V bias, as indicated by the arrows in Fig. 3a, but not on those deposited at higher bias voltages. Such an evolution of the coating morphology is closely related to the maximum deposition temperature and the temperature variation per revolution of the sample carousel (Table 2). Due to the large thermal expansion coefficient of the rubber, the amount of expansion/shrinkage of the rubber substrate during each revolution of the sample carousel is high enough (up to 0.64% area strain) to break up the coatings when the adhesion between the coating and the rubber substrate is strong enough (at –100, –200 and –300 V bias). Assuming linear elasticity, it is understandable that the size of the coating patches is inversely proportional to the temperature variation of the substrate, namely, 70 to 10 μm versus 2 to 14 $^{\circ}\text{C}$. Delamination bands may form in the case of poor adhesion (–50 V bias), due to the large size of patches and the release of thermal strain of rubber substrate during the cooling phase after deposition. On the contrary, the dense crack networks that separate the smaller coating patches formed at higher bias voltages may effectively accommodate the thermal strain of the rubber substrate even when cooled down from higher deposition temperatures. Such segmented structures were never seen on DLC and DLC-based coatings deposited on metallic or Si

substrates. The reason is apparently that the coefficient of thermal expansion of those substrate materials is very small compared to that of HNBR rubber, and nearly matches that of the coatings.

Fig. 4 shows the hardness of Ti-DLC deposited on a Si wafer. Upon increasing the bias voltage from –50 to –300 V, the coating hardness increases from 9.4 to 16.2 GPa. The increase of coating hardness with increasing bias voltage has been reported mainly due to two processes: adsorption of species at the growing interface and the implantation at the subsurface, which depend mainly on the ion energy and thus bias voltage [18]. Under low voltages, the ion energy is not high enough to knock the adatoms to penetrate through the interface and most of the ions are only trapped on the growing interface, resulting in the formation of a loosely cross-linking with low density and low sp^3 fraction, i.e. with a low hardness. Under high bias voltages, the ion species have sufficient energy to penetrate

Fig. 2. Ti-DLC coating on Si wafer deposited at –100 V bias.

Fig. 3. Surface morphology of Ti-DLC coating on HNBR rubber deposited at different bias voltages: (a) –50 V, (b) –100 V, (c) –200 V and (d) –300 V. Two arrows indicate the partially delaminated bands at the bulges of coating 50 V-HNBR (a).

into the subsurface. The ion implantation is associated with a compressive stress and densification that in turn lead to an increase of sp^3 bond fraction and thus higher hardness. It should be noted that excessive heat generated by the impinging of over-energetic ions may reduce the hardness through the graphitization of amorphous carbon network. This explains the only slight increase of coating hardness (from 15.8 to 16.2 GPa) when the bias voltage was increased from –200 to –300 V. However, as already mentioned, the structure of coatings deposited on rubber is rather different from that on Si wafer and therefore their hardness may be also different. Since it is rather difficult to measure precisely the hardness of the coatings deposited on rubber, the coatings on Si wafer are used as reference. Under the same deposition condition, the hardness of the coating on rubber might be lower than that of the coating on Si due to the release of the residual stresses, but the trend of hardness increase as a function of bias voltage is expected to be the same.

Fig. 5a shows the CoF curves of Ti-DLC coatings deposited on HNBR rubber and Si wafer under different bias voltages. Since the friction curves of the coatings on Si wafer deposited at different bias voltage are hardly distinguishable, only the ones of the coating 100 V-Si and 200 V-Si are added in this figure for the sake of comparison. With the coatings on Si wafer, the average CoF at the steady-state is about 0.15, but the curves show large and dense fluctuations. This observation is different from the results of tribotests performed at higher normal loads [19], where only a few large peaks were observed due to breakdown of the relatively dense transfer films. Although local surface graphitization of the DLC matrix [20,21] may operate under the normal load of 1 N only, the compaction of the transfer film of graphite-rich solid lubricant is likely low so that it may collapse very often on the wear scar of the ball counterpart, leading to fluctuations in the friction curves. With

the coatings on HNBR rubber, it is clear that the friction decreases with increasing bias voltage. The coating 300 V-HNBR exhibited the lowest coefficient of friction of 0.21 and it is stable during the whole test. The friction of the coating 200 V-HNBR is a little bit higher (0.23) and almost stable during the whole test. However, at the end of the test, a few tiny fluctuations are seen and indicate that some wear debris has been generated. The coefficient of friction of the coating 100 V-HNBR gradually increases with some fluctuations during the test and reaches a value of 0.26 by the end of the test. The coating 50 V-HNBR exhibits the highest coefficient of friction (~0.45) with large fluctuations from the beginning of the test. This trend

Fig. 4. Hardness as a function of the bias voltage of Ti-DLC coatings deposited on Si wafer.

Fig. 5. Coefficients of friction versus sliding laps: (a) Ti-DLC coatings deposited at different bias voltages on HNBR rubber and on Si wafer and (b) coating 300 V-HNBR under different normal loads.

indicates that a serious wear of the coating occurred just after a few rotation laps and a large amount of wear debris has been generated from the coating. Compared to the CoF of uncoated HNBR rubber (more than 1.30 [14]), Ti-DLC-coated rubber exhibits much lower friction (3–6 times lower, depending on the deposition condition). Much lower friction obtained with the coated rubber can be mainly attributed to the chemical inertness of Ti-DLC (which hinders the bonding between the coating and the counterpart) and the lubricating effect of graphite-like clusters, which exist in carbon matrix. At higher normal load of 3 N, the CoF of the coating 300 V-HNBR decreases to 0.19–0.2 (Fig. 5b), but is still higher than the CoF of the coated Si wafer. Because of the soft contact between coated rubbers and a counterpart [15], the effect of surface graphitization seems to be limited during tribo-operation of Ti-DLC coatings deposited on the rubber as it does with the coatings on rigid substrate such as Si wafer. It is well known that the critical condition for surface graphitization process to occur is the peak stresses of the asperities under contact should be high enough [20]. Due to the huge elastic deformation resulting from the extremely low elastic modulus of rubber substrates, the maximum contact pressure with a ø6 mm 100Cr6 steel ball at 1 N normal load is about 2 MPa according to Hertzian theory of elastic contact, in comparison with the maximum contact pressure of 610 MPa on the coated Si wafer. Under such a low contact pressure namely a “soft” contact, the peak stresses on the asperities of the coated rubber is likely insufficient to

promote the surface graphitization. Another possible reason for the different CoFs of the coated rubber and of the coated Si wafer is that the difference in the accommodation modes of HNBR rubber and Si wafer may induce a difference in the energy-dissipation processes during the friction shearing between the transfer film and the Ti-DLC coating in the presence of water vapor, due to the viscoelastic nature of rubbers. Such a significant elastic deformation may contribute to dissipate energy responsible for the friction increase.

The wear tracks of coated HNBR rubbers are shown in Fig. 6. The coating 50 V-HNBR was heavily worn (Fig. 6a), partly due to the low hardness. It can be seen that the damage occurs at a very early stage of the tribotest leading to a high friction of about 0.5 (see Fig. 5a). Therefore, the poor adhesion is likely the main reason causing the local coating failure and the formed debris acts as the third body that results in severe wear of the coating. This is consistent with the SEM observation of surface morphology, where the delamination bands after deposition were observed (Fig. 3a). The partial exposure of rubber substrate due to coating failure naturally increases the friction. It should be noted that although the coating was partially damaged there are still coating-steel counterpart contacts. Therefore the friction is only about one third of that of uncoated HNBR rubber (0.46 compared to >1.3). The coatings deposited under higher voltages (–100, –200 and –300 V) are all functional after tribotests and the higher hardness of the coatings results in less wear. The crack networks, which separate the coatings into patches, play an important role in maintaining the coating flexibility. Since the coatings are not flat and have a segmented structure, the worn areas were seen only on the top of the patches, meaning that the contact mainly occurs at these areas. The wear debris on the contact spots of the coatings 100 V-HNBR and 200 V-HNBR (Fig. 6b and c) is the cause of the fluctuation observed on friction curves (Fig. 5). It can be seen that a high bias voltage gives the coatings good adhesion, which guarantees a good tribological performance of Ti-DLC coatings on rubber. However, some intra-patch cracks are observed on the wear track of coating 300 V-HNBR (Fig. 6d), indicating that a too high bias voltage may reduce the toughness of the coating.

4. Conclusion

Ti-DLC coatings deposited on HNBR via unbalanced magnetron reactive sputtering normally exhibit a columnar structure, due to the very rough interface of the rubber substrate. The columnar structure can only be restrained when a high bias voltage of –300 V is applied in the case of DC magnetron reactive sputtering. For comparison, a bias voltage of –100 V totally restrains the columnar structure and gives a very dense and smooth coating on Si wafer. However, the deposition rates for the coatings on rubber and Si are nearly the same. A segmented morphology of the coatings on HNBR rubber is formed as a result of the large difference in thermal expansion between the coating and HNBR rubber. The size of the patches reduces with increasing bias voltage and thus the variation of deposition temperature. Under dry sliding condition, Ti-DLC reduces the friction of HNBR rubber by 3–6 times depending on the bias voltage applied during deposition. Low coefficients of friction (<0.25) were obtained with the coatings deposited under –200 and –300 V bias. High bias voltage enhances the hardness of Ti-DLC coating and the rubber-coating adhesion, and guarantees a good tribological performance. Ti-DLC coating can be considered as a promising coating for enhancing the tribological performance of rubbers.

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Fig. 6. SEM micrographs showing the middle part of the wear track of Ti-DLC coating on HNBR rubber deposited at different bias voltages: (a) –50 V, (b) –100 V, (c) –200 V and (d) –300 V. An arrow indicates the sliding direction of the ball counterpart for all the tribotests (tribotest conditions: 1 N normal load, 10 cm/s sliding velocity and 35% relative humidity). The inset of (a) shows the delamination spot at the border of the wear track.

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References

- [1] J.F. Silvain, J.J. Ehrhardt, *Thin Solid Films* 236 (1993) 230.
- [2] I.S. Tashlykov, A.V. Kasperovich, G.K. Wolf, *Surf. Coat. Technol.* 116–119 (1999) 848.
- [3] I.S. Tashlykov, A.V. Kasperovich, G.K. Wolf, *Surf. Coat. Technol.* 158–159 (2002) 498.
- [4] S. Vasquez, C.A. Achete, C.P. Borges, D.F. Franceschini, F.L. Freire Jr, E. Zanghellini, *Diamond Relat. Mater.* 6 (1997) 551.
- [5] N.V. Novikov, M.A. Voronkin, S.N. Dub, I.N. Lupich, V.G. Malogolovets, B.A. Maslyuk, G.A. Podzyarey, *Diamond Relat. Mater.* 6 (1997) 574.
- [6] K. Donnelly, D.P. Dowling, M.L. McConnell, R.V. Flood, *Diamond Relat. Mater.* 8 (1999) 538.
- [7] G.A. Abbas, S.S. Roy, P. Papakonstantinou, J.A. McLaughlin, *Carbon* 43 (2005) 303.
- [8] T. Nakahigashi, Y. Tanaka, K. Miyake, H. Oohara, *Tribol. Int.* 37 (2004) 907.
- [9] Y. Aoki, N. Ohtake, *Tribol. Int.* 37 (2004) 941.
- [10] S. Yoshida, M. Okoshi, N. Inoue, *J. Phys.: Conf. Ser.* 59 (2007) 368.
- [11] H. Takikawa, N. Miyakawa, S. Minamisawa, T. Sakakibara, *Thin Solid Films* 457 (2004) 143.
- [12] N. Miyakawa, S. Minamisawa, Y. Iwasaki, H. Takikawa, T. Sakakibara, K. Takemura, T. Matsushita, *J. IAPS* 11 (2003) 81.
- [13] H. Takikawa, N. Miyakawa, J. Toshifuji, S. Minamisawa, T. Matsushita, K. Takemura, T. Sakakibara, *IEEE Trans. FM* 123 (2003) 738.
- [14] Y.T. Pei, X.L. Bui, X.B. Zhou, J.Th.M. De Hosson, *Surf. Coat. Technol.* 202 (2008) 1869.
- [15] Y.T. Pei, X.L. Bui, X.B. Zhou, J.Th.M. De Hosson, *J. Vacuum Sci. Technol.* 26 (4) (2008), doi:10.1116/1.2889443.
- [16] Y.T. Pei, C.Q. Chen, K.P. Shaha, J.Th.M. De Hosson, J.W. Bradley, S.A. Voronin, M. Cada, *Acta Mater.* 56 (2008) 696.
- [17] N. Miyakawa, S. Minamisawa, H. Takikawa, T. Sakakibara, *Vacuum* 73 (2004) 611.
- [18] S. Zhang, X.L. Bui, Y.Q. Fu, *Surf. Coat. Technol.* 167 (2003) 137.
- [19] Y.T. Pei, P. Huizenga, D. Galvan, J.Th.M. De Hosson, *J. Appl. Phys.* 100 (2006) 114309.
- [20] A.A. Voevodin, A.W. Phelps, J.S. Zabinski, M.S. Donley, *Diamond Relat. Mater.* 5 (1996) 1264.
- [21] Y. Liu, A. Erdemir, E.I. Meletis, *Surf. Coat. Technol.* 86–87 (1996) 564.