

Substrate effect on the optical properties and thickness of diamond-like carbon films deposited by the RF PACVD method

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ABSTRACT

The paper presents analyses of the optical properties and thickness of diamond-like carbon (DLC) films deposited on oxidized silicon wafers and silicon wafers with various resistivity and different crystallographic orientations. The influence of the parameters of the radio frequency plasma-assisted chemical vapor deposition (RF PACVD) process, notably the duration of the deposition process and the negative self-bias voltage of RF-powered electrode, on the optical properties and thickness of the DLC film were investigated. These properties were determined by spectroscopic ellipsometry. To the best of our knowledge, this is the first comparative analysis of these properties for various silicon and oxidized silicon substrates. Our results show that the substrate has a significant influence on both the optical properties and the thickness of the DLC film. The differences observed are highly dependent on the discussed process parameters.

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1. Introduction

Diamond-like carbon (DLC) is a metastable form of amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) that has a significant content of sp^3 bonds [1]. The DLC films are often deposited using the radio frequency plasma-assisted chemical vapor deposition (RF PACVD) method, which makes it possible to deposit carbon films exhibiting a wide range of optical and electrical properties [1–3]. The method has already been widely used in the microelectronic industry, due to low-cost deposition and high efficiency. It allows for large-area deposition of the films not only on flat surfaces, but also on more complex shapes and structures [4,5]. DLC films show good adhesion to many substrates, can be deposited in relatively low-temperature processes (from room temperature to 250 °C [3,5]) and with a high deposition rate [4]. Due to their high hardness and chemical resistance, the films have already found application as protecting coatings for metals (stainless steel, Al, and Cr), semiconductors (Si, Ge), dielectrics (SiO_2 , Si_3N_4 , $LiTaO_3$, and $LiNbO_3$) and ceramics (Al_2O_3 –TiC) [6–10]. Successful deposition of DLC on various polymers, e.g., silicone rubber [11], PMMA [12], PET [4] or polyurethane [13], has also been demonstrated. For most applications, where DLC serves to provide mechanical protection, all that is required is good adhesion and tribological properties. For coatings for medical implants, where DLC is

assumed to be one of the best materials, two other properties are essential: biocompatibility and resistance to bacteria colonization on the coating's surface [13–15].

During the last decade, it was shown that there was a need for coatings of nanometric thickness, where specific properties of the films were required and had to be well defined [10,13,16]. For optical applications (e.g. [5,17]), the most important parameters of the film are thickness, refractive index (n) and optical absorption, which is usually represented by the extinction coefficient (k). Thanks to DLC's high refractive index and optical transparency over a wide spectral range, these films have been applied as both protective and antireflective coatings for optical devices and silicon solar cells [18]. Recently, DLC films have also been used for optical sensing applications [19–21] that are even more demanding in terms of well defined thickness and specific optical properties of the films. To investigate their properties, researchers usually deposit thin films on polished silicon wafers or silica glass plates. The use of these substrates allows for very precise measurement of the optical properties and the thickness of thin films using a spectroscopic ellipsometer [5]. For certain materials where adhesion of the DLC film is weak (e.g., $LiTaO_3$), typically thin silicon-related interlayers such as SiC [9], SiO_2 [22] or a-Si [15,23] may be used instead, because the ultra-thin SiC that forms at the interface improves adhesion [24]. Authors of a number of papers assumed that the properties of the films deposited on silicon wafer [12,25] or silica glass plate [11,13] agreed well with the properties of the films deposited on other substrates by the same deposition process. However, Tian et al. [26] noticed that DLC film deposited on $LiTaO_3$ substrate showed a lower refractive index than DLC film on the

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silicon reference sample. We believe the optical properties and thickness of thin DLC films must be discussed in terms of substrate effect before they can properly be applied in novel optical devices.

The aim of this work is to compare for the first time the properties of thin DLC films deposited by the RF PACVD process on the most commonly used optical substrates: oxidized Si substrates and Si wafers of different crystallographic orientation and resistivity. The investigative work reported here is motivated by the need to optimize the performance of DLC coated optical devices in terms of such characteristics as their sensitivity and fabrication repeatability. We focus on the dependence of the optical properties and thickness of DLC films on parameters of the RF PACVD process such as negative self-bias voltage (V_b) and deposition time. In the case of the RF PACVD method, one of the most important characteristic parameters is a negative self-bias voltage (V_b), which represents energy transferred to the film from the plasma during deposition [1]. An increase in V_b leads to an increase in the number of active particles in the plasma and also to an increase in their total energy. Besides the V_b , the deposition time is a critical process parameter from the point of view of film thickness [23,28].

2. Experimental method

The DLC films were deposited using the RF PACVD method [1–3]. The chamber pressure was 50 Pa and methane flowed at a rate of 50 ml/min. The negative self-bias voltages of the RF-powered electrode were 200 to 600 V with deposition times of 3, 4 and 5 min. The samples were placed close together in the center of the water-cooled electrode ($T = 20^\circ\text{C}$). The substrates were p-type $\langle 111 \rangle$ and $\langle 100 \rangle$ polished silicon wafers with a resistivity of 0.01 and 6–8 $\Omega\text{ cm}$, respectively. The films were simultaneously deposited on wet oxidized $\langle 100 \rangle$ silicon wafers. Before plasma deposition and oxidation, all samples were cleaned according to the common practice in micro-electronics RCA procedures. The oxidation process was performed in a furnace heated to 1000 $^\circ\text{C}$. The oxidized wafers were then cooled down and used immediately for deposition of the DLC films.

The investigated parameters, i.e., index of refraction (n), extinction coefficient (k) and thickness, were determined by a Horiba-Jobin-Yvon UVISSEL spectroscopic ellipsometer in the wavelength range from 260 to 2100 nm. The equipment was calibrated before each measurement. To fit the measurement data to a physical model, a single-layer Tauc–Lorentz dispersion model [16] of DLC film was applied and fitted with $\chi^2 < 0.5$. In order to minimize error coming from precision of angle of incidence, which was initially set to 70° , the angle of incidence in addition to the other parameters was determined using the fitting procedure. In the case of oxidized samples, the model contained a first SiO_2 layer covering the silicon substrate and a second DLC layer. The thickness of the SiO_2 layer was measured at 420 nm.

3. Experimental results

During our experiments, we found that the optical properties and the thickness of DLC films strongly depend on self-bias voltage and deposition time, as well as on the substrate material. Fig. 1 shows the relation between thickness and the deposition process parameters for films deposited on $\langle 100 \rangle$ and $\langle 111 \rangle$ oriented Si substrates. Films deposited on low-resistivity Si $\langle 111 \rangle$ substrates are, in general, thicker than those deposited on higher-resistivity Si $\langle 100 \rangle$ substrates. The DLC films deposited on oxidized Si (not shown in the figure for the sake of simplicity) are comparable in thickness or slightly thinner than those obtained on bare Si $\langle 100 \rangle$. For films obtained with longer processes at higher V_b , the influence of the substrate on their thickness is greater than for those obtained with shorter processes at lower V_b . It seems that the substrate has less influence on thickness at the initial stage of film growth, especially when the process is conducted at low V_b .

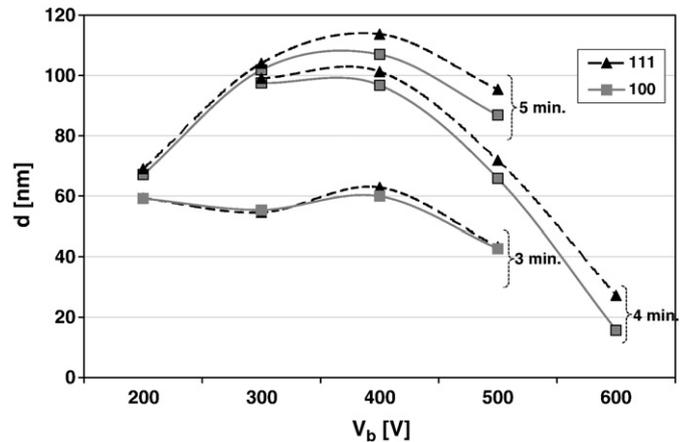


Fig. 1. Thickness (d) of the DLC films deposited with various negative self-bias voltages ($V_b = -200$ to -600 V) and process durations (3, 4 and 5 min) on $\langle 111 \rangle$ and $\langle 100 \rangle$ -oriented bare silicon substrates.

Fig. 2 shows the dispersion characteristics of the optical properties of DLC films deposited on all three types of substrates at $V_b = -400$ V with a process duration of 4 min. Both the optical properties and the thickness of the DLC films significantly depend on the substrate material. The difference of optical properties is most marked in the visible and near-infrared wavelength range. The film obtained on the oxidized substrate exhibits a lower refractive index (n) than the films deposited on bare Si substrates in the whole spectral range we investigated. There is also a difference in the refractive index for films deposited on Si $\langle 100 \rangle$ and Si $\langle 111 \rangle$, but it is relatively small. Films deposited on Si $\langle 111 \rangle$ show a slightly higher refractive index than those deposited on Si $\langle 100 \rangle$.

Investigating the influence of the extinction coefficient (k) on the substrate, we find that film deposited on oxidized substrate also strongly differs from film deposited on bare Si. Since the extinction coefficient refers to absorption, it should reach values low enough to make this substrate practical for optical devices. For film deposited on oxidized Si, we see a significantly higher k than for film deposited on bare Si. However, for wavelengths greater than $\lambda = 1250$ nm, all the investigated films show a negligible extinction coefficient.

In optical systems, light sources with a wavelength of $\lambda = 1550$ nm and around $\lambda = 600$ nm are often used, therefore values of n were compared in this spectral range for different deposition process parameters. Figs. 3 and 5 show that at certain values of V_b (300 V/500 V), the refractive index reaches its maximum value and begins to decrease as the self-bias voltage increases further. For devices operating in the visible spectral range (e.g., $\lambda = 600$ nm), both V_b and deposition time have a stronger influence on n than they do on devices that use the infrared (IR) light range (e.g., $\lambda = 1550$ nm). The effect of the substrate on the refractive index is hardly visible if we consider the films deposited on both bare Si substrates. In the IR range, films deposited with high V_b on Si $\langle 111 \rangle$ substrates show a slightly higher refractive index. The refractive index of films deposited on oxidized Si substrates is on the average 0.06 and 0.025 lower than for films on bare Si substrates, at $\lambda = 600$ nm and $\lambda = 1550$ nm respectively (Fig. 5).

DLC films show negligible optical absorption in the IR range (Fig. 2). Extinction coefficient values were therefore compared in the visible (e.g., $\lambda = 600$ nm) and the UV ranges (e.g., $\lambda = 400$ nm), as set out in Fig. 4. Around $V_b < 500$ V, k slightly increases and above that point, the increase is significant. At $\lambda = 400$ nm, the influence of deposition time on the extinction coefficient of the films is more evident. The 3-minute process makes it possible to obtain films that are slightly less absorbing in the UV range. The substrate influence on the extinction coefficient is clearly visible for $V_b = -600$ V, where films deposited on Si $\langle 111 \rangle$ are significantly more absorbing. In the

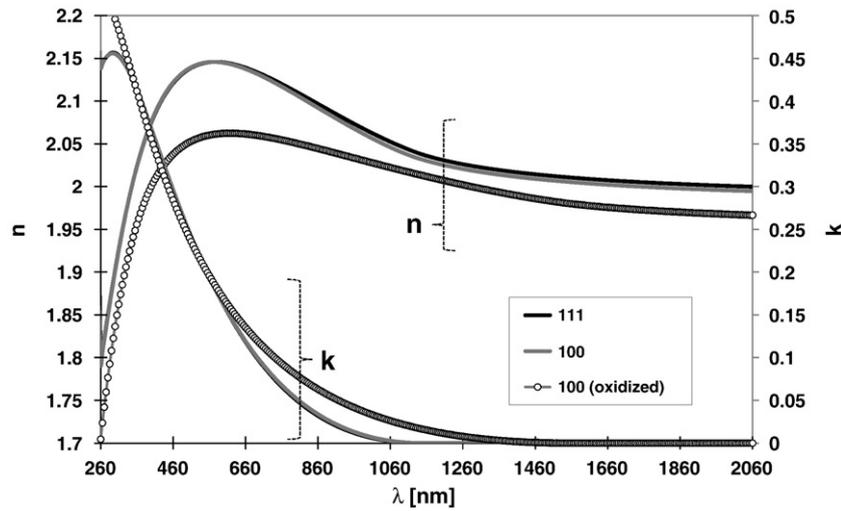


Fig. 2. Refractive index (n) and extinction coefficient (k) of the DLC films deposited with negative self-bias voltage $V_b = -400$ V and 4-minute process duration on $\langle 111 \rangle$ and $\langle 100 \rangle$ bare silicon substrates and oxidized $\langle 100 \rangle$ substrate.

case of films deposited on oxidized substrates, their extinction coefficient in the visible range is on average 0.02 higher than for films deposited on bare Si $\langle 100 \rangle$ (Fig. 5).

4. Discussion

The influence of various parameters of the deposition process, including V_b , on the properties of DLC films is widely reported in the literature of plasma CVD methods [1,3,10,16,23,27–31]. The published results as well as ours are in agreement with the subplantation DLC growth model [1,32]. When the energy of the ions is low (i.e., for $V_b = -200$ V), they tend to stick to the surface and remain at their lowest energy state, which is sp^2 . These films have a low refractive index and a low extinction coefficient. When the ions are in a higher energy state (typically $V_b = -300$ to -400 V), they can penetrate the surface and enter the subsurface interstitial state, increasing local density. The local bonding will then reform according to change of the density and transform to sp^3 one. At that voltage, the films have a maximum refractive index and exhibit a typical diamond-like character. The extinction coefficient, which strongly depends on the bonding structure in DLC film, barely changes in this range of V_b . An

increase of V_b leads not only to an increase in total ion energy but also to an increase in the number of active particles in the plasma. This phenomenon has a good correlation with the increase of DLC thickness in that range of V_b . When their energy is high (usually for $V_b > 500$ V), the ions can penetrate more deeply into the film and dissipate their energy, displacing the atoms and forming sp^2 clusters, and simultaneously decreasing the film's refractive index and increasing its extinction coefficient. Intense ion sputtering can also take place in this V_b range, so films are thinner than those obtained at lower V_b .

In terms of dependence on deposition time, i.e., the length of time required to deposit the film, shorter processes produce films that exhibit a lower refractive index and a lower extinction coefficient (in the UV range) than do films deposited under longer processes in the same investigated range of V_b . Generally speaking, for longer times, the film thickness changes in parallel with the refractive index (Figs. 1 and 3). By varying the length of the thin film deposition process when using the RF PACVD method, we can determine the thickness of the films and also change their optical properties by modifying their structure. To date, a number of authors have discussed the influence of thickness on the mechanical properties of DLC films. Lemoine et al. [10], for example,

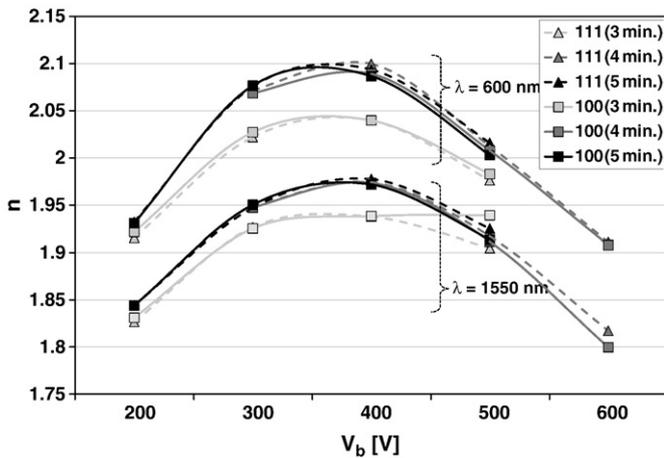


Fig. 3. Refractive index (n) of the DLC films deposited with various negative self-bias voltages ($V_b = -200$ to -600 V) and process durations (3, 4 and 5 min) on $\langle 111 \rangle$ and $\langle 100 \rangle$ bare silicon substrates. The refractive index values are given for $\lambda = 600$ and 1550 nm.

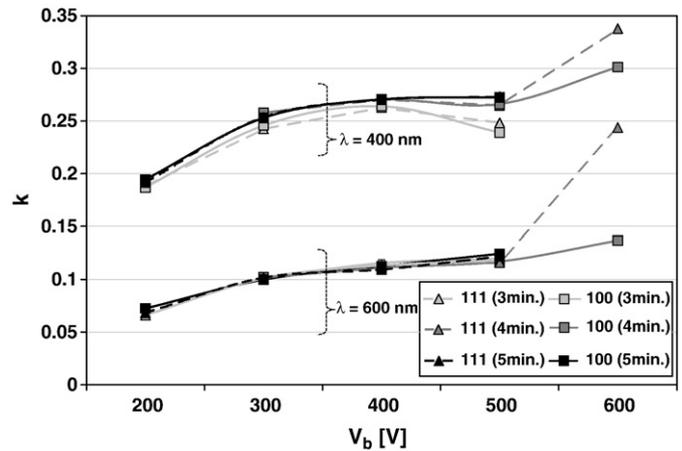


Fig. 4. Extinction coefficient (k) of the DLC films deposited with various negative self-bias voltages ($V_b = -200$ to -600 V) and process durations (3, 4 and 5 min) on $\langle 111 \rangle$ and $\langle 100 \rangle$ bare silicon substrates. The extinction coefficient values are given for $\lambda = 400$ and 600 nm.

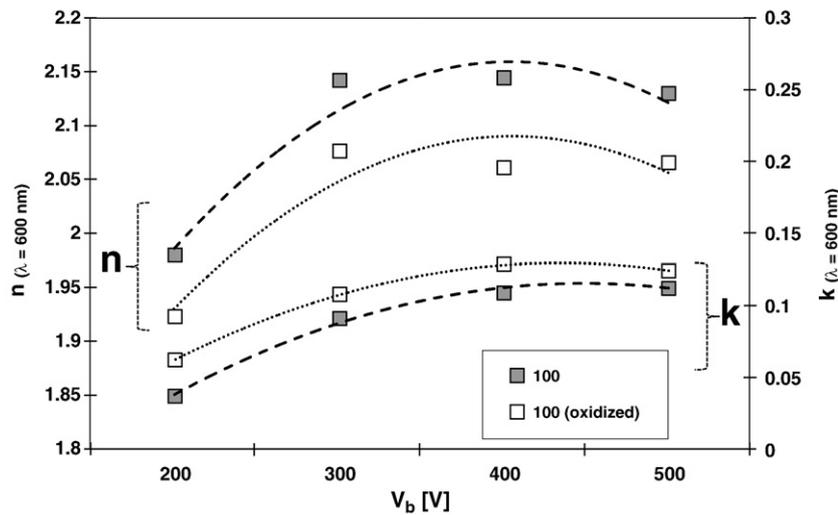


Fig. 5. Refractive index (n) and extinction coefficient (k) of the DLC films deposited with various negative self-bias voltages ($V_b = -200$ to -500 V) and 4-minute process duration on bare $\langle 100 \rangle$ and oxidized $\langle 100 \rangle$ silicon substrates. The values of both optical properties are given for $\lambda = 600$ nm.

found that the hardness of DLC films increases with their thickness. McCann et al. [33] noticed an increase in the density of carbon films corresponding with an increase in their thickness. Finally, the authors of [24] concluded that the refractive index is exclusively correlated with the film density. Our results appear to be in line with those obtained by other authors. We have directly proved that the optical properties of DLC films also depend on film thickness in the range we investigated.

The substrate affects both the optical properties and the thickness of DLC films. Investigated by other authors [10], the relation between the hardness and the thickness of DLC films was found to follow the same pattern for various substrates. We show that the relation also holds for the optical properties of films deposited on different substrates. For all substrates, an increase in film thickness is closely correlated with an increase in refractive index. However, using bare Si $\langle 111 \rangle$ substrates, we were able to obtain slightly thicker films than with either bare or oxidized Si $\langle 100 \rangle$ substrates. The difference is dependent on both the deposition time and V_b . The influence of the substrate is lower at a low V_b , where the radicals mostly stick to the surface, and it increases with ion energy. We believe that the resistivity of the silicon substrate plays an important role in determining the thickness of the deposited DLC films. Following [3], for substrates of lower resistivity the ion bombardment leads to increased fragmentation of the hydrocarbon species arriving at the surface into ever more hydrogen-deficient radical species, resulting in an increased sticking coefficient on the bombarded surface. Moreover, when the substrate shows lower resistivity (in our case Si $\langle 111 \rangle$), it is more likely that ions can effectively penetrate the film's surface. The significant difference in the extinction coefficient for films deposited at $V_b = -600$ V is proof of that mechanism. Ions striking the surface with high energy are more able to penetrate films deposited on a lower resistivity substrate thus increasing the formation of sp^2 clusters, which in turn results in a higher extinction coefficient in the films.

From the point of view of optical properties, films deposited on oxidized substrates exhibit a significantly lower refractive index and a higher extinction coefficient than films deposited on bare Si. The reason for this phenomenon may lay in the differing thermal properties of Si and SiO_2 or in differences in the density of ions in the plasma above the two surfaces. The thermal conductivity of SiO_2 is over two orders of magnitude lower than that of Si. At a higher substrate temperature, sp^2 sites form large aromatic clusters that are responsible for the higher extinction coefficient and lower refractive index [1,3]. That effect can be clearly observed in Fig. 5. Tian et al. [26] also reported a 0.03 higher refractive index for DLC film deposited on Si

substrate than for the same film on $LiTaO_3$. Since the thermal conductivity of $LiTaO_3$ is significantly lower than that of Si, their result is in agreement with the proposed relation. On the other hand, it has been shown [34] that material present on the RF electrode is one of several factors that influence discharge characteristics and the composition of species present in the discharge. In the case of SF_6/Ar plasma, it was found that the use of silicon and silicon dioxide surfaces produces significant differences in the electron and negative ion densities [35]. Authors of [35] reported that the negative ion density above the oxide surface was significantly greater than the density above a silicon surface. We believe that in the case of methane plasma we are dealing with a similar phenomenon resulting in the lower refractive index and higher extinction coefficient of DLC film deposited on oxidized silicon substrate.

5. Conclusions

Diamond-like carbon film deposited by RF PACVD is a promising nanocoating for novel optical applications, but its use requires consideration of how the substrate influences both the thickness and the optical properties of the film. We found that films deposited on silicon substrate of lower resistivity are thicker than those deposited on higher-resistivity substrates. The difference in the thickness of films deposited on Si substrates of various degrees of resistivity increases with both self-bias voltage and deposition time. For a 5-minute process at $V_b = -500$ V, the difference in thickness can reach over 10%. The increase in thickness correlates well with an increase in the refractive index for all the investigated substrates. Films deposited on oxidized Si substrates exhibit significantly higher absorption (k at $\lambda = 600$ nm, on average 0.02 higher) and lower refractive index (n at $\lambda = 600$ nm, on average 0.06 lower) than those deposited on bare Si substrates. The origins of that phenomenon may lie in differences between the two substrates in their thermal conductivities and the density of ions in their plasma. All the investigated films show negligible absorption in infrared light, which makes them suitable for optical applications working in this spectral range. In order to maintain the optical properties and thickness of the films deposited on silicon substrates with various levels of resistivity, we recommend deposition at low self-bias voltage using processes of short duration. We proved that DLC films deposited on bare silicon wafers can stand as a limited reference of thickness and optical properties for those deposited on other substrates, including oxidized silicon wafers.

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References

- [1] J. Robertson, *Mat. Sci. & Engin.* R37 (2002) 129.
- [2] S. Mitura, E. Mitura, A. Mitura, *Diam. Relat. Mater.* 4 (1995) 302.
- [3] A. Grill, *IBM J. Res. Develop.* 43 (1999) 147.
- [4] A. Shirakura, M. Nakaya, Y. Koga, H. Kodama, T. Hasebe, T. Suzuki, *Thin Solid Films* 494 (2006) 84.
- [5] L. Martinu, D. Poitras, *J. Vac. Sci. Technol. A* 18 (2000) 2619.
- [6] I. Ahmad, P.D. Maguire, P. Lemoine, S.S. Roy, J.A. McLaughlin, *Diam. Relat. Mater.* 13 (2004) 1346.
- [7] S.-J. Cho, J.-W. Chung, K.-R. Lee, *Diam. Relat. Mater.* 14 (2005) 1270.
- [8] E. Salgueiredo, M. Vila, M.A. Silva, M.A. Lopes, J.D. Santos, F.M. Costa, R.F. Silva, P.S. Gomes, M.H. Fernandes, *Diam. Relat. Mater.* 17 (2008) 878.
- [9] Q. Zhang, S.F. Yoon, S. Zhgoon, V. Ligatchev, M.B. Yu, J. Ahn, *Diam. Relat. Mater.* 10 (2001) 1843.
- [10] P. Lemoine, J.P. Quinn, P.D. Maguire, J.F. Zhao, J.A. McLaughlin, *Appl. Surf. Sci.* 253 (2007) 6165.
- [11] K. Donnelly, D.P. Dowling, M.L. McConnell, M. Mooney, *Thin Solid Films* 394 (2001) 102.
- [12] M. Ban, T. Yuhara, *Surf. Coat. Tech.* 203 (2009) 2587.
- [13] D.S. Jones, C.P. Garvin, D. Dowling, K. Donnelly, S.P. Gorman, *J. Biomed. Mater. Res. B Appl. Biomater.* 78B (2006) 230.
- [14] A. Grill, *Diam. Relat. Mater.* 12 (2003) 166.
- [15] F.R. Marciano, L.F. Bonetti, L.V. Santos, N.S. Da-Silva, E.J. Corat, V.J. Trava-Airoldi, *Diam. Relat. Mater.* 18 (2009) 1010.
- [16] M. Gioti, S. Logothetidis, C. Charitidis, Y. Panayiotatos, I. Varsano, *Sensors Actuators A* 99 (2002) 35.
- [17] Z. Gu, Y. Xu, *Meas. Sci. Technol.* 18 (2007) 3530.
- [18] M.H. Oliveira Jr., D.S. Silva, A.D.S. Cortes, M.A.B. Namani, F.C. Marques, *Diam. Relat. Mater.* 18 (2009) 1028.
- [19] M. Smietana, J. Szmids, M. Dudek, P. Niedzielski, *Diam. Relat. Mater.* 13 (2004) 954.
- [20] M. Smietana, J. Szmids, M.L. Korwin-Pawłowski, W.J. Bock, J. Grabarczyk, *Diam. Relat. Mater.* 16 (2007) 1374.
- [21] M. Smietana, M.L. Korwin-Pawłowski, W.J. Bock, G.R. Pickrell, J. Szmids, *Meas. Sci. Technol.* 19 (2008) 085301.
- [22] J. Tian, Q. Zhang, Q. Zhou, R. Gruenwald, M. Huesgen, S.F. Yoon, J. Ahn, *Surf. Coat. Tech.* 198 (2005) 198.
- [23] V.J. Trava-Airoldi, L.F. Bonetti, G. Capote, L.V. Santos, E.J. Corat, *Surf. Coat. Tech.* 202 (2007) 549.
- [24] P. Patsalas, S. Logothetidis, P.C. Kelires, *Diam. Relat. Mater.* 14 (2005) 1241.
- [25] D.W. Han, S.M. Jeong, H.K. Baik, S.J. Lee, N.C. Yang, D.H. Suh, *Thin Solid Films* 420–421 (2002) 190.
- [26] J. Tian, Q. Zhang, Q. Zhou, S.F. Yoon, J. Ahn, S.G. Wang, J.Q. Li, D.J. Yang, *Appl. Surf. Sci.* 239 (2005) 255.
- [27] M. Smietana, J. Szmids, M.L. Korwin-Pawłowski, N. Miller, A.A. Elmustafa, *Diam. Relat. Mater.* 17 (2008) 1655.
- [28] K.J. Clay, S.P. Speakman, N.A. Morrison, N. Tomozeiu, W.I. Milne, A. Kapoor, *Diam. Relat. Mater.* 7 (1998) 1100.
- [29] R. Clergereaux, D. Escaich, S. Martin, F. Gaillard, P. Raynaud, *Thin Solid Films* 482 (2005) 216.
- [30] M. Smietana, M.L. Korwin-Pawłowski, J. Grabarczyk, J. Szmids, *Mater. Sci. Eng. B* 165 (2009) 132.
- [31] N. Maitre, S. Camelio, A. Barranco, Th. Girardeau, E. Breelle, J. NonCrystalline Solids 351 (2005) 877.
- [32] Y. Lifshitz, S.R. Kasi, J.W. Rabalais, W. Eckstein, *Phys. Rev. B* 41 (1990) 10468.
- [33] R. McCann, S.S. Roy, P. Papakonstantinou, G. Abbas, J.A. McLaughlin, *Diam. Relat. Mater.* 14 (2005) 983.
- [34] E.V. Barnata, G.A. Hebner, *J. Appl. Phys.* 98 (2005) 13305.
- [35] G.A. Hebner, I.C. Abraham, *J. Appl. Phys.* 91 (2002) 9539.