Diamond & Related Materials 20 (2011) 221–226

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Mechanical properties of MWPECVD diamond coatings on Si substrate via nanoindentation ☆

M.A. Nitti [a,*], G. Cicala [b], R. Brescia [b,1], A. Romeo [a], J.B. Guion [c], G. Perna [d], V. Capozzi [d]

[a] Dipartimento Interateneo di Fisica, Università degli Studi di Bari-Via G. Amendola 173, 70126 Bari, Italy
[b] IMIP-CNR, Sezione di Bari-Via G. Amendola 122/D, 70126 Bari, Italy
[c] CSM Instruments-4 rue de la gare, 2034 Peseux, Switzerland
[d] Dipartimento di Scienze Biomediche, Università degli Studi di Foggia-Viale Pinto, 71100 Foggia, Italy

ARTICLE INFO

Available online 8 December 2010

Keywords:
Nanoindentation
Hardness
Young's modulus
Polycrystalline diamond coatings

ABSTRACT

The mechanical properties of polycrystalline diamond coatings with thickness varying from 0.92 to 44.65 μm have been analysed. The tested samples have been grown on silicon substrates via microwave plasma enhanced chemical vapour deposition from highly diluted gas mixtures CH_4–H_2 (1% CH_4 in H_2). Reliable hardness and elastic modulus values have been assessed on lightly polished surface of polycrystalline diamond films.

The effect of the coating thickness on mechanical, morphological and chemical-structural properties is presented and discussed. In particular, the hardness increases from a value of about 52 to 95 GPa and the elastic modulus from 438 to 768 GPa by varying the coating thickness from 0.92 to 4.85 μm, while the values closer to those of natural diamond (H = 103 GPa and E = 1200 GPa) are reached for thicker films (>5 μm). Additionally, the different thickness of the diamond coatings permits to select the significance of results and to highlight when the soft silicon substrate may affect the measured mechanical data. Thus, the nanoindentation experiments were made within the range from 0.65% to 10% of the film thickness by varying the maximum load from 3 to 80 mN.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The high values of hardness (H), the topmost position of Mohs scale, and Young's modulus (E) of natural diamond make it appealing for mechanical and wear resistant applications. For this reason, synthetic diamond films produced by chemical vapour deposition (CVD), have been and are still investigated as coatings for cutting and polishing tools used for machining high-strength materials [1,2].

CVD diamond has also been used for abrasive purposes either exploiting the sharp-edged roughness of as-grown polycrystalline diamond films [3] or designing abrasive diamond structures on the surface [4].

In recent works the instrumented nanoindentation testing (INT) has been proved to be a very useful technique in the mechanical characterization of synthetic diamond films [5,6] and superhard materials such as c-BC_x [7]. In particular, the mechanical measurements are not simple for polycrystalline diamond (PCD) coatings which are among the hardest materials with H values comparable to that of the diamond indenter. In this case, in order to validate the results, a particular attention has to be devoted to the integrity of the indenter all along the measurements. Besides, the indenter cannot be considered rigid and its deformation cannot be neglected as well argued by Veprek et al. [8] who consider the diamond indenter as an elastic body when superhard coatings are analysed.

Another particular care has to be devoted to the influence of the substrate during mechanical measurements of thin coatings. To avoid this, the penetration depth for the indentation should be kept within 10% of the overall film thickness, as a rule-of-thumb [8–10].

The advantage of the nanoindentation method with respect to the conventional Vickers micro hardness compression test is that at low loads it does not require an imprint imaging of the residual indent area for accurate measurements; and, at high loads it allows to avoid localised damages due to cracking within residual indent sites [5].

In particular, the INT permits accurately controlling the load, namely the normal force (in the scale of mN), and measuring the penetration depth into the material (in the scale of nm).

In the nanoindentation technique H and E are determined by the Oliver and Pharr (O&P) method [10], with H defined as: $H = F_{max}/A_p(h_c)$, where F_{max} is the maximum applied load, and $A_p(h_c)$ is the projected area of contact of the indenter at distance h_c from the tip. E is obtained from the equation for the reduced modulus E_r of the indentation contact: $\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i}$, where ν_i and E_i are the

☆ Presented at NDNC 2010, the 4th International Conference on New Diamond and Nano Carbons, Suzhou, China.

* Corresponding author.
E-mail address: mariangela.nitti@ba.infn.it (M.A. Nitti).

[1] Present address: IIT, Genova, Italy.

0925-9635/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2010.12.002

Table 1
Discharge conditions for the set of polycrystalline diamond films with different thickness grown on Si substrates with the total flow rate and the pressure fixed at 200 sccm and 50 mbar, respectively, and variable CH_4 percentage, power, deposition temperature and rate. The grain sizes and the surface roughness of the PCD films, as determined by SEM images and the profilometer, respectively, are also reported.

Thickness (μm)	CH_4 (%)	Power (W)	Deposition temperature (°C)	Deposition rate (μm/h)	Grain size (μm)	Roughness as-grown (nm)	Roughness Calotest polished (nm)
0.92	1	1250	767	0.29	0.3–0.8	4.09	4.83
1.84	1	1250	769	0.27	0.3–1	19.20	4.85
4.85	1	1250	748	0.26	0.4–1.5	19.60	2.58
18.21	1	1250	738	0.22	2–7	136	16.9
30.10	1	1250	832	0.39	3–8	151	6.93
	0.5			0.20			
	0.4			0.13			
44.65	1	1000	804	0.45	1–5	44.60	7.06

Poisson's ratio (0.07 for diamond) and the Young's modulus of the indenter, while ν_s and E_s are the Poisson's ratio and the Young's modulus of the sample.

In this work, the effect of the PCD coating thickness on mechanical properties such as hardness and Young's modulus is presented and discussed together with the morphological and chemical-structural properties. Specifically, this paper deals with how to establish the significance and accuracy of experimental H and E values of PCD superhard coatings on a soft silicon substrate ($H_{Si} = 10.4$ GPa and $E_{Si} = 130$ GPa [11]). In this case indentation experiments were performed both at a fixed load (25 mN) and also within the range from 0.65% to 10% of the PCD film thickness to determine the load at which the substrate influence becomes important.

2. Experimental

2.1. Sample preparation

PCD films were deposited on square pieces of 2×2 cm^2 polished p-doped (B) silicon (100) substrates by microwave plasma enhanced CVD (MWPECVD) technique, in a home-made cylindrical stainless steel Astex-type reactor. Before the growth process the Si was treated ultrasonically for 1 h in an ethanol suspension of diamond powder (40–60 μm).

The deposition was performed in discharges where the total flow rate and the pressure were fixed at 200 sccm and 50 mbar, respectively, as summarized in Table 1 for the investigated set of PCD samples. As the 30.10 μm thick sample, the CH_4 percentage in the gas mixture CH_4–H_2 was fixed at 1% for the bottom layer (17 μm) and 0.5% and 0.4% for the intermediate and upper layers (9.8 and 3.3 μm, respectively).

During the deposition process the substrate surface temperature, the deposition rate and the thickness were monitored *in-situ* and in real-time by the pyrometric interferometry technique [12] using a dual-wavelength ($\lambda_1 = 2.1$ and $\lambda_2 = 2.4$ μm) infrared pyrometer (Williamson Pro 92 40).

2.2. Scanning electron microscopy

The film surface morphology was observed by using an EVO scanning electron microscope (SEM, model Zeiss 50XVP) in secondary electrons mode, with an operating voltage of 15 kV.

The SEM images of the six samples are reported in Fig. 1. The thicker PCD films exhibit larger grains than those of the thinner ones. The exception is the 44.65 μm thick sample, the only one grown at 1000 W, which evidences clear pyramidal structures with grain sizes smaller than those of the 18.21 and 30.10 μm thick coatings. The grain sizes of each film, as estimated from the SEM images of Fig. 1, are reported in Table 1. SEM analyses of the samples before and after polishing do not show any appreciable variation in the surface microstructure of the films.

2.3. Micro-Raman spectroscopy

The chemical-structural features of PCD films were determined at room temperature by means of a Raman confocal micro-spectrometry apparatus (Labram from Jobin–Yvon Horiba) in the backscattering configuration using an Ar-ion laser beam (488 nm, laser output power 4.5 mW). The spot size on the samples was approximately 1 μm

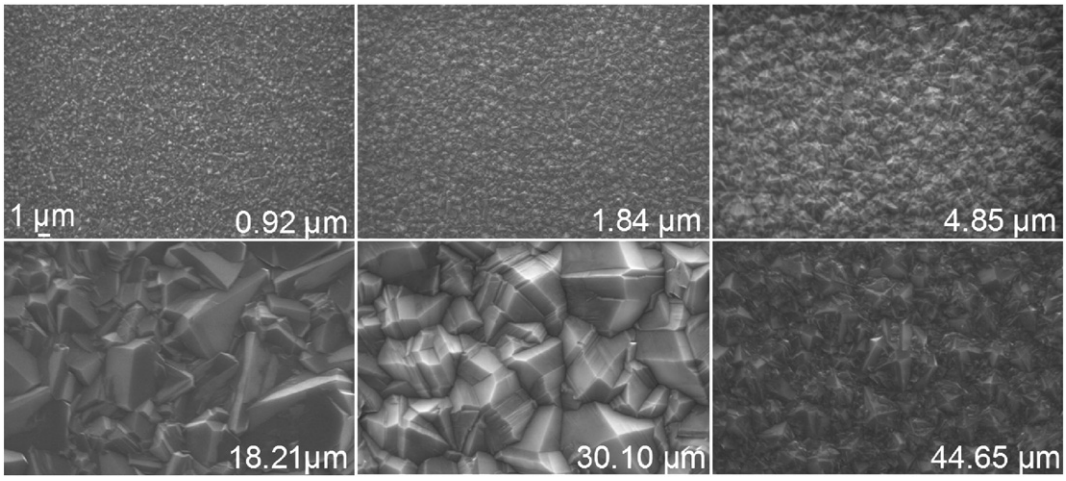

Fig. 1. Secondary electron microscopy images of polycrystalline diamond films with different thickness.

diameter by using a 100× dry objective. At least three measurements were acquired from different regions on the samples. The Raman spectra of PCD films, recorded between 500 and 2250 cm^{-1}, are represented in Fig. 2. These spectra are characterized by a typical diamond sharp peak around at 1332 cm^{-1}, a broad band at about 1500 cm^{-1} attributed to non-diamond phase due to sp^2 bonds localized principally at the grain boundaries, a peak at 520 cm^{-1} evident only in the thin sample (≤18 μm) spectra, due to the Si substrate, and a fluorescence background due to structural defects and impurities of the PCD samples. In particular, the fluorescence background in the examined samples increases with the film thickness from 0.92 μm to 4.85 μm, whereas it decreases with increasing the film thickness from 4.85 μm to 30.10 μm; such behaviour is in agreement with that reported by Ali et al. [13] and Ternyak et al. [14], respectively. Besides, the 44.65 μm thick sample presents the highest fluorescence background because of the specific growth parameters: in fact, it has been deposited with lower deposition power and higher deposition rate (see Table 1) with respect to the other samples. A quality factor, R, is determined by the equation $R = 100 \cdot \frac{I_{sp^3}}{I_{sp^3} + I_{fl} + \sum_k I_k}$, where I_{sp3}, I_{fl} and $\Sigma_k I_k$ are the intensities of the diamond peak at 1332 cm^{-1}, the fluorescence background and the non-diamond phases, respectively, at the position of the diamond peak as reported in ref. [15].

Moreover, the percentage of sp^3 component with respect to sp^2 one can be estimated by means of the ratio $P_{sp^3} = 100 \cdot \frac{A_{sp^3}}{A_{sp^3} + A_{sp^2}}$, where A^3_{sp} and A^2_{sp} are the areas of the relative Raman features measured in the spectra.

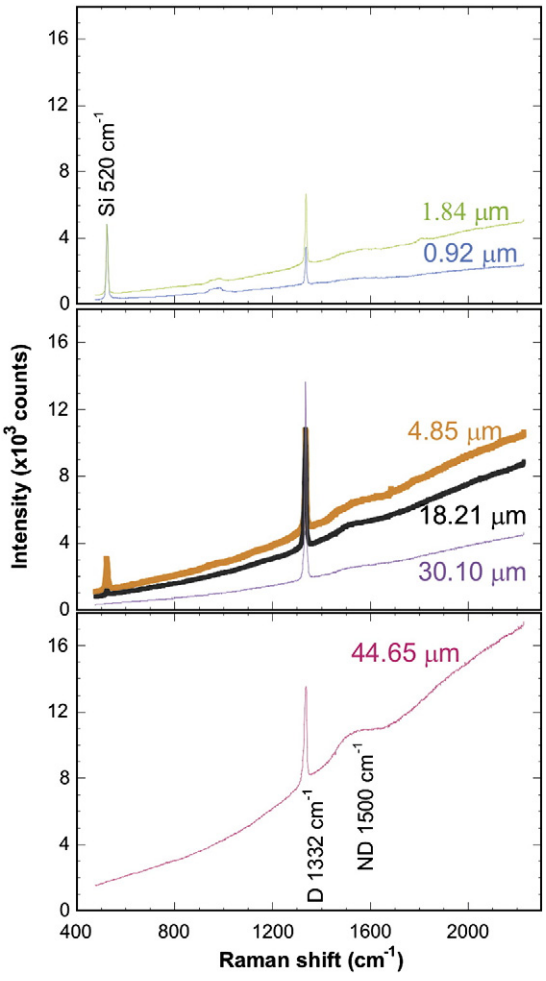

Fig. 2. Typical Raman spectra of polycrystalline diamond films with different thickness.

2.4. Nanoindentation

The nanoindentation technique was used to determine the mechanical properties of the PCD films grown on silicon substrates with a thickness ranging between 0.92 and 44.65 μm. The measurements were performed at the CSM-Instruments Laboratory using a Nano-Hardness Tester (NHT) operating with a maximum displacement and load of 500 μm and 500 mN, respectively.

The following indentation parameters were used for the investigated samples: various applied loads (3–80 mN), loading/unloading rate of 50 mN/min, pause time at maximum load of 10 s to avoid thermal drift between loading and unloading cycles, contact load of 50 μN, load and displacement resolution of 40 nN and 0.3 nm.

A Berkovich diamond indenter with a three sided pyramidal geometry and total included angle of 142.3° was employed, that was driven into and withdrawn from a specific site of film, while the loads and the displacements were measured. At each stage of the nanoindentation experiment the position of the indenter relative to the sample surface was precisely monitored with a differential capacitive sensor.

Typical loading/unloading cycles, with the applied load value plotted against the corresponding penetration depth of the indenter, are reported in Fig. 3a for a rough (as-grown) 1.84 μm thick sample. The maximum penetration depth of the indentations was limited to the 10% of the coating thickness to minimise the substrate influence

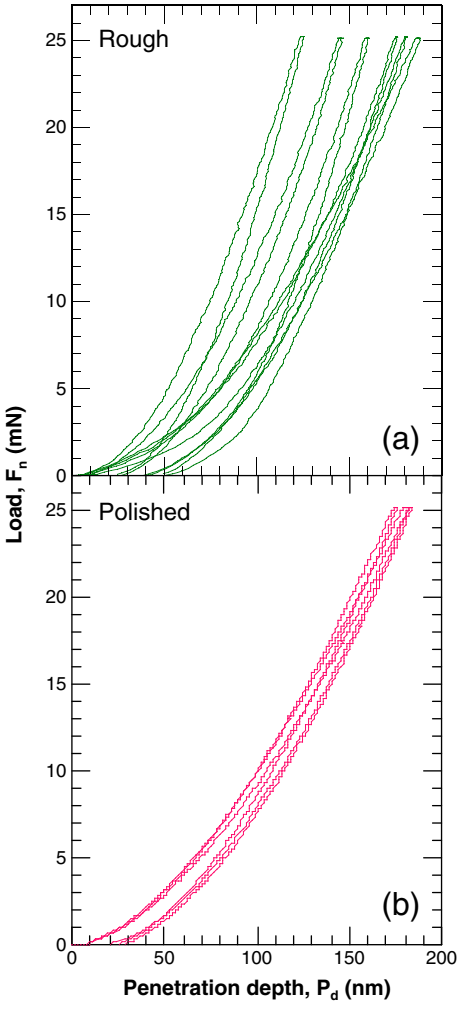

Fig. 3. Typical load-penetration depth curves of a polycrystalline diamond film (1.84 μm thick) with: (a) rough (as-grown) and (b) polished (Calotest-treated) surfaces.

on the measurements. The 10% value is generally accepted as rule-of-thumb. In spite of the compliance with the 10% rule-of-thumb, the load–penetration depth (L–P_d) curves obtained on rough surfaces are highly dispersed. As a consequence, the hardness is sometimes overestimated, sometimes underestimated. Due to the strong effect of the roughness on the dispersion of load/displacement curves it is necessary to ensure that the surface of the tested material is smooth to avoid a miscalculation of the hardness. Thus, before tests each PCD coating was lightly polished with Calotest method. The parameters used for the polishing were: diamond paste 0.5 μm, arm speed 500 rpm, time 30 s (for the thinnest samples) and 3 min (for 18.21, 30.10 and 44.65 μm thick PCD films, the roughest ones). This treatment avoids any change in surface properties due to work hardening effects and allows even limited damages of the diamond indenter. The surface roughness of the PCD coatings, measured using a Contact profilometer Talysurf Series 2 from Taylor Hobson Ltd ISO 4287, as-grown and after Calotest polishing, is reported in the Table 1.

As a result of the foregoing, Fig. 3b shows that the L–P_d curves obtained on polished surface are less dispersed and almost superimposed (see Table 2), being the smoothed surface more homogeneous. The maximum depths obtained with the rough (as-grown) sample are scattered between 110 and 190 nm, whereas with the polished one they are all around 180 nm. Moreover, the value of the surface roughness (R_a) in the rough sample is about 19.20 nm, instead in the polished sample it is about 4.85 nm, so the P_d/R_a ratio ranges from 5.7 to 9.9 for rough PCD film and it is 37 (overcoming 20) for the lapped one. A $P_d/R_a \geq 20$ represents the recommended value for minimising the influence of surface morphology and the dispersion of results. This last outcome confirms the fact that the Calotest is a good method to improve reliability of results in the measurements of the mechanical properties. Additionally, the polishing is required, from economical point of view, to preserve the indenter integrity or lifetime of the indenter tip.

Our results are opposite to those reported by De Fazio et al. [16], who observed high dispersion in maximum penetration depths although their samples were polished, perhaps due to the fact that the reported surface roughness of their lapped samples is 50–100 nm and the reported indentation depth values (see Fig. 1 of Ref. [16]) are scattered between 250 and 370 nm. These last P_d values are far away from the advised 1000–2000 nm in order to obtain a P_d/R_a ratio around 20.

The analysis of the above load–penetration depth curves, through an already established power law method developed by O&P [10], provides the estimation of the mechanical H and E data of the film under examination.

The integrity checking of Berkovich tip geometry was carried out doing regular indentations on a soft metal like copper ($H_{Cu} = 1.1$ and $E_{Cu} = 128.1$ GPa), during the measurements. In fact, the copper enables to have a kind of mirror image of the tip, because of its high plasticity. At least three measurements were made at each load at different locations over the PCD sample surfaces to check the consistency of results and estimate an accurate mean value. The indenter employed for the nanoindentation measurements was properly calibrated by standard fused silica ($H_{SiO2} = 9.7$ and $E_{SiO2} = 72$ GPa).

A CSM Micro Scratch Tester (MST) was also used in order to determine the scratch resistance of one film and its adhesion on the substrate. The MST is especially suited to test mechanical properties of hard coatings on soft substrates as well as soft coatings on hard substrates.

The high surface roughness of the sample together with the high hardness, form an extremely abrasive combination which constitutes a serious problem during scratches. In fact, the tip wear makes repeatable scratch tests impossible. A new tip would be required for each scratch; so as it is not a realistic solution, this type of analysis was dismissed.

3. Results and discussion

The evaluation of hardness and elastic modulus of PCD coatings is not simple since the examined samples exhibit mechanical properties comparable with the diamond Berkovich indenter. In order to derive meaningful values of H and E we have to consider the value of penetration depth to exclude the substrate influence and to prove the validity of the Oliver–Pharr model.

3.1. Film thickness effect on the nanoindentation test at 25 mN

In Fig. 4 the L–P_d curves with a maximum load of 25 mN for the polished samples of the set (see Table 1) are reported. The L–P_d curves of Fig. 4 confirm the rather elastic behaviour of CVD diamond, showing a low degree of hysteresis, except for the thinnest sample (0.92 μm), which shows a loading curve not coincident with the unloading one, and a slope lower than those of the others. This could be attributed to the plastic work, and/or to the silicon substrate influence.

In Fig. 5a the hardness and the elastic modulus, derived from the L–P_d curves shown in Fig. 4, are reported as a function of the PCD film thickness. Except for the two thin samples (0.92 μm and 1.84 μm), it is well evident that the thicker samples achieve H values close to or higher than that of the natural diamond (H = 103 GPa) and E values

Table 2
Hardness (H) and Young's modulus (E) derived by the load-penetration depth curves from nanoindentation using a maximum load of 25 mN (Fig. 2a and b) of a polycrystalline diamond film (1.84 μm thick).

	H (GPa) rough	H (GPa) polished	E (GPa) rough	E (GPa) polished
Data 1	55.14	74.34	1094.90	579.30
Data 2	83.67	69.73	1122.09	528.87
Data 3	49.95	67.56	731.64	519.46
Data 4	55.04		503.55	
Data 5	46.53		694.30	
Data 6	103.07		2475.95	
Mean	65.57	70.54	1103.74	542.54
Std dev	22.63	3.46	714.10	32.18
% std dev	34.51	4.91	64.70	5.93

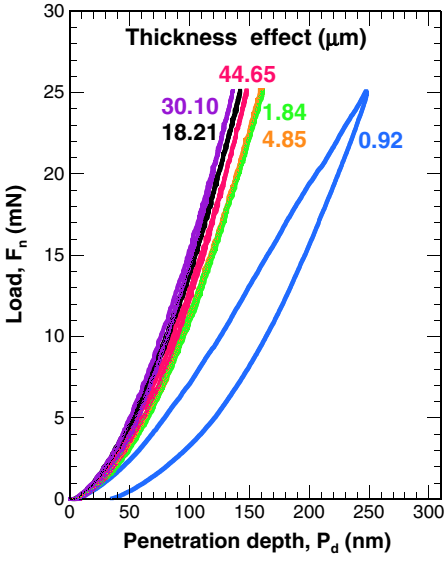

Fig. 4. Load-penetration depth curves of the samples with different thickness from nanoindentation using maximum load of 25 mN.

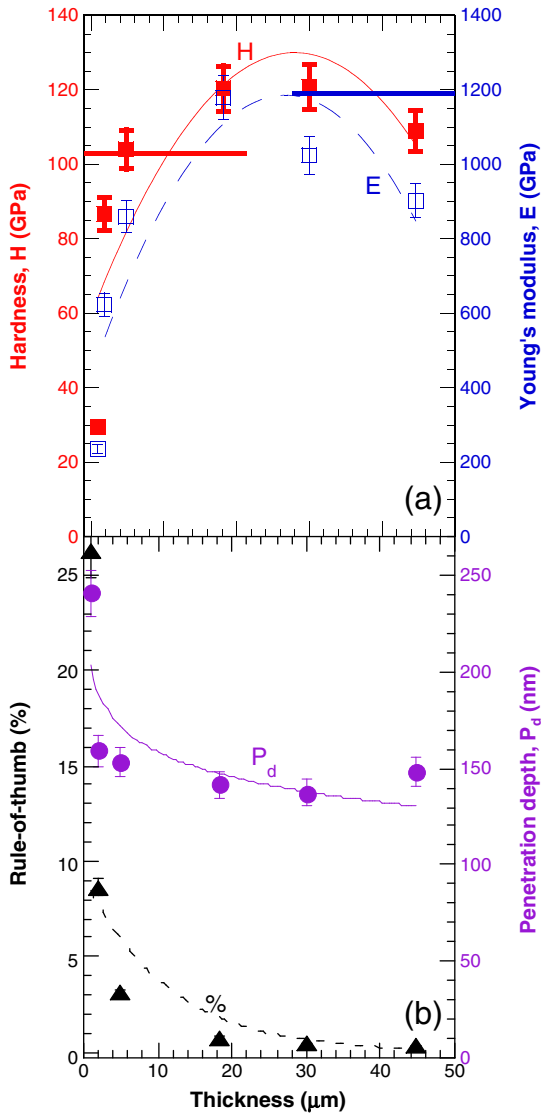

Fig. 5. (a) Hardness (full squares) and elastic modulus (empty squares), (b) penetration depth (circles) and rule-of-thumb (triangles) measured at a maximum load of 25 mN as a function of the PCD film thickness. The continuous and dashed curves on the experimental H and E, P_d and % rule-of-thumb points, are not fits to the data, but eye-guides. The horizontal lines that intercept the y-axis on the left and right side of Fig. 4a are the reference values of H (103 GPa) and E (1200 GPa) of natural diamond.

up to about 1179 GPa, not far from the value of the Young's modulus of the natural diamond (E = 1200 GPa). Fig. 5b shows the penetration depth measured at the maximum load (25 mN) and the calculated rule-of-thumb values (defined as the ratio between the P_{dMax} and the film thickness multiplied by 100) as a function of the film thickness. Except for the high value of penetration depth (241 nm) for the thinnest film (0.92 μm), the other ones vary from 137 to 161 nm for thicker films. The penetration depth decreases suddenly from 241 nm to 160 nm going from film thickness of 0.92 μm to 1.84 μm and then it remains almost constant around a value of 150 nm for film thickness ≥ 1.84 μm. Furthermore, since the thickness of the examined PCD films changes from 0.92 to 44.65 μm, the corresponding values of rule-of-thumb decreases from 26.2% to 0.3%, maintaining the maximum load fixed at 25 mN. These results suggest that it should be better to set the recommended value (≤10%) of rule-of-thumb [8–10] to exclude the soft substrate influence rather than to apply a fixed load regardless of the sample thickness.

3.2. Limitation of the rule-of-thumb and O&P model

The hardness and the elastic modulus of the three thinner samples (0.92 μm, 1.84 μm and 4.85 μm) are reported in Fig. 6a, b and c, respectively, as a function of the penetration depth. The numbers indicated on each point of the graphics are the calculated values of rule-of-thumb. In Fig. 6a the 6.1% rule-of-thumb corresponds to a maximum penetration depth of 56 nm. Even though the value of 6.1% is within the 10% rule-of-thumb the corresponding penetration depth is below 70 nm. The 70 nm value represents the lower limit for the validity of the O&P model as established by highly dispersed H and E values obtained on standard fused silica. Thus, the H and E

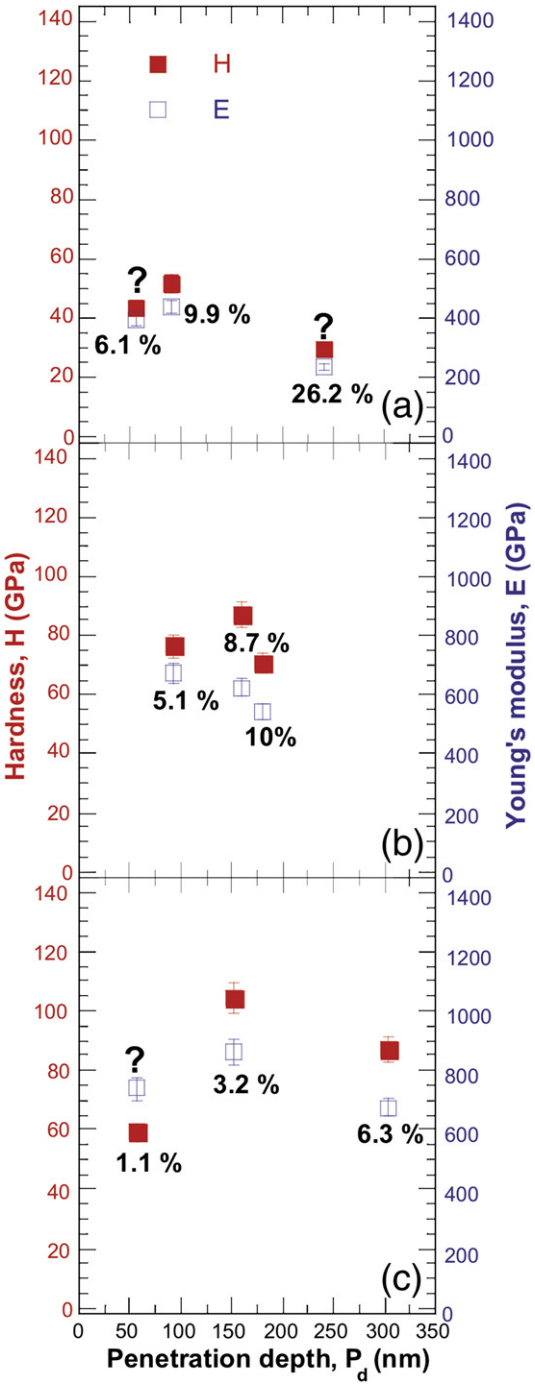

Fig. 6. Hardness and elastic modulus as a function of the penetration depth of: (a) 0.92 μm; (b) 1.84 μm; (c) 4.85 μm thick samples.

values at this P_{dMax} cannot be considered reliable. Instead the H and E values obtained using a 26.2% rule-of-thumb could be influenced by the soft substrate. Thus, for the thinnest sample (0.92 μm) the reliable values of H and E are those at 9.9% rule-of-thumb.

Fig. 6b shows that the indentation tests at the three values of maximum load provide P_{dMax} values varying in the range 70 nm ≤ P_{dMax} ≤ 180 nm; on one hand they ensure the validity of the O&P method and on the other hand they comply with the rule-of-thumb. As a consequence the meaningful H and E values for this PCD film (1.84 μm) is the average of the three experimental data.

In Fig. 6c the indentation measurement to be excluded corresponds to a P_{dMax} of about 57 nm, for which the O&P model fails, even though it satisfies the 1.1% rule-of-thumb. For this sample the accurate H and E values are the average of the two data at 3.2% and 6.3% rule-of-thumbs.

3.3. Correlation between Raman quality factor and "reliable" hardness values

The Raman quality factor R, the sp^3 percentage P_{sp3} and the chosen reliable H values of the examined samples are shown in Fig. 7 as a function of thickness. Except for the two thinnest (0.92 μm and 1.84 μm) coatings, the H, R and P_{sp3} trends are similar. For this correlation, we can say that *the higher the P_{sp3}, the better is the film quality R and the harder is the PCD coating*. In the thicker films the areas probed during Raman and nanoindentation measurements are close to the growth surface having quality and mechanical properties comparable to those of natural diamond. However, in the 44.65 μm thick film the smaller grain size (see Table 1) due to the lower deposition power (1000 W) and the consequent higher concentration of grain boundaries, i.e. higher sp^2 carbon phase (see Fig. 2), deteriorate the diamond quality and it becomes therefore less hard although the coating is the thickest.

The disappearance of this correlation for the thinnest sample could be explained considering the fact that the substrate influence becomes dominant as proved by Raman and nanoindentation measurements. In fact, in the Raman spectra (see Fig. 2) a silicon line is observed and in the nanoindentation measurements the slope of load-penetration depth curves is low (see Fig. 4 at 25 mN and also at various maximum loads not reported here) with respect to those of thicker films. Due to the columnar nature of PCD growth a worsening of the mechanical properties is found moving towards the thinner films. In this case the film-substrate interface, where we expect Si impurities [17] and also higher concentration of the grain boundaries, is closer to the probed and measured region. In fact, the interface is a highly inhomogeneous and defective transition region where the initial diamond nuclei start to increase until the grains coalesce to form a continuous film.

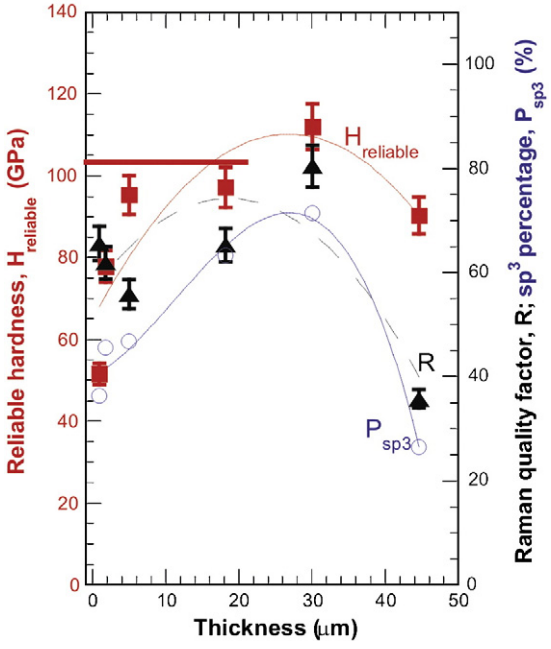

Fig. 7. Raman quality factor (triangles), sp^3 percentage (empty circles) and "reliable" hardness values (full squares) as a function of PCD film thickness. The continuous and dashed curves on the experimental $H_{reliable}$, P_{sp3} and R (%) points, respectively, are not fits to the data, but eye-guides. The horizontal line that intercepts the y-axis on the left side is the reference value H (103 GPa) for natural diamond.

4. Conclusions

A set of PCD films grown on silicon substrates and having different thickness has been characterized by means of nanoindentation technique, scanning electron microscopy and micro-Raman spectroscopy in order to measure the mechanical, the surface morphology and the chemical-structural properties, respectively.

It has been found that the PCD samples have to be lightly polished by the Calotest method before nanoindentation testing for reducing the surface roughness and therefore for obtaining less dispersed and more reproducible results.

Besides, the load-penetration depth curves obtained at fixed load for PCD films of different thickness do not give reliable values of hardness and Young's modulus for all the samples of the investigated set because the probed penetration depth in the thinnest film overcomes the 10% of the film thickness by violating the rule-of-thumb conventionally accepted by the scientific community. It has been suggested that the nanoindentation measurements of the present set have to be carried out at various values of maximum load to get penetration depth ≥ 70 nm to be sure that Oliver–Pharr model used to calculate the mechanical parameters is still valid and a penetration depth value ≤ 10% of the thickness film to exclude the silicon substrate influence.

The mechanical properties and the quality factor R of PCD films having thickness ≥ 4.85 μm seem to be strongly affected by the sp^3 content.

Acknowledgements

This work was carried out in the frame of the "Progetto Strategico" ATS PS_136 of Regione Puglia (Italy).

References

[1] J. Hu, Y.K. Chou, R.G. Thompson, J. Burgess, S. Street, Surf. Coat. Technol. 202 (2007) 1113.
[2] Q. Liang, C.-S. Yan, Y. Meng, J. Lai, S. Krasnicki, H.-K. Mao, R. Hemley, J. Phys. Condens. Matter 21 (2009) 364215.
[3] J. Gäbler, S. Pleger, Int. J. Mach. Tools Manuf 50 (2010) 420.
[4] R. Gåhlin, H. Björkman, P. Rangsten, S. Jacobson, Wear 233–235 (1999) 387.
[5] S. Chowdhury, E. de Barra, M.T. Laugier, Surf. Coat. Technol. 193 (2005) 200.
[6] A. Richter, R. Smith, N. Dubrovinskaia, E. Mcgee, High Pressure Res. 26 (2006) 99.
[7] A. Richter, C.P. Daghlian, R. Ries, V.L. Solozhenko, Diam. Relat. Mater. 15 (2006) 2019.
[8] J.L. He, S. Veprek, Surf. Coat. Technol. 163–164 (2003) 374.
[9] ASTM Standard Test Method E-384, Annual Book of Standards 3.01, American Society for Testing and Materials, Philadelphia, PA, 1989, p. 469.
[10] Z.W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
[11] P. Bruno, G. Cicala, A.M. Losacco, P. Decuzzi, Surf. Coat. Technol. 180–181 (2004) 259.
[12] G. Cicala, R. Brescia, M.A. Nitti, A. Romeo, D. Altamura, C. Giannini, M. Capitelli, P. Spinelli, S. Schutzmann, Surf. Coat. Technol. 204 (2010) 1884.
[13] N. Ali, Q.H. Fan, W. Ahmed, J. Gracio, Thin Solid Film 420–421 (2002) 155.
[14] O. Teryak, A.A. Cimmino, S. Prawer, A. Hoffman, Diam. Relat. Mater. 14 (2005) 272.
[15] H. Chatei, J. Bougdira, M. Rémy, P. Alnot, C. Bruch, J.K. Krüger, Diam. Relat. Mater. 6 (1997) 107.
[16] L. De Fazio, S. Syngellakis, R.J.K. Wood, F.M. Fugiuele, G. Sciumé, Diam. Relat. Mater. 10 (2001) 765.
[17] G. Cicala, R. Brescia, M.A. Nitti, A. Romeo, M. Ambrico, L. Schiavulli, G. Perna, V. Capozzi, Diam. Relat. Mater. 19 (2010) 470.