

**LNF-96/072**

**Temperature-Dependent Orientation of Diamond Films on  
Titanium and Structural Evolution of Interfacial Layers**

G. Cappuccio, V. Sessa, M.L. Terranova

*Appl. Phys. Lett.* 69, 27, 4176-4178, (1996)

# Temperature-dependent orientation of diamond films on titanium and structural evolution of interfacial layers

Giorgio Cappuccio<sup>a)</sup>

*Istituto di Strutturistica Chimica, CNR, Monterotondo Staz., and Laboratorio Dafne Luce, INFN-LNF, P.O.B. 13, 00044 Frascati, Italy*

Vito Sessa and Maria Letizia Terranova

*Dipartimento di Scienze e Tecnologie Chimiche, Università di Tor Vergata, and Consorzio Interuniversitario di Chimica dei Materiali, Via della Ricerca Scientifica, 00133 Roma, Italy*

(Received 8 July 1996; accepted for publication 28 October 1996)

X-ray diffraction analytical techniques have been used to investigate the influence of the deposition temperature (650–850 °C) on the composition and microstructure of the transition layers formed at the interface between titanium substrates and diamond thin films. The diamond coatings were produced by hot-filament chemical vapor deposition using a 1% methane/hydrogen mixture. X-ray diffraction analysis, performed both through  $\theta$ - $2\theta$  scans and at grazing incidence, allowed investigation of the crystallographic properties and of the structural evolution of the various phases (TiC, TiH<sub>2</sub>,  $\alpha$ -Ti) generated inside the intermediate reaction layers. The temperature-dependent orientation of diamond crystallites is discussed with reference to the complex structure of these interfacial layers. © 1996 American Institute of Physics. [S0003-6951(96)03053-7]

Many modern high-technological areas, such as optoelectronics, x-ray lithography, tool and engine mechanics, biomedical prostheses, etc., require high-quality diamond coatings characterized by a particular grain orientation and by strong adhesion of the polycrystalline films to nondiamond substrates. However, in the case of chemical vapor deposition (CVD), both the substrate material and the process parameters play a fundamental role not only with respect to grain growth and the consequent formation of textured diamond layers but also in the creation of spurious phases at the substrate/diamond interface. It is worth noting that the formation of such reaction layers may have either beneficial or detrimental effects on the properties of diamond coatings. In fact, the mismatch between the different lattice parameters of the various phases is expected to cause stress-strain effects and give rise to adhesion problems. On the other hand, intermediate layers with specific structures are found to promote heteroepitaxial growth of diamonds; for instance, on silicon substrates, highly oriented growth of diamond crystallites can be achieved when the nucleation occurs on oriented  $\beta$ -SiC layers generated ad hoc during the early stages of the process.<sup>1-8</sup> It is clear that for each material substrate, detailed research work is needed in order to select the conditions for the textured growth of diamond films.

In the case of titanium, previous investigations<sup>9</sup> have shown that during the deposition process of diamond by hot-filament CVD, two crystalline phases are generated at the film/substrate interface: titanium carbide (TiC) and titanium hydride (TiH<sub>2</sub>). By using a combination of several structural probes, it was possible to define the stratification sequence of the various phases inside the complex interfacial layer produced at 650 °C.<sup>10</sup> Some measurements, however, indicated that the substrate temperature plays a fundamental role in the TiH<sub>2</sub> and TiC formation as well as in determining the crys-

tallographic properties of the diamond films. The present work was undertaken to ascertain whether the composition and the temperature-dependent structural evolution of the intermediate layers influence the features of diamond deposition.

The deposition processes were performed in a CVD reactor<sup>10</sup> using 1% CH<sub>4</sub>/H<sub>2</sub> mixtures activated by hot-filament, kept at 2180±10 °C. Polycrystalline diamond films were grown on 1-mm-thick titanium plates according to the following conditions: pressure 36 Torr, gas flow rate 200 sccm, deposition time 240 min. The substrate temperature was changed from 650 to 850 °C in steps of 50 °C. Before deposition the substrates were scratched under controlled conditions with a 0.25  $\mu$ m diamond paste and thoroughly cleaned ultrasonically in an acetone bath. Substrate penetration and gas phase conditions were identical for all samples.

To characterize such diamond films, we used many complementary techniques, such as scanning electron microscopy, reflection high-energy electron diffraction, Raman spectroscopy, etc.<sup>10</sup> In the following, we refer to x-ray diffraction (XRD) measurements made with a two-axis diffractometer in the Bragg-Brentano parafocusing geometry, together with a graphite monochromator and a Cu x-ray tube. To investigate the complex structure of the samples, full diffraction patterns were collected, through  $\theta$ - $2\theta$  scans, from 34° up to 122°. Moreover, two spectral regions were carefully examined: 34°–46° and 73°–79°, where the reflections from {111} and {220} diamond planes are present together with many other peaks belonging to the Ti, TiC, and TiH<sub>2</sub> phases.<sup>11</sup>

Using the same diffractometer, x-ray grazing incidence diffraction measurements were also performed by changing the incidence angle  $\theta$  of the sample in one-degree steps and by scanning the  $2\theta$  axis between 34° and 46°. A typical set of data files obtained after profile fitting and background subtraction<sup>12</sup> is shown in Fig. 1. The intensity evolution of the peaks produced by the various phases shows the relative

<sup>a)</sup>Electronic mail: cappuccio@vaxInf.Infn.it

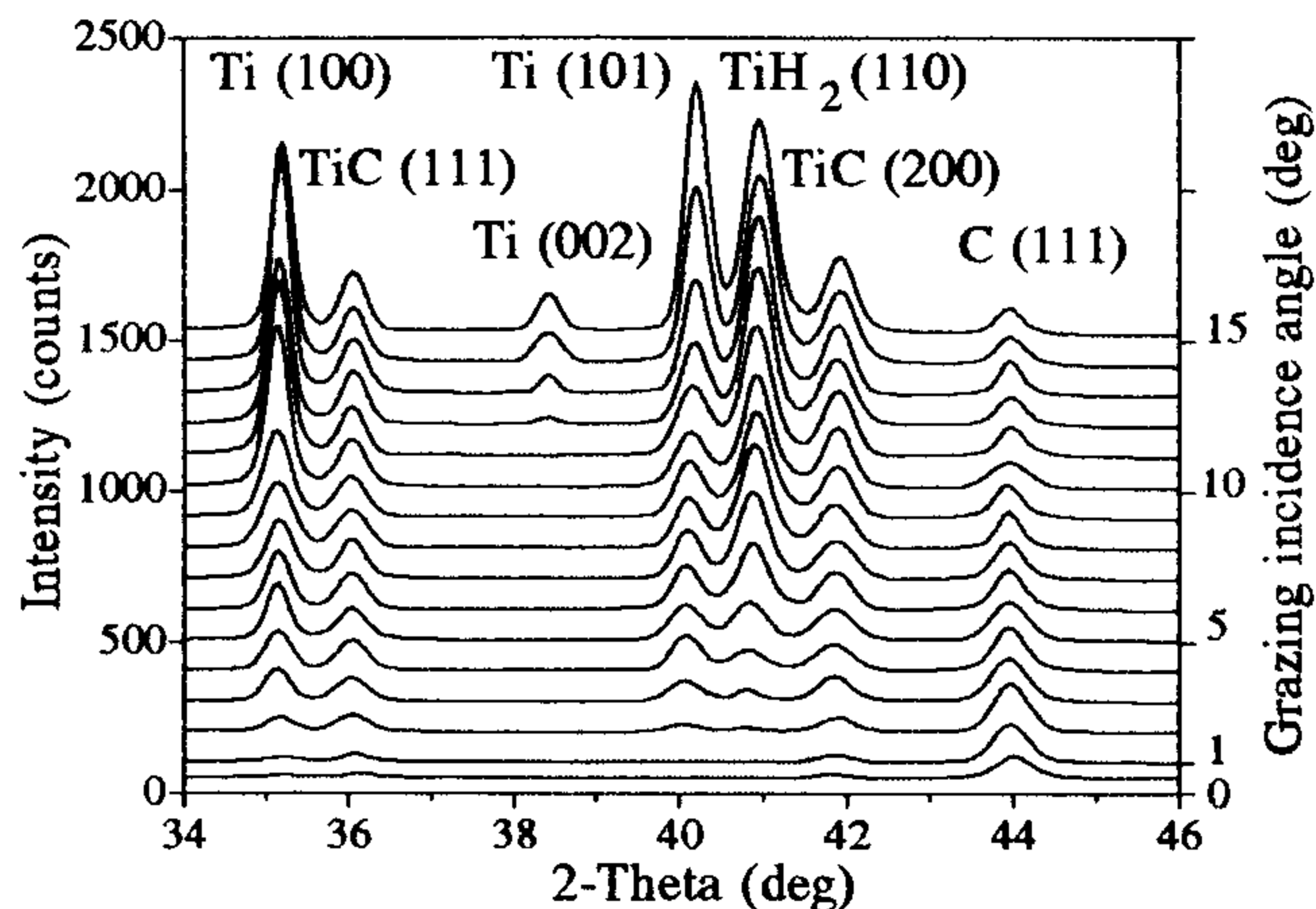


FIG. 1. X-ray grazing incidence diffraction spectra taken from a diamond film deposited at 650 °C.

depth inside the intermediate layer and the growth sequence, which, starting from the topmost layer, is diamond, TiC, TiH<sub>2</sub>, and  $\alpha$ -Ti.

A Pseudo-Voigt profile fitting<sup>12</sup> of the XRD spectra, obtained through  $\theta$ - $2\theta$  scans in the range of 34°–46°, allowed us to deduce the values of net integrated intensity for the C(220), C(111), TiH<sub>2</sub>(110), TiC(111), and TiC(200) diffraction peaks. The trend exhibited by these quantities in the temperature range 650–850 °C can be observed in Fig. 2(a) for the diamond reflections, and in Fig. 2(b) for the reflections due to TiH<sub>2</sub> and TiC.

Figure 2(a), clearly shows that at 650 °C the diamond crystallites are preferentially oriented in the  $\langle hh0 \rangle$  direction. According to previous measurements,<sup>13</sup> at 650 °C the interface has a polycrystalline structure (mean grain size 15–25

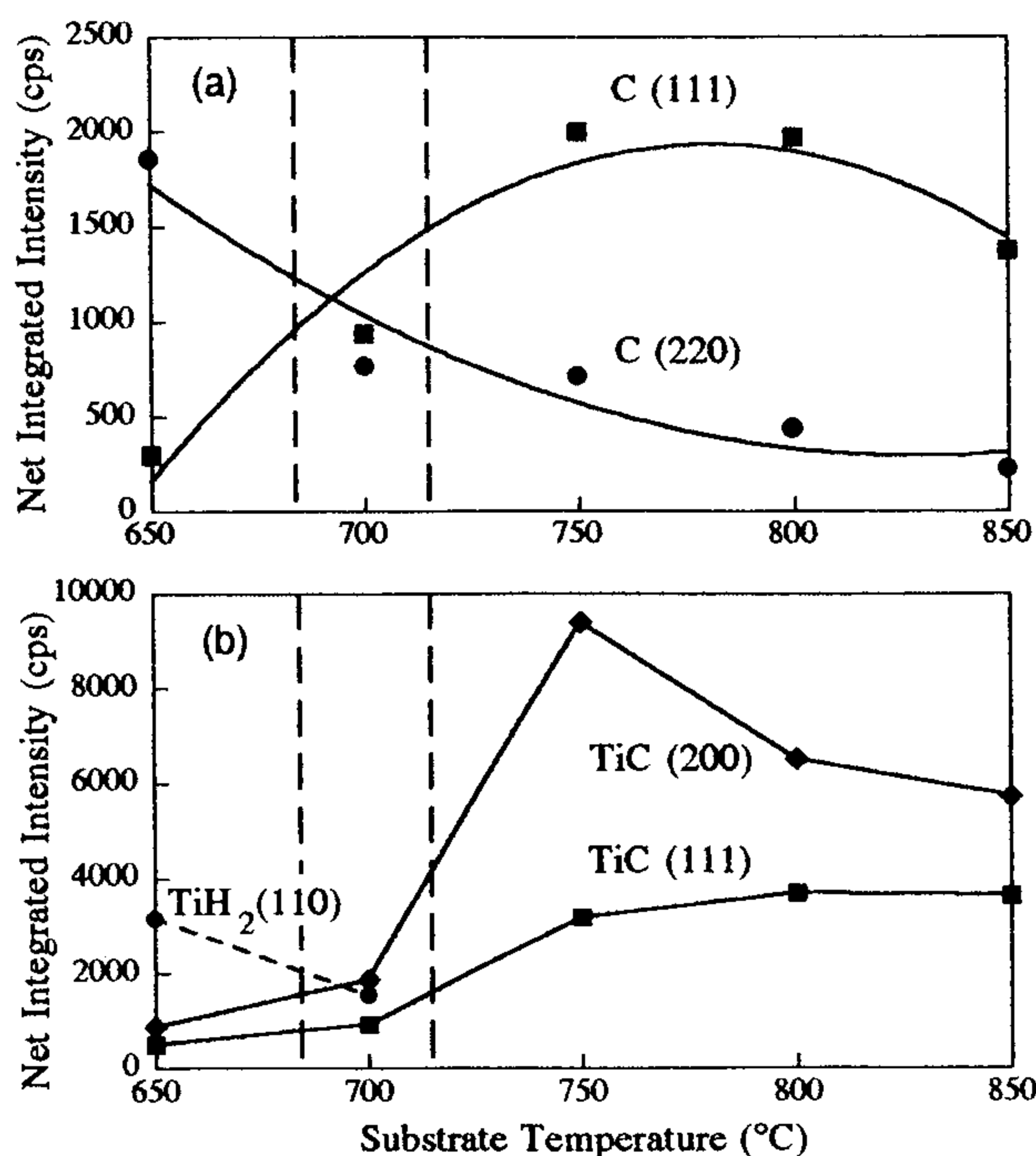


FIG. 2. Net integrated intensity as a function of the deposition temperature on (a) for the diamond (220) and (111) diffraction peaks and (b) for the TiH<sub>2</sub> (110), TiC(200), and TiC(111) peaks. The dashed lines define the critical zone around 700 °C.

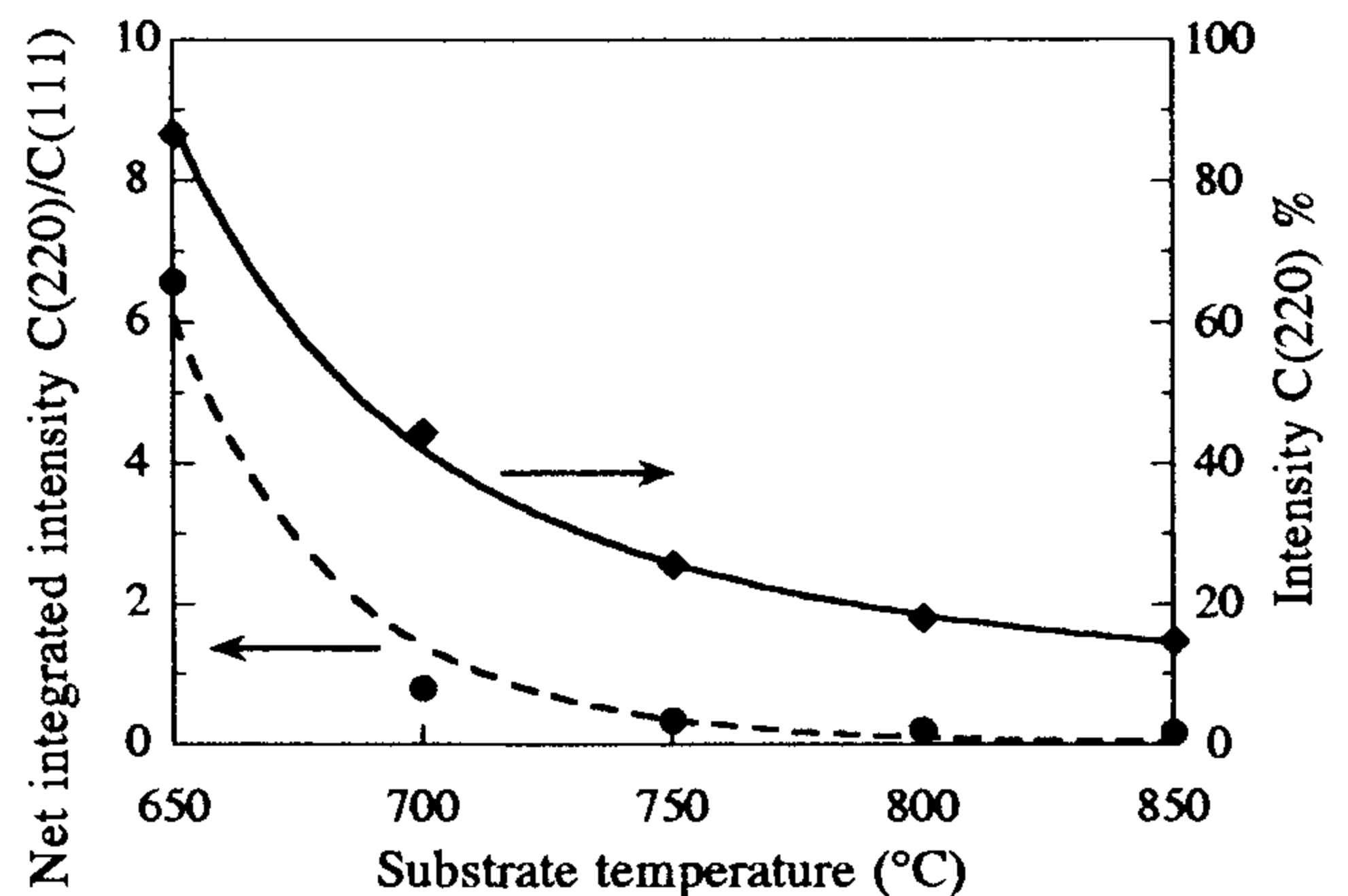


FIG. 3. Preferential orientation of diamond films expressed as a percentage of  $\langle 220 \rangle$  texture (full line, right scale) and C(220)/C(111) intensity ratio (dashed-line, left scale).

nm) mainly formed by randomly oriented TiC, and by the TiH<sub>2</sub> grains oriented in the direction  $\langle hh0 \rangle$ , with a prevalence of the TiH<sub>2</sub> phase in the mixed TiC/TiH<sub>2</sub> layer.

The formation of a diamond film textured for about 87% (Fig. 3) along the  $\langle hh0 \rangle$  direction occurs, therefore, on a mixed TiC/TiH<sub>2</sub> layer characterized by the preponderant presence of hydride grains aligned along the  $\langle hh0 \rangle$  direction.

With increasing substrate temperature, the  $\langle hh0 \rangle$  orientation of the diamond crystallites progressively converts to  $\langle hhh \rangle$ . At 700 °C only ~45% of the grains are aligned in the  $\langle hh0 \rangle$  direction. Concerning the structure of the interfacial layers, present results indicate that going from 650 to 700 °C, the integrated intensity of the TiH<sub>2</sub> line is halved, and the titanium hydride signal no longer appears in the 750 °C diffraction pattern. In this temperature range, the lowering of the TiH<sub>2</sub>( $hh0$ ) signal mimics the trend of the diamond (220) peak intensity. On the contrary, the formation of the TiC phase is enhanced at temperatures higher than 700 °C, as witnessed by the increasing values of intensity for both ( $hh0$ ) and ( $hhh$ ) TiC reflections. From inspection of Figs. 2(a) and 2(b), the general outline is that, under the conditions of the present experiments,  $T \cong 700$  °C represents a critical value for the diamond deposition process.

A further increase in deposition temperature, up to about 750 °C, is found to promote  $\langle 111 \rangle$  textured growth of diamond films. The formation of progressively thicker carbide layers probably explains the observed disappearance of the Ti peaks from the diffraction patterns at  $T > 750$  °C. Moreover, the decrease in the full width at half-maximum (FWHM) values<sup>14</sup> obtained for the TiC reflections (111), (200), and (222) after normalization of each ( $hkl$ ) peak to the same height (Fig. 4), indicates an increase in the titanium carbide grain size with deposition temperature. After 800 °C, however, both the net integrated intensity [Fig. 2(b)] and the FWHM (Fig. 4) show a trend variation, probably due to some saturation effect in the TiC growth process. It is, indeed, worth stressing that when the TiC layer reaches a critical thickness, further growth of the carbidic phase is limited by titanium diffusion through the carbidic layer itself.<sup>15</sup> At temperatures higher than about 800 °C, also observed is a decrease in the net integrated intensity for the C(111) peaks

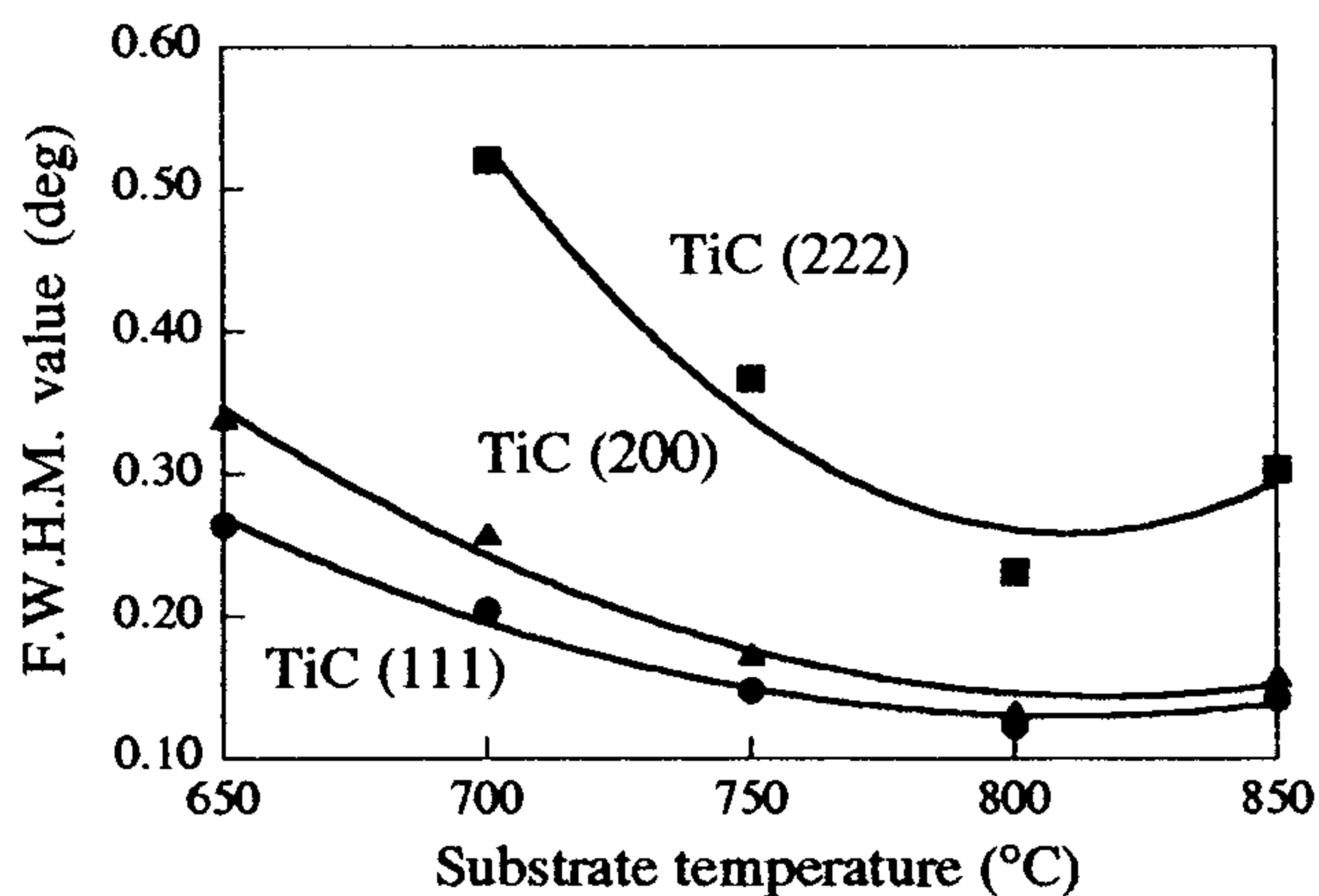


FIG. 4. Trend of the FWHM values for the TiC peaks vs substrate temperature.

[Fig. 2(a)]. This result can be rationalized if we consider that for  $T > 750$  °C the CVD process on titanium progressively yields an increasing amount of codeposited nanocrystalline graphite and/or amorphous diamond-like carbon,<sup>16</sup> which has a detrimental effect on diamond nucleation.

The trend of preferred orientation for diamond crystallites in the whole temperature range investigated is better demonstrated in Fig. 3. The  $C(220)/C(111)$  intensity ratio shows an exponential decrease, with values going from 6.57 at 650 °C to 0.17 at 850 °C.

A completely inverted trend, i.e., a gradual enhancement of the  $\langle hh0 \rangle$  growth direction with increasing temperature was, conversely, found by other researchers<sup>17</sup> for diamond coatings on silicon. The discrepancy noted at first a glance between the two sets of data (cf. Table II of Ref. 17, and Fig. 3, present work) can be, however, rationalized if one considers that the reported trends refer to different substrate materials, namely, silicon and titanium. The difference in growth mode exhibited by diamond films according to whether deposited on silicon or titanium can safely be ascribed to differences in the process of nucleation and growth on surface layers characterized by different kinetics of carbon diffusion, adsorption, desorption, and carbide formation. Moreover, in the case of titanium, the formation of the hydride phase must be taken into consideration.

We wish to emphasize that, in our CVD conditions, the film's thickness seems to enhance the degree of preferential orientations, whereas the crystallite's growth direction remains unchanged. According to previous results<sup>9</sup> at 650 °C the degree of preferential orientation along  $[hh0]$  as a function of the deposition time, and therefore of the film thickness, was found to be of the order of 30% for 20 min deposition time, and to approach the value of 90% for 180 min grown films.<sup>18</sup>

Overall, the present findings indicate some relationship between the preferred orientation of diamond films and the structural characteristics of the layers generated at the titanium surface during the CVD process, and agree with the conclusions of studies performed on the Si/SiC/diamond system.<sup>8</sup>

Preliminary results obtained by using silica-glass<sup>19</sup> and Ta<sup>20</sup> substrates also suggested that the final texturing of the

diamond films strongly depends on the composition and microstructure of the interfacial layers deposition. Unfortunately, whereas many studies have investigated the competitive growth mechanism for the various diamond planes<sup>21</sup> on silicon substrates,<sup>22-31</sup> only scarce information is currently available for other substrate materials used for diamond deposition.

We hope that present results can help to identify and select the experimental conditions that promote textured growth of diamond films on various materials via epitaxial relationship with the underlying structures.

The authors wish to thank C. Veroli of the CNR-ICM (Montelibretti, Italy) for his collaboration in doing the XRD measurements. This work was partly supported by the INFN-Legnaro National Laboratories.

- <sup>1</sup>B. R. Stoner and J. T. Glass, *Appl. Phys. Lett.* **60**, 698 (1992).
- <sup>2</sup>B. R. Stoner, S. R. Sahaida, J. P. Bade, P. Southworth, and P. J. Ellis, *J. Mater. Res.* **8**, 1334 (1993).
- <sup>3</sup>S. D. Wolter, B. R. Stoner, J. T. Glass, P. J. Ellis, D. S. Buhaenko, E. E. Jenkins, and P. Southworth, *Appl. Phys. Lett.* **62**, 1215 (1993).
- <sup>4</sup>X. Jiang, C. P. Klages, R. Zachai, M. Hartweg, and H. J. Füsser, *Appl. Phys. Lett.* **62**, 3438 (1993).
- <sup>5</sup>R. Kohl, C. Wild, N. Herres, P. Koidl, B. R. Stoner, and J. T. Glass, *Appl. Phys. Lett.* **63**, 1792 (1993).
- <sup>6</sup>M. Shreck, R. Hessmer, S. Geier, B. Rauschenbach, and B. Stritzker, *Diam. Relat. Mater.* **3**, 510 (1994).
- <sup>7</sup>S. Barrat and E. Bauer-Grosse, *Diam. Relat. Mater.* **4**, 419 (1995).
- <sup>8</sup>H. Kawarada, T. Suesada, and H. Nagasawa, *Appl. Phys. Lett.* **66**, 583 (1995).
- <sup>9</sup>G. Cappuccio, V. Sessa, M. L. Terranova, and C. Veroli, *Mater. Sci. Forum* **166-169**, 325 (1994).
- <sup>10</sup>M. L. Terranova, V. Sessa, M. Rossi, G. Vitali, G. Cappuccio, and C. Veroli, *J. de Phys. IV C5*, 879 (1995).
- <sup>11</sup>JCPDS-ICDD-Powder Diffraction File (1988): Diamond 6-675, TiC 32-1383, TiH<sub>2</sub> 9-371, Ti 5-682.
- <sup>12</sup>E. Burattini, G. Cappuccio, P. Maistrelli, and S. Simeoni, *Mater. Sci. Forum* **133-136**, 309 (1993).
- <sup>13</sup>G. Cappuccio, M. Leoni, P. Scardi, V. Sessa, and M. L. Terranova, *Mater. Sci. Forum* **203**, 285 (1996).
- <sup>14</sup>B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley, Reading, MA, 1978), p. 102.
- <sup>15</sup>S. Sarin, *J. Appl. Phys.* **40**, 3515 (1969).
- <sup>16</sup>M. Rossi (private communication, 1996).
- <sup>17</sup>H. Windischmann, G. F. Epps, Y. C. Cong, and R. W. Collins, *J. Appl. Phys.* **69**, 2231 (1991).
- <sup>18</sup>M. Rossi, G. Vitali, M. L. Terranova, and V. Sessa, *Proceedings ICEM 13-PARIS*, 951 (1994).
- <sup>19</sup>M. L. Terranova, M. Rossi, V. Sessa, and G. Vitali, in *Proceedings of the Second AIMAT (Trento, Italy, 1993)*, Vol. 2, p. 653.
- <sup>20</sup>M. L. Terranova, V. Sessa, and M. Rossi (unpublished).
- <sup>21</sup>A. Van der Drift, *Philips Res. Rep.* **22**, 267 (1967).
- <sup>22</sup>Ch. Wild, N. Herres, and P. Koidl, *J. Appl. Phys.* **68**, 973 (1990).
- <sup>23</sup>C. Wild, P. Koidl, W. Mueller-Sebert, and T. Ecerman, *Electrochem. Soc. Proc.* **91/8**, 224 (1991).
- <sup>24</sup>R. E. Clausing, L. Heatherly, L. L. Horton, E. D. Specht, G. M. Begun, and Z. L. Wang, *Diam. Relat. Mater.* **1**, 411 (1992).
- <sup>25</sup>C. J. Chu, R. H. Hauge, J. L. Margrave, and M. P. D'Evelyn, *Appl. Phys. Lett.* **61**, 1393 (1992).
- <sup>26</sup>C. Wild, P. Koidl, W. Mueller-Sebert, H. Walcher, R. Kohl, N. Herres, R. Locher, R. Samlenski, and R. Brenn, *Diam. Relat. Mater.* **2**, 158 (1993).
- <sup>27</sup>N. Fujimori, *Proceedings of Advanced Materials '94*, edited by M. Kamo, H. Kanda, Y. Matsui, and T. Sekine (NIRIM, Japan, 1994), p. 146.
- <sup>28</sup>C. Wild, R. Kohl, N. Herres, W. Mueller-Sebert, and P. Koidl, *Diam. Relat. Mater.* **3**, 373 (1994).
- <sup>29</sup>S. Barrat, I. Dieguez, H. Michel, and E. Bauer-Grosse, *Diam. Relat. Mater.* **3**, 520 (1994).
- <sup>30</sup>S. Barrat and E. Bauer-Grosse, *Diam. Relat. Mater.* **4**, 419 (1995).
- <sup>31</sup>H. Maeda, K. Ohtsubo, M. Irie, N. Ohya, K. Kusakabe, and S. Morooka, *J. Mater. Res.* **10**, 3115 (1995).