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Photoelectron spectroscopy of CVD diamond*

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Abstract

We report a study of the electronic structure of thin diamond films by core state (X-ray photoelectron spectroscopy (XPS)) and valence band (UV photoelectron spectroscopy (UPS)) photoelectron spectroscopy. These techniques were used to investigate the different phases in the initial growth of polycrystalline diamond films on Si(100) substrates. The films were deposited by a standard microwave technique as well as by bias-enhanced microwave plasma chemical vapour deposition in a dilute mixture of methane in hydrogen. The influence of sample preparation (such as prebiasing or prescratching of the silicon surface with different sized diamond powder prior to deposition) on nucleation density and electronic structure was also investigated by scanning electron microscopy and photoelectron spectroscopy (PES) respectively. The surface composition was probed as a function of deposition time. The XPS data reveal the formation of an SiC phase at the early stage on nucleation, preceding the gradual growth of diamond. At intermediate stages a combination of different carbon phases was observed. The atomic structure of the interface phases is discussed and a growth model is proposed. Valence band spectra of the different samples show the extreme sensitivity of PES to impurities and to surface properties such as reconstruction. The obtained data were compared to valence band measurements of natural diamond and other forms of carbon and to some extent to data obtained with Raman spectroscopy.

1. Introduction

Since the discovery of the microwave plasma chemical vapour deposition (CVD) technique to produce diamond and diamond-like carbon films, huge effort was put in obtaining ever better quality films. One important step in this evolution was the establishment of various nucleation enhancement procedures in order to increase the deposition rate and nucleation density. It is a well-known fact that the surface density of diamond particles per unit substrate area is enhanced on scratched substrate surfaces. In particular, surface polishing by diamond grit seems to be the most efficient, compared to surface treatments with other abrading materials [1].

It is the aim of the present paper to participate in the discussion about the differences of different pretreating methods on the growth of diamond films. Because of the surface sensitivity of photoelectron spectroscopy (PES), this technique is ideal for studying the initial stages of nucleation and growth of diamond on a non-diamond substrate [2]. The possible potential of PES in characterizing CVD diamond films will be discussed here.

2. Experimental details

Our diamond films were deposited by a standard microwave-plasma-assisted chemical vapour deposition (MWCVD) in the downstream configuration. The apparatus consisted mainly of a quartz tube with 41 mm inner diameter in which the incoming methane and hydrogen mixture was activated to a plasma. The composition of the mixture was regulated by flow meters, and the temperature of the sample was measured by a one-colour pyrometer.

The Si(100) wafer pieces were scratched for several minutes using diamond polishing dust of sizes 0.1, 1 and 3 μm, then ultrasonically cleaned in acetone and dried by nitrogen. In the case of the biased sample an Si(111) wafer was exposed to a 5% CH_4–H_2 plasma for 25 min while a biasing voltage of -250 V was applied to the substrate holder. Afterwards the bias voltage was set to zero and normal deposition parameters were used, such as: pressure, 30 mbar; CH_4/H_2, 0.7%; flow, 150 standard cm^3 min^{-1}; temperature, 950 °C.

The UPS measurements were performed on either a Leybold EA 10/100 or Leybold EA 11/100 spectrometer. The spectra were recorded by operating the spectrometer at a constant retardation ratio. The energy solutions for the two photon energies used here are 0.1 and 0.2 eV for the He I ($h\nu = 21.22$ eV) and He II ($h\nu = 40.8$ eV) excitation lines respectively. X-ray photoelectron

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spectroscopy (XPS) was performed using non-monochromatic Mg Kα (XPS) radiation with a photon energy of 1253.6 eV on a Leybold EA 10/100 spectrometer. These spectra were recorded with constant pass energies resulting in an energy resolution of 0.7 eV. Unless otherwise stated, all spectra here are shown without any data treatments such as background or satellite subtraction. Some of the diamond valence band spectra have been aligned in order to compensate for charging effects that may occur when performing PES on the highly insulating films.

3. Results

3.1. *Influence of the sample preparation on electronic structure and nucleation density*

The number of diamond crystallites per square centimetre was calculated from scanning electron microscopy pictures. In the case of the virgin Si(100) substrate, the deposition density of diamond particles was only several hundred per square centimetre. On the scratched samples deposition density was increased by a factor of 10^6, but nucleation density did not, as we expected, increase significantly with diminishing size of diamond polishing particles. The results were: 1.7×10^8 cm^{-2}, 3.4×10^8 cm^{-2} and 2.2×10^8 cm^{-2} for 0.1 μm, 1 μm and 3 μm sized particles respectively. This could mean that no residual diamond particles, acting as nucleation centres, were left and nucleation took place only on hydrocarbon residuals. Other authors already have pointed out the enhancing of heterogeneous diamond nucleation on Si by the presence of surface carbides [3]. It was reported that polishing time [4] as well as strength [5] are playing a crucial role in determining exact differences in nucleation density. We therefore have to carry out further research on this topic.

Fig. 1 shows three different forms of carbon and the initial stage of the growth of the biased sample #209 (see Table 1). The UPS valence band spectra are dominated by p-electron states due to the much higher excitation cross-section at these low photon energies [6]. The deposited material on sample #209 can be best ascribed to sputtered carbon.

A thorough inspection of the sample surface composition is important in order to find additional information regarding the structures observed in Fig. 1 (and Fig. 3; see below). Although the samples have not been cleaned in the photoelectron spectrometer once exposed to air, the contamination by oxygen on the closed films is unusually low. An oxygen contamination level between 0.5 and 2.8 at.% has been calculated out of the XPS data. The features observed in Figs. 1 and 3 do not scale with oxygen contamination. Table 1 shows the chemical surface compositions of the samples as determined from integrated core level intensities and theoretical pho ionization cross-sections [7].

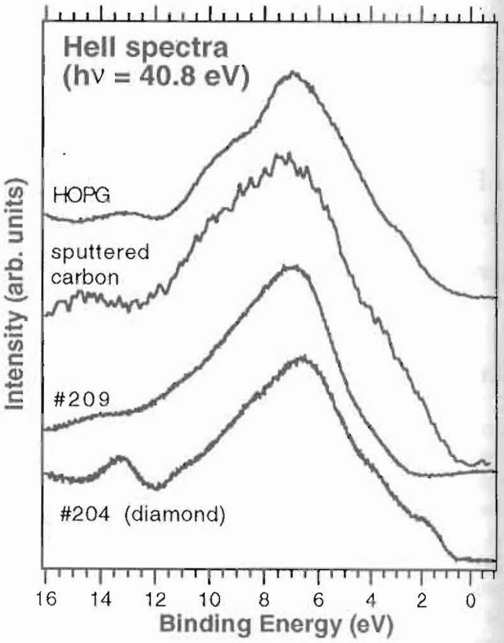

Fig. 1. UPS He II spectra of different carbon phases and of
#209 and #204.

TABLE 1. Surface composition of the presented samples

Sample	Fig.	Deposition time (min)	Surface concentration		
			O	C	S
Si(100) S	2	0	36	17	47
207 S	2	10	27	25	48
206 S	2	30	26	28	47
205 S	2	60	8	68	24
208 S	2	120	10	89	2
212 S	2	165	2	98	0
204 S	1	300	0	100	0
209 B	1	70	21.6	27.9	50.4
66 S	4	240	0.9	99.0	0.1
78 B	4	245	0.6	99.2	0.2

S, scratched; B, biased.

3.2. *Si–diamond interface formation*

Films grown for increasing deposition times
10 min to several hours) were analysed for the
composition by XPS. All samples were prescrat
with 1 μm diamond grit and deposition parameters
held constant as mentioned in Section 2. Fig. 2 sh
the core level intensities of the C 1s and Si 2p sign
a function of deposition time. Spectra a, b and
adjusted to an arbitrary intensity for a better underst
ing. At the early growth stages the forming of an
interface between the Si substrate and the diam
particles growing on it can be observed in the C

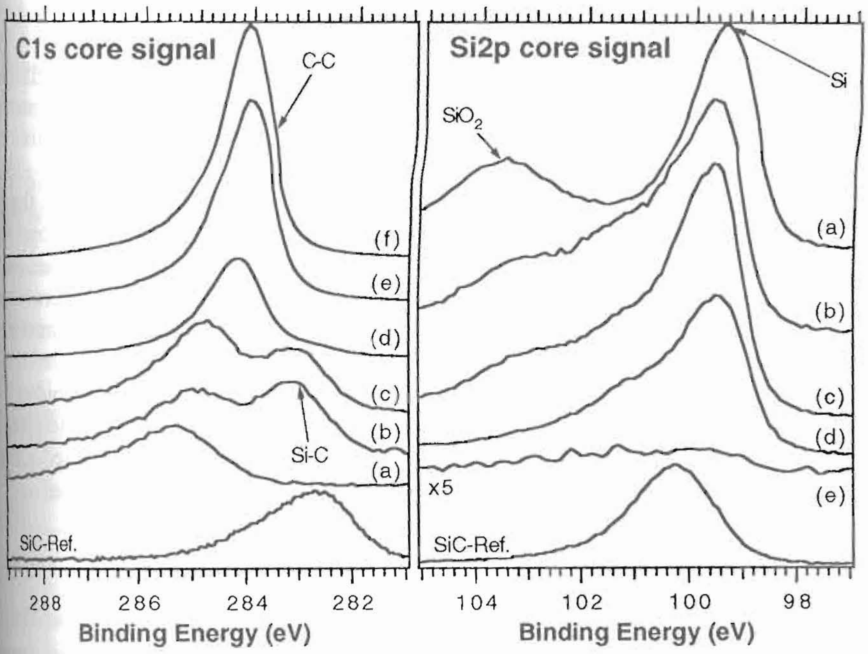

Fig. 2. XPS C 1s and Si 2p spectra of MWCVD films at 0 min (spectrum a), 10 min (spectrum b), 30 min (spectrum c), 1 h (spectrum d), 2.8 h (spectrum e) and 4 h (spectrum f) deposition time, and an SiC reference spectra.

well as in the Si 2p region. After a prolonged time only the diamond signal can be observed and the Si 2p region shows no features even at high magnification. The 1 μm diamond-grit-scratched Si(100) sample showed no sign of SiC or diamond particles left on the surface; only some carbonaceous residuals are observed (see spectrum a on the left). The SiO_2 peak originates from the native oxide layer on the Si wafer. For comparison, the spectra of an SiC reference sample are shown.

3.3. *Surface properties of CVD diamond films: reconstruction*

The He II spectra of some closed CVD diamond films, together with a spectrum of a natural (110) diamond window, are shown in Fig. 3. The diamond window was heated in situ up to 850 °C as a cleaning procedure. Spectra b and c refer to samples prepared by MWCVD, but have not been measured in situ. The spectra are very similar and show the same features at 6–7 eV originating from p–σ bondings and around 13 eV from the 'diamond peak'. Compared with spectrum a the polycrystalline and the (100)-structured CVD diamond films show a distinct peak at 1.5 eV binding energy. It is known from scanning tunnelling microscopy (STM) investigations that CVD-grown films apparently show a 2 × 1 reconstruction in air. After heating the (100)-structured film in a hydrogen plasma up to 900 °C for several minutes a strong peak at 1.5 eV emerges (see spectrum d). Synchrotron radiation measurements of this film showed a very distinctive intense peak at the same position for radiation energies between 30 and 50 eV. UPS He II spectra of natural 2 × 1 surface-reconstructed (100) diamond show similar features [8]. We therefore conclude that the observed peak at 1.5 eV belongs to a surface state associated with a 2 × 1 hydrogen-free reconstructed surface.

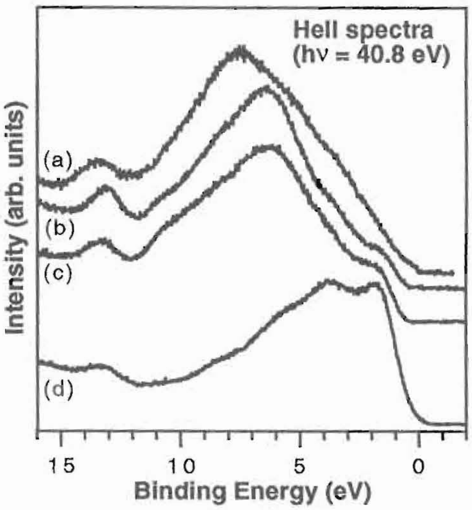

Fig. 3. UPS He II spectra of natural (110) diamond (spectrum a), polycrystalline diamond film (spectrum b) (100)-structured CVD diamond film (spectrum c), and the same film after H plasma heating (spectrum d).

3.4. *Raman spectroscopy*

As a well-established method, Raman spectroscopy was used to monitor the differences between normal

MWCVD and bias-enhanced MWCVD films. Raman spectra of sample #78 (a closed bias-enhanced MWCVD film) and of sample #66 (an MWCVD film) were taken in the backscattering configuration by the use of a 514 nm argon ion laser. The appearance of the characteristic crystalline diamond line at 1332 cm^{-1} clearly shows the formation of the diamond phase for both samples.

Fig. 4 shows the Raman spectra of sample #78 (spectrum b), #66 (spectrum c) and of amorphous carbon (spectrum a). Sample #66 shows a broad feature at 1550 cm^{-1} that can be best ascribed to amorphous carbon. This amorphous carbon originates most probably from the domain boundaries between the diamond crystals. In the case of the biased sample this feature is absent. Broad peaks at around 1460 and 1610 cm^{-1} could be the proof for other disordered sp^2-bonded carbon material acting as interface. Yarbrough and Roy report a peak around 1470 cm^{-1} which is classified as diamond precursor [9]. Although biased deposition increased the nucleation density the quality of the measured film was poorer than that of the normally deposited film. The smaller intensity is due to smaller crystallites and the high amount of non-diamond carbon products in the interface and grain boundaries.

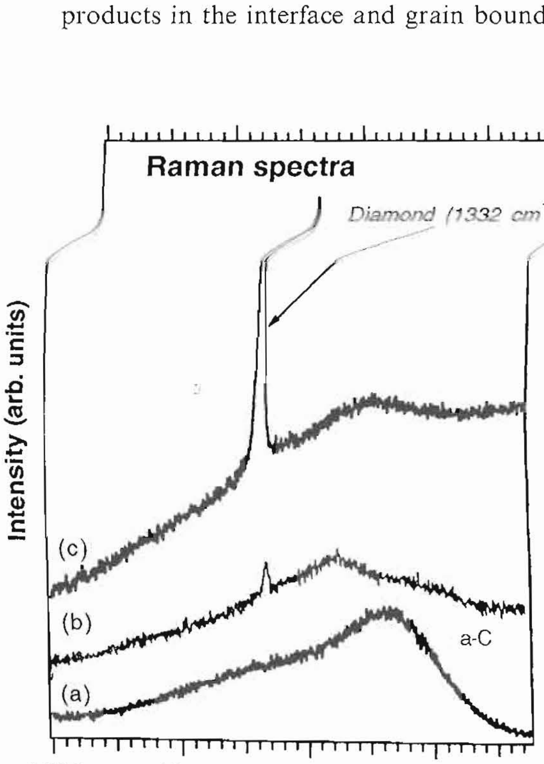

Fig. 4. Raman spectra of amorphous carbon (spectrum a), biased MWCVD film #78 (spectrum b) and "normal" MWCVD diamond film #66 (spectrum c).

4. Conclusion

As pointed out in earlier work [2,10
powerful tool to investigate the Si–diam
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substrates with diamond dust greatly enha
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SiC or on disordered sp^2-bonded carbon
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Even though our samples have not been
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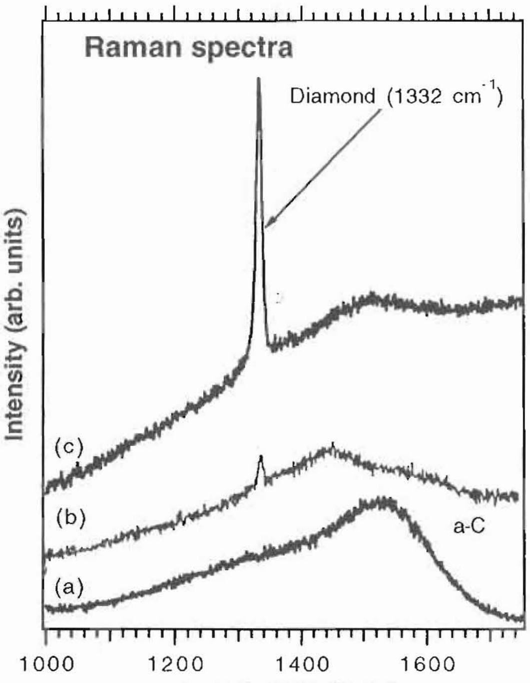

Fig. 4. Raman spectra of amorphous carbon (spectrum a), biased MWCVD film #78 (spectrum b) and "normal" MWCVD diamond film #66 (spectrum c).

4. Conclusion

As pointed out in earlier work [2,10] PES is a powerful tool to investigate the Si–diamond interface formation and surface properties of polycrystalline diamond films. We have shown that scratching silicon substrates with diamond dust greatly enhances the diamond nucleation. PES and Raman spectroscopy indicated that diamond particles start to grow either on the SiC or on disordered sp^2-bonded carbon sources as in the case of bias-enhanced MWCVD. The high nucleation density observed on biased samples could be due to these heterogeneously distributed surface carbides.

Even though our samples have not been measured in situ, surface states associated with reconstructed surfaces have been observed by UPS.

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