

# Mechanisms of CVD diamond nucleation and growth on mechanically scratched and virgin Si(100) surfaces

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## Abstract

The diamond nucleation and growth processes on a scratched and a virgin Si(100) surface were studied by both electron spectroscopies (XPS) and microstructural probes (SEM, TEM) in order to connect the nature of surface species with the structural changes. We have shown that a preliminary scratching of the substrate surface hugely enhances the nucleation kinetics relative to the virgin sample. This is explained by the much faster formation of stable diamond nuclei in correspondence of suitable nucleation sites. The results have been modeled, considering the covered surface  $S$  as the unique parameter.  $S$  obeys an Avrami plot of the form  $S = 1 - \exp(-kt^n)$  where the exponent  $n \approx 2.5 \pm 0.4$  over a wide range of deposition is indicative of a constant linear growth rate with decreasing nucleation rate. © 1997 Elsevier Science S.A.

**Keywords:** Diamond nucleation; Electron spectroscopies; Silicon; Silicon carbide

## 1. Introduction

The success in growing diamond films by using the chemical vapor deposition (CVD) process has stimulated an enormous interest in the unique properties of diamond for new technological applications [1,2]. However attempts to grow diamond on non-diamond substrates yielded poorly adhesive polycrystalline films consisting of randomly oriented crystals which contain non-diamond carbons and numerous defects. One main reason for this is the poor understanding of nucleation and growth in the early stages, diamond being a metastable form of carbon under the deposition conditions. We have performed a comparative study of diamond nucleation and growth processes on mechanically scratched and virgin Si(100) surfaces, respectively. In a previous work [3], we have established that nucleation on virgin Si(111) and Si(100) surfaces occurs through a three-step process already described [4,5]. The experiments were carried out in a synthesis chamber directly connected to a surface analysis chamber, allowing sequential monitoring of the diamond nucleation and growth by electron spectroscopies (X-ray photoemission (XPS),

Auger electron (AES) and electron loss (ELS) spectroscopies) without air exposure. A set of depositions on independent samples were performed separately for microstructural investigations including scanning electron (SEM), atomic force (AFM) and transmission electron (TEM) microscopies.

## 2. Experimental

The samples were obtained by polishing a B-doped ( $17\text{--}23 \Omega \cdot \text{cm}$ ) Si(100) wafer with diamond paste with a final polishing at  $0.25 \mu\text{m}$ . Surface structural defects are generated by randomly distributed scratches as well as by subplanted carbon residues left on the substrate. Before being introduced in the preparation chamber, they were ultrasonically cleaned in  $\text{CCl}_4$  and ethanol. The only surface impurities that could be detected were carbon and oxygen. The initial surface exhibits a silicon oxide layer as displayed in Fig. 1(A). Its depth is estimated to  $1.5\text{--}1.6 \text{ nm}$ , according to Auger calibrations. In general no in situ surface treatment was attempted. The reasons for this are discussed in detail in Ref. [6], but soon this leads to changes in the nucleation kinetics and the density at saturation. The virgin

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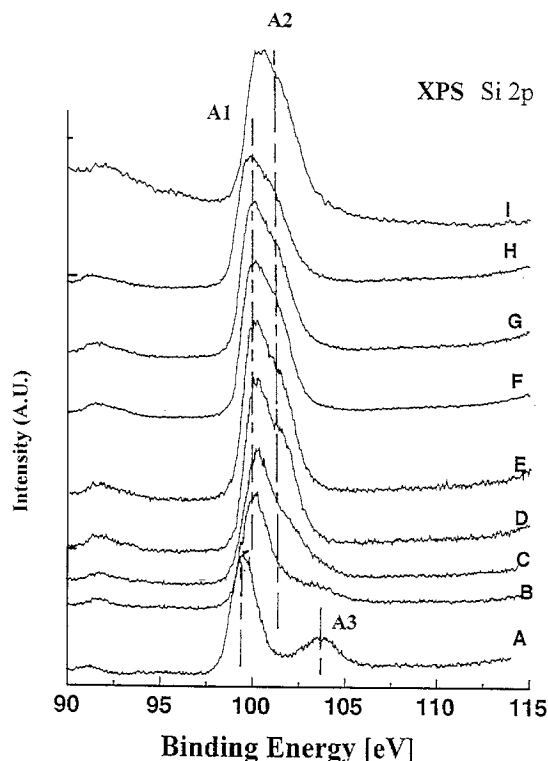


Fig. 1. Evolution of the Si 2p core level with the cumulative deposition time. Scratched Si(100) sample. (A) Initial surface; (B) 2 min; (C) 4 min; (D) 21 min; (E) 56 min; (F) 97 min; (G) 112 min; (H) 162 min; (I) 302 min. The assignment of the A1, A2 and A3 lines is reported in the text.

Si(100) samples were prepared by mechanical scratching, chemical etching and finally UHV cleaning at about 1200 K. AES analysis then displays a single Si LVV contribution at 89 eV [7].

CVD growth by the hot filament process was carried out in a chamber described elsewhere [3]. The experimental conditions are: distance between the tungsten filaments and the substrate:  $5 < d < 7$  mm; activation power:  $185 \pm 5$  W, corresponding to a temperature of the filaments of  $2400 \pm 25$  K; temperature of the substrate:  $1073 \pm 5$  K; total gas flow: 200 sccm; methane content: 0.5%; total pressure: 3 kPa.

Surface analyses by electron spectroscopies (XPS, AES, ELS) were performed in an UHV chamber equipped with a VSW hemispherical analyser described elsewhere [3]. The energy resolution of the XPS analyses was 0.6 eV. The electron beam energy was 1 keV for AES, 1.2 keV and 250 keV for ELS and impinged on an area of about  $2 \text{ mm}^2$ .

Microstructural investigations were performed by SEM, TEM and AFM. The SEM lateral resolution was estimated to  $0.05 \mu\text{m}$ . Morphological data such as the covered surface were determined by using the image processing software Khoros. Samples were characterized by AFM on a multimode Nanoscope III apparatus from

Digital Instruments. The observations were performed in the tapping mode. The samples for TEM were prepared by the extractive replica technique. After coating by an amorphous carbon layer the silicon support is dissolved by a HF:  $\text{CH}_3\text{COOH}$ :  $\text{HNO}_3$  solution (1:3:2 by vol.). Thin films of the carbon islands are then coated on 1000-mesh copper grids. The observations were performed on a Topcon EM-002B apparatus with an accelerating voltage of 200 kV.

### 3. Results

A sequence of Si 2p core level is displayed in Fig. 1 with increasing cumulative deposition time for the scratched Si (100) sample. As stated above, the surface of the initial substrate is oxidized, so that a large oxide contribution  $\text{SiO}_x$  (A3) merges around 104 eV besides the elemental silicon at 99.6 eV (A1). This oxide contribution disappears after the first deposition sequence, but a new one is detected at 101.9 eV (A2) as a shoulder of the main silicon contribution. This new feature becomes clearly visible as soon as 21 min of deposition time. It could be assigned to silicon carbide [8,9]. On the other hand the elemental silicon contribution A1 shifts by about 0.6 eV to higher energies. This shift corresponds to a change in the work function as soon as the silicon surface is cleaned by oxygen removal and the carbon deposition starts. Above 21 min of deposition, we only detect these two contributions with a relative ratio which does not change very much. A small tail around 103 eV still indicates the occurrence of some substoichiometric silicon oxide. This is consistent with a small but constant O 1s contribution.

In a similar way, the evolution of the C 1s core level with the cumulative deposition time is displayed in Fig. 2. The broad initial peak denoted B2 at 284.6 eV corresponds to contamination carbon and to hard carbon residues left by the scratching process. These residues were first evidenced by Iijima [10] and they were assumed to explain the diamond growth by an initial seeding process. Attempts to eliminate this carbon contribution by sequences of  $\text{Ar}^+$  ion bombardments and thermal treatments were unsuccessful, by contrast with unscratched Si(100) and Si(111). Subsequent carbon depositions led to two contributions. The first one at 283.15 eV (denoted B1) is the most intense up to about 115 min. This contribution can clearly be assigned to silicon carbide formation [8]. Furthermore, we note that the binding energy difference between the C 1s and the Si 2p core levels of silicon carbide quotes to  $B1 - A2 \approx 182.25 \pm 0.1$  eV, in good agreement with the 182.15 eV difference reported elsewhere on clean SiC [9]. The second contribution at 284.6 eV (B2) is initially very weak, but is rapidly increasing. It could be clearly evidenced above 56 min and becomes the unique one

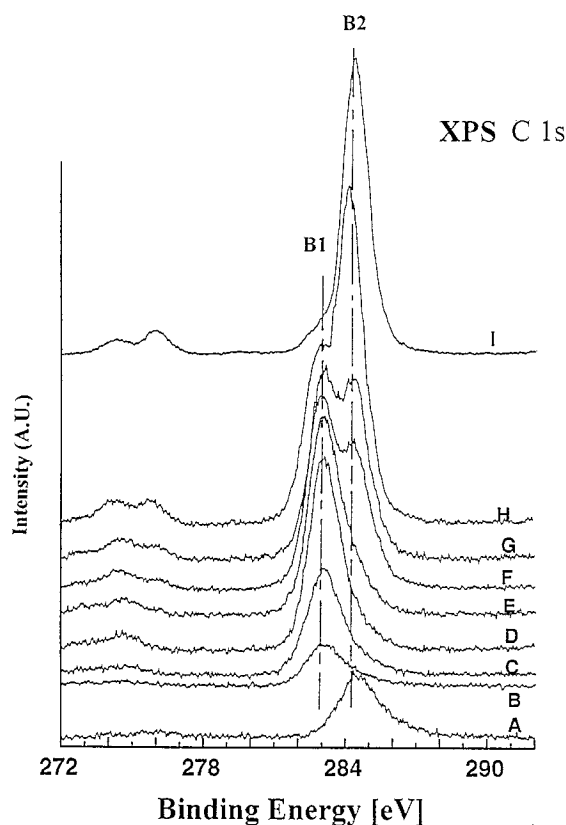


Fig. 2. Evolution of the C 1s core level with the cumulative deposition time. Scratched Si(100) sample. A) Initial surface; B) 2 min; C) 4 min; D) 21 min; E) 56 min; F) 97 min; G) 112 min; H) 162 min and I) 302 min. The assignment of the B1 and B2 lines is reported in the text.

above 302 min. We attribute it to diamond or to amorphous carbon, as reported in the literature [11,12]. Let us note that elemental carbon exhibits one single line around 284.6 eV whatever its structural form (graphitic, amorphous, diamond,...). The nature of this carbon species can thereby hardly be assessed from the unique consideration of this XPS line. However, both the AES lineshape of the C KVV line and energy loss spectra (ELS) clearly suggest that the carbon is mainly of the diamond type.

The evolution on the virgin Si(100) sample exhibits quite a similar behaviour on both the Si 2p and the C 1s core levels (not shown here), although on a much wider time scale.

The relative intensities of the silicon carbide signal  $I_{SiC}$ , determined both from the B1 and the A2 contributions, and the diamond signal  $I_D$  (contribution B2) are displayed as a function of the cumulative deposition time for both samples (Figs. 3 and 4, respectively). They are normalized to the signal of the substrate  $I_{Si}$  (contribution A1) and only the first 500 min are reported.

In both cases, the intensity of silicon carbide rapidly reaches a constant level which is larger on the scratched sample than on the virgin one (Fig. 3). By contrast, the

diamond signal increases on the scratched sample (Fig. 4), whereas a significant increase occurs only after 1200 min of carbon deposition. This is consistent with SEM, AFM and TEM observations as a diamond film is obtained after 300 and 3000 min on the scratched and virgin samples, respectively. As it is well known that diamond growth occurs through island formation, i.e. a Volmer–Weber mode, we modeled the XPS intensities, normalized to the substrate signal, by assuming first the formation of an homogeneous layer of silicon carbide of depth  $z$  onto which the diamond nucleates and grows in a 3D mode with a surface covering  $S$  [13].

The silicon carbide contribution can be expressed in two independent ways, considering the Si 2p and the C 1s signals:

$$I(\text{Si,SiC})/I(\text{Si,Si}) = \Lambda_{SiC} \{1 - \exp[-(z/\lambda_{SiC} \cos \theta)]\} / \Lambda_{Si} \exp(-z/\lambda_{SiC} \cos \theta) \quad (1)$$

$$I(\text{C,CSi})/I(\text{Si,Si}) = \Lambda_{CSi} \lambda_{CSi} \{1 - \exp[-(z/\lambda_{CSi} \cos \theta)]\} / \Lambda_{Si} \lambda_{SiC} \exp(-z/\lambda_{SiC} \cos \theta) \quad (2)$$

where  $\Lambda_{AB}$  and  $\lambda_{AB}$  are experimental constants and attenuation length that depend on the matrix AB and on the elements A and B, respectively, and  $\theta$  is the angle of the detector with the direction normal to the surface. From both Eqs. (1) and (2), the depth  $z_{\infty}$  of the silicon carbide layer can be extracted. This depth  $z_{\infty}$  is determined to 1.2 and  $1.0 \pm 0.1$  nm for the scratched and the virgin samples, respectively, using  $\lambda_{SiC} = 1.5$  nm. This last value, extracted from the literature [14], is known within 0.3 nm, so that the true error (experimental + systematic) on  $z_{\infty}$  is probably higher than 0.1 nm. Moreover they are probably slightly underestimated as we include the small signal of substoichiometric silicon oxide in the overall signal of the substrate. Similarly the diamond signal can be expressed as:

$$I(\text{C,D})/I(\text{Si,Si}) = \Lambda_D \lambda_D S / \Lambda_{Si} \lambda_{SiC} \times \exp(-z/\lambda_{SiC} \cos \theta) (1 - S) \quad (3)$$

The covered surface  $S$  has been determined from image analysis of the SEM, AFM and TEM pictures. We found that it obeys an Avrami law similar to a phase transformation process [15] (Fig. 5):

$$S = 1 - \exp(-kt^n), \quad (4)$$

where  $k$  is a kinetic constant and  $n$  an exponent which is characteristic of the growth mechanism. We find  $n \approx 2.5 \pm 0.4$  over a wide range of deposition time. In the case of a constant growth rate and constant nucleation rate, an  $n$  value of 3 is expected. On the other hand, in the case of constant growth rate and Dirac  $\delta$  nucleation [16],  $n$  quotes to 2. Thereby intermediate  $n$  values between 2 and 3 means that, in the range of deposition times considered, the nucleation rate is decreasing, whereas the activated species directly

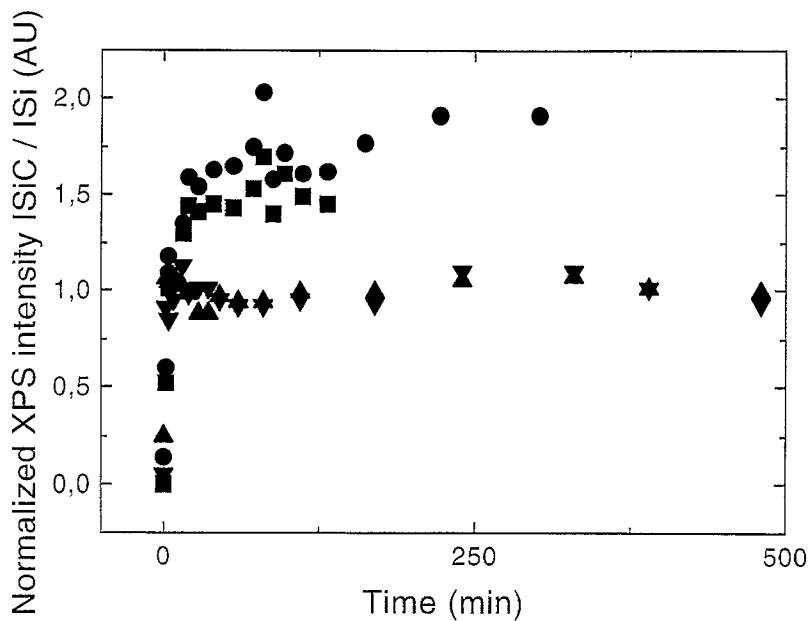


Fig. 3. Evolution of the silicon carbide XPS signal normalized to the silicon substrate. Scratched sample: Solid square: Si 2p core level; solid circle: C 1s core level. Virgin sample: Down triangle: Si 2p core level; Up triangle: C 1s core level.

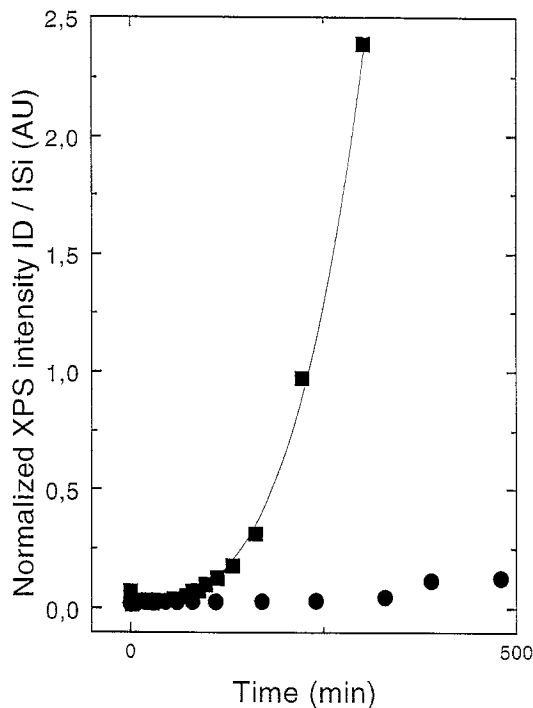


Fig. 4. Evolution of the diamond XPS signal normalized to the silicon signal. (Solid square): scratched Si(100); (solid circle): virgin Si(100). The solid line corresponds to a fit according to Eqs. (1), (3) and (4).

impinges on the diamond island from the gas phase. By including the expression of  $z$  extracted from Eq. (1) or Eq. (2) and putting Eq. (4) into Eq. (3), the evolution of the XPS diamond signal can be fitted Eq. (4) and the kinetic constants  $\ln k$  are estimated to  $-14.8$  and  $-18$  in  $\text{min}^{-2.5}$  for the scratched and the virgin samples,

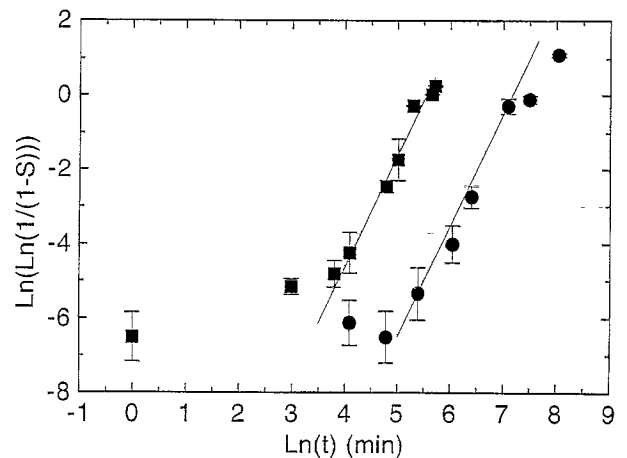


Fig. 5. Evolution of the logarithm of the uncovered surface as a function of deposition time on a logarithmic scale. Solid square, scratched sample; solid circle, virgin sample; solid line, fit according to Eq. (4) with  $n=2.5$  and  $\ln k = -14.8$  and  $-18$  in  $\text{min}^{-2.5}$  for the scratched and the virgin samples, respectively.

respectively. The agreement however is not satisfactory for the virgin sample at the start of the process. This is probably because the nucleation needs a large induction time with a poor density (around  $10^6$  nuclei/cm<sup>2</sup>), leading to a growth process limited by surface diffusion of the activated species. Let us conclude on two remarks:

(1) First, the very fast formation of the silicon carbide layer is independent of the pretreatment of the substrate, unlike the subsequent diamond nucleation. Thus we believe the silicon carbide layer plays a minor role in the diamond nucleation process.

(2) The faster diamond nucleation cannot be attrib-

uted only to the occurrence of carbon residues left on the surface of the scratched sample. In fact most of these carbon residues are transformed into silicon carbide at the first stages of the process (Fig. 2A and B). We believe that a carbon phase, possibly amorphous, is in equilibrium with this silicon carbide and that the microstructural defects created by the mechanical scratching also play a decisive role in the diamond nucleation.

#### 4. Conclusions

Electron spectroscopy (XPS) is a powerful probe to monitor the nucleation and growth of CVD diamond on silicon. Thereby by comparing these processes on a scratched and virgin Si(100) surfaces, we offer this evidence:

- (1) The rapid formation of a silicon carbide layer on both substrates of depth around 1–2 nm.
- (2) However, a quite different behaviour concerning the subsequent nucleation and growth of diamond. The growth has been modeled with an expression where surface coverage is the only parameter to be introduced.
- (3) The kinetic behaviour of the nucleation and growth can be extracted from the evolution of surface coverage with time. Thereby both on scratched and virgin Si(100) the slope of 2.5 determined from the Avrami's plot of the surface coverage suggests a linear growth rate and a decreasing nucleation rate on most of the deposition range.

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