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CVD diamond nucleation and growth on scratched and virgin Si(100) surfaces investigated by in-situ electron spectroscopy

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Abstract

The nucleation and growth of CVD diamond has been investigated on scratched and virgin Si(100) by photoemission spectroscopy. In both cases, a silicon carbide layer of a depth of 1–2 nm forms rapidly. The formation of this layer is apparently independent of subsequent diamond nucleation, which occurs after a long induction time on the virgin sample. The results are rationalized using Avrami's law of the kinetics of surface coverage by diamond islands.

Keywords: Chemical vapor deposition; Diamond; Growth; Nucleation; Silicon oxides; X-ray photoelectron spectroscopy

1. Introduction

The success in growing diamond films using the chemical vapor deposition (CVD) process has stimulated an enormous interest in the unique properties of diamond for new technological applications [1]. 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 a poor understanding of the early stages of the nucleation and growth of diamonds, which is a metastable form of carbon under the deposition conditions.

We have performed a comparative study of the diamond nucleation and growth process on

mechanically scratched and virgin Si(100) surfaces. The scratching treatment is performed with diamond paste (0.25 μm). Thereby, randomly distributed surface structural defects are generated and subplanted carbon residues are left on the surface. These residues are thought to be the surface sites and germ centers where diamond can grow further during the CVD process. It is important to compare this mechanism with the true mechanism which occurs on the virgin surface, where the presence of carbon residues can be excluded.

2. Experimental

All the Si(100) samples (10 mm $\times$ 10 mm) came from the same wafer supplied by Wacker. The scratched samples were prepared by polishing with

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diamond paste (15, 10, 3, 1 and finally 0.25 μm). The samples were cleaned ultrasonically in CCl_4 and ethanol solutions (10 min), before being introduced into the preparation chamber. The only surface impurities which could be detected were carbon and oxygen. The initial surface exhibits a silicon oxide layer, as shown in Fig. 1a, the depth of which is estimated to be 1.5–1.6 nm according to Auger calibrations. In general, no in-situ surface treatment was attempted. The reasons for this are discussed in detail in Ref. [2], but briefly, this leads to a change in the nucleation kinetics and the density at saturation. The virgin Si(100) samples were prepared by subsequent treatments of mechanical scratching, chemical etching and UHV cleaning at about 1200 K. AES analysis displayed a single Si LVV contribution at 89 eV [3].

The CVD growth of diamond was carried out under the following conditions. The distance between the tungsten filaments and the substrate was $5 < d < 7$ mm, the activation power was

185 ± 5 W (corresponding to a filament temperature of 2400 ± 25 K), the temperature of the substrate was 1073 ± 5 K, the total gas flow was 200 l min^{-1} , the methane content was 0.5%, and the total pressure was 3000 Pa.

The standard conditions for surface analysis by X-ray photoemission spectroscopy have been reported elsewhere [2]. Briefly, the UHV chamber was a custom-built system equipped with a VSW hemispherical analyzer. Photoelectrons were collected normal to the substrate. The X-ray source was an unmonochromatized PHI Mg anode providing photons (kinetic energy 1253.6 eV) with an incident angle of 30° with respect to the sample. The acceleration voltage was 13 kV and the power was 300 Watt. The resolution was 0.60 eV, as measured by the broadening of the 4f core level of a clean gold foil. The procedure of starting and stopping a deposition sequence and of transferring the sample to the surface-analysis chamber has been described previously [2].

Fig. 1. Evolution of the Si 2p core level of the scratched Si(100) sample with cumulative deposition time. (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 lines A1, A2 and A3 is reported in the text.

3. Results

The evolution of the 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 (line A3 in Fig. 1) emerges at around 104 eV as well as elemental silicon (line A1 in Fig. 1) at 99.6 eV. This oxide contribution disappears after the first deposition sequence, but a new contribution (line A2 in Fig. 1) is detected at 101.9 eV as a shoulder of the main silicon contribution. This new feature becomes clearly visible as early as 21 min of deposition time, and could be assigned to silicon carbide [4,5]. On the other hand, the elemental silicon contribution (line A1 in Fig. 1) shifts by about 0.6 eV to higher energy. This shift corresponds to a change in the work function as soon as the silicon surface is cleaned by oxygen removal and the deposition of carbon starts. Above 21 min of deposition, we detect only these two contributions, with a relative ratio which does not change very much. A small tail around 103 eV still indicates the existence of some substoichiometric silicon

oxide. This is consistent with a small and constant O 1s contribution.

In a similar way, the evolution of the C 1s core level with cumulative deposition time is displayed in Fig. 2. The broad initial peak denoted B2 at 284.6 eV corresponds to carbon contamination and to hard carbon grains left by the scratching process. These residues were first observed by Iijima et al. [6], and were assumed to represent seed where diamond growth occurs. Attempts to eliminate this carbon contribution by cycles of Ar^+ -ion bombardment and thermal treatment were unsuccessful, in contrast to unscratched Si(100) and Si(111). Subsequent carbon depositions lead to two contributions. The first (denoted B1 in Fig. 2), at low binding energy (283.15 eV) is the most intense up to about 115 min. This contribution can clearly be assigned to the formation of silicon carbide [5]. Furthermore, we note

Fig. 2. Evolution of the C 1s core level of the scratched Si(100) sample with cumulative deposition time. (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 lines B1 and B2 is reported in the text.

that the binding-energy difference between the C 1s and the Si 2p core levels of silicon carbide amounts to $B1 - A2 \approx 182.25 \pm 0.1$ eV, in good agreement with the difference of 182.15 eV reported elsewhere on clean SiC [6]. The second contribution (denoted B2 in Fig. 2) at 284.6 eV is initially very weak, but increases rapidly. It could be seen clearly above 56 min and becomes the only contribution above 302 min. We attribute it to diamond or to amorphous carbon, as reported in the literature [7,8]. Elemental carbon exhibits one line at around 284.6 eV, whatever its structural form (graphitic, amorphous, diamond, etc.). The nature of this carbon species can therefore hardly be deduced from consideration of this single line. However, both AES of the C KVV line and ELS clearly suggest that the carbon is of the diamond type [9].

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

The intensity 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 in Figs. 3 and 4, respectively. Both signals have been normalized to the signal of the substrate I_{Si} (contribution A1), and only the first 500 min are discussed here.

In both cases, the silicon carbide intensity rapidly reaches a constant level which is larger on the scratched sample than on the virgin sample (Fig. 3). By contrast, the diamond signal increases on the scratched sample, whereas a significant increase occurs only after 1200 min of carbon deposition (Fig. 4). This is consistent with SEM, AFM and TEM observations of a diamond film obtained after 300 and 3000 min on the scratched and the virgin samples, respectively. As it is well known that the diamond growth occurs through island formation (i.e. a Volmer–Weber mode), we modeled the XPS intensities, normalized to the substrate signal, by first assuming the formation of a homogeneous layer of silicon carbide of a depth z onto which the diamond nucleates with a density of islands N and grows in a 3D mode with a surface coverage S [10].

The silicon carbide contribution can be

Fig. 3. Evolution of the silicon carbide XPS signal normalized to the silicon substrate. Scratched sample: solid squares represent the Si 2p core level and solid circles the C 1s core level. Virgin sample: downward-pointing triangles represent the Si 2p core level and upward-pointing triangles the C 1s core level.

expressed in two independent ways, considering the Si 2p and the C 1s signals

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

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

where A_{AB} and λ_{AB} are experimental constants and attenuation lengths, respectively, which depend on the matrix AB and on the elements A and B , and θ is the angle of the detector normal to the surface. From Eq. (1) and Eq. (2), the depth z_{∞} of the silicon carbide layer can be extracted. This depth z_{∞} is around 1.2 and 1.0 ± 0.1 nm for the scratched and the virgin samples, respectively, using $\lambda_{\text{SiC}} = 1.5$ nm. These values are probably slightly underestimated as we have included the small

Fig. 4. Evolution of the diamond XPS signal normalized to the silicon signal. Solid squares: scratched Si(100); solid circles: virgin Si(111). The solid line corresponds to a fit according to Eq. (1), (3) and (4).

signal of substoichiometric silicon oxide in the overall signal of the substrate.

Similarly, the diamond signal can be expressed as

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

and we found that the covered surface S obeys an Avrami law, similar to a phase-transformation process [11]

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

where k is a kinetic constant and n an exponent which is characteristic of the growth mechanism. We found generally $n \approx 2.5 \pm 0.4$ over a wide deposition time. This corresponds to a constant growth rate, where the activated species directly impinge the diamond island from the gas phase, and a decreasing nucleation rate. By including the expression of z extracted from Eq. (1) or (2) and the

expression of S (Eq. (4)), determined by image analyses of the SEM pictures, into Eq. (3), the evolution of the diamond signal can be fitted. The kinetic constants k are estimated to be 7.4×10^{-9} and $8 \times 10^{-11} \text{ min}^{-2.5}$ for the scratched and the virgin samples, respectively. The agreement, however, is not satisfactory for the virgin sample at the start of the process. This is probably because nucleation needs a large induction time with a poor density (around $10^6 \text{ nuclei cm}^{-2}$), leading to an initial growth process limited by the surface diffusion of the activated species.

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 that the silicon carbide layer plays a minor role in the diamond nucleation process.

The faster diamond nucleation cannot be attributed only to the occurrence of carbon residues left on the surface on the scratched sample. In fact, most of these carbon residues are transformed into silicon carbide in the first stages of the process (Fig. 2). We believe that a carbon phase, possibly amorphous, is in equilibrium with the silicon carbide, and that the microstructural defects created by the mechanical scratching play a decisive role in diamond nucleation.

4. Conclusions

X-ray photoemission spectroscopy is a powerful probe to monitor the nucleation and growth of

CVD diamond on silicon. By comparing these processes on scratched and virgin Si(100) surfaces, we found a rapid formation of a silicon carbide layer on both substrates, but a quite different behaviour concerning the subsequent nucleation and growth of diamond on the two substrates.

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