

IN SITU CHARACTERIZATION OF DIAMOND NUCLEATION AND GROWTH BY XPS

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Abstract

Filament assisted chemical vapor deposition (CVD) diamond film growth on Si(100) was studied using X-ray Photoelectron Spectroscopy (XPS) to examine the sample at selected intervals during the nucleation and growth processes. The sample was transferred under vacuum from the growth chamber to the attached XPS analysis chamber without exposure to air. Before growth XPS showed that the Si sample is covered by a layer of SiO₂ and carbonaceous residue; however, after 15 minutes of growth both of these substances are removed and replaced by a distinct SiC layer [Si(2p)=100.3 eV and C(1s)=282.7 eV]. Between 15 minutes and 4.5 hours the SiC layer grows and diamond nucleation begins. The XPS signal from diamond [C(1s)=284.3 eV] saturated after 17 hours. The identification of diamond was confirmed with Raman spectroscopy. This work identifies SiC as the substrate for diamond nucleation and growth during filament assisted CVD diamond growth on Si.

Introduction

Diamond films grow at relatively low pressures (≤ 1 atm) and temperatures (≤ 1300 K) when the proper mixture of CH₄ and H₂ flows over a substrate that is near a hot filament [1-3] or electric discharge [4-6]. This method of diamond production offers the possibility for inexpensive diamond coatings on tools, wear surfaces, and optical components. Single crystal diamonds ultimately could be prepared for use as high performance electronic devices. New technologies involving chemical vapor deposition (CVD) diamond films have not yet been implemented in part because there is no understanding of the chemical and physical processes which control the properties of the diamond films. In particular, there have been no adequate characterizations of the surfaces on which the films grow.

In order to examine the surface chemistry of diamond film growth we coupled a diamond growth chamber to an ultrahigh vacuum (UHV) system equipped with X-ray photoelectron spectroscopy (XPS). By stopping the growth at selected intervals we are able to obtain a time dependent characterization of the surface during the nucleation and growth processes without exposure to air. This experiment, which is the first to offer such a time dependent monitoring of the surface during diamond growth, allows us to characterize the surface on which diamonds are actually grown as opposed to the substrate we place in the growth chamber. These data may assist in developing better models for diamond growth [7]. In this experiment we examined growth on Si because such a large amount of work has been done on this material. We identified three distinct phases of diamond film growth: removal of initial substrate contaminants, formation of a SiC layer, and nucleation and growth of diamonds. From these results we can conclude that diamonds form on SiC as opposed to clean Si, Si oxides, or a carbonaceous layer.

Experimental Aspects

The experiments were performed in a system that coupled a UHV analytical chamber to a diamond growth chamber. The UHV chamber is a custom built system that contains a Leybold-Heraeus EA11, 150 mm hemispherical analyzer with multichannel detection and is isolated from the growth chamber with a gate valve. The sample was transferred between the two chambers on a bellows motion. The growth chamber is a 6-way 2 3/4 inch cross pumped with a 50 l/sec turbo pump. The gas supply was a premixed 0.2% CH₄ in H₂ cylinder that was connected to the growth chamber with a 100 sccm flow controller. The outlet of the growth chamber was connected through a stainless steel leak valve to a rotary vane pump that controlled the total pressure at 50 Torr as measured by a capacitance manometer. A 0.020 inch diameter W filament was mounted 2 mm from the Si(100) substrate at a temperature of 2350 K as measured by an optical pyrometer. The Si sample was cut from a Si(100) wafer, polished using 1 micron diamond paste, and washed with acetone followed by methanol prior to mounting on the transfer device. After growing for a prescribed time the pressure was reduced to 10⁻⁷ Torr before opening the gate valve and introducing the sample into the analytical chamber. XPS data were obtained about 30 minutes after stopping the growth.

Results and Discussion

Prior to growth ($t=0$) the Si(100) substrate was introduced into the analytical chamber and characterized with XPS by obtaining a survey scan and high resolution scans of the C(1s), Si(2p), and O(1s) regions. The survey scan shows that only C, O, and Si are present on the surface. The C(1s) region (fig. 1a) contains one relatively broad transition at 285.1 eV due to adventitious carbon whose probable source is hydrocarbons deposited on the sample prior to introduction. The Si(2p) region (fig. 2a) indicates the presence of both reduced Si (at 99.0 eV - used for calibration) and SiO₂ (at 102.7 eV) [8]. Similar data were obtained from three different Si samples suggesting that a carbon covered SiO₂ surface is typical for Si substrates treated in the manner reported above.

Following the initial Si(100) characterization the sample was returned to the growth chamber for a 15 minute growth. XPS data obtained at that point (fig. 2b) show no Si(2p) peak from SiO₂ (102.7 eV), but instead a new peak at 100.3 eV which we assign to SiC [8]. The elemental Si peak at 99.0 eV is reduced by 50% (fig. 2b) compared to the sample prior to growth (fig. 2a) indicating that the SiC is on top of the Si. Identification of the Si(2p) peak at 100.3 eV as SiC, is confirmed by the observation of a new C(1s) peak at 282.7 eV (fig. 1b) of the proper intensity and energy for carbide-type carbon [8,9]. In addition, the adventitious carbon seen in fig. 1a is removed during the first 15 minutes of growth. These four spectra (figs. 1a,b and 2a,b) show that after only 15 minutes of diamond growth the SiO₂ and carbon contamination are replaced by a SiC layer.

After 45 minutes XPS (figs. 1c and 2c) shows an increased SiC intensity in both the Si(2p) and C(1s) regions. Between 45 minutes and 4.5 hours the SiC Si(2p) peak increases in intensity while the elemental Si peak decreases to less than 5% of its original intensity (fig. 2e). By assuming a SiC layer of uniform thickness and a Si(2p) escape length of 25 Å, we estimate from fig. 2e that the SiC layer is greater than 90 Å thick. Another observation after 4.5 hours is the detection of a new type of carbon with a C(1s) peak at 284.3 eV (fig. 1e).

For longer growth periods (figs. 1f,g and 2f,g) two phenomena occur: the C(1s) peak at 284.3 eV increases in intensity concurrent with a decline in the SiC feature (282.7 eV) and the

Si intensity drops very low with no change in peak position. Figures 1f,g and 2f,g show that the surface is being covered with the new form of carbon that exhibits a C(1s) peak at 284.3 eV. The XPS survey scan after 17 hours of growth shows only a single form of carbon and a very small amount of Si. No further changes were observed by XPS after 17 hours of growth. To confirm that the C(1s) peak at 284.3 eV was due to diamond, the sample was removed from the apparatus and a Raman spectrum was obtained which exhibited the characteristic diamond line at 1332 cm^{-1} .

Conclusions

The application of XPS has for the first time elucidated some of the surface chemistry which occurs during the nucleation and growth of diamond films. We characterize the nature of the substrate prior to growth showing that the Si(100) is covered with a layer of SiO_2 and carbonaceous contamination. After a short period the SiO_2 layer and the carbonaceous contamination are removed and replaced by a layer of SiC which increases in thickness with time. Finally, diamonds nucleate and grow on the SiC layer. No other forms of carbon are observed. This experiment represents a significant improvement in the level of understanding of diamond film growth.

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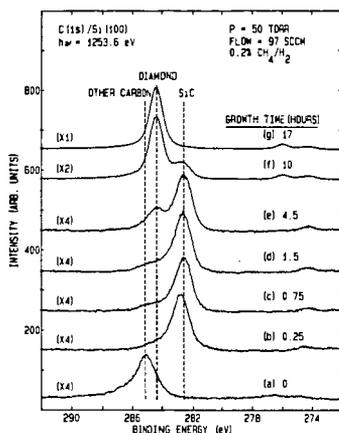


Fig. 1: XPS spectra of the C(1s) region for different growth times. Data for the substrate prior to growth, $t=0$, show carbon contamination typical for Si cleaned with methanol prior to introduction. The other spectra, b-g, show the formation of a carbide layer (282.7 eV) followed at later times by diamond growth (284.3 eV).

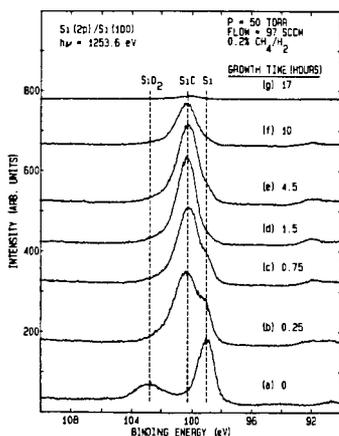


Fig. 2: XPS spectra of the Si(2p) region for different growth times. Data for the substrate at $t=0$, prior to growth, show that the Si(100) is covered with a thin layer of SiO_2 . Data at later times show that the oxide is replaced by a carbide layer (100.3 eV) which then declines in intensity as the surface is covered with diamond.