

Surface Processes Associated with Diamond Growth From Water Alcohol Deposition Chemistries

R. E. Thomas, R. A. Rudder, and R. J. Markunas

Center for Semiconductor Research, Research Triangle Institute, Research Triangle Park, NC 27709,
U.S.A.

Electron energy loss spectroscopy (EELS) and low energy electron diffraction (LEED) have been used to study the effects of atomic oxygen dosing and atomic hydrogen dosing on the diamond (100) surface. Terminated surfaces appear very similar with EELS although the oxygenated surface gives a 1x1 LEED pattern and the hydrogenated surface gives a 2x1 LEED pattern. Annealing of both surfaces gives rise to a new loss peak at approximately 5 eV from the elastic peak. This peak is thought to arise from dangling bonds on the surface

1. INTRODUCTION

Although a wide variety of growth chemistries and techniques have been developed for the chemical vapor deposition of diamond, fundamental questions remain unresolved concerning surface processes during diamond growth. A number of diamond growth mechanisms have been proposed which involve atomic hydrogen and hydrocarbon species[1]. In addition, numerous growth studies have shown that oxygen, in the form of CO, H₂O, or alcohols, can contribute to diamond formation[1]. Previous surface studies have shown that atomic oxygen will convert a C:(100)-2x1: surface to 1x1 configuration[2]. Upon heating the oxygen leaves the surface predominantly in the form of CO with some CO₂ also desorbed. The maximum desorption rate for CO occurs at approximately 600°C for a heating rate of 5C/s, and significant desorption occurs at temperatures less than 400°C, well below the peak maximum. As CO desorbs from the surface the surface reverts to the 2x1 configuration. The desorption of CO from the surface at relatively low temperatures has the potential for opening sites for the addition of carbon to the diamond lattice. However, the nature of these sites is unclear. In the present

study we have used electron energy loss spectroscopy (EELS) and low energy electron diffraction (LEED) to study the transition from the 1x1 to the 2x1 structure upon CO evolution and to probe the surface sites resulting from CO desorption. Comparisons are made of both hydrogen and oxygen terminated surfaces and graphite surfaces.

2. EXPERIMENTAL PROCEDURES

A full description of the experimental procedure is available in earlier publications and only a brief review is given here[2]. EELS and LEED observations were performed in a stainless steel UHV system. Sample heating was accomplished by clipping the crystals to a 0.25 mm thick molybdenum resistive strip heater. The sample temperature was measured by a 0.125 mm diameter chromel/alumel thermocouple threaded through a laser drilled hole in the diamond and held in tension against the crystal face. Two type IIa (100), 5x5x0.25 mm, diamond crystals were used in the course of the present study. To clean the surfaces, the samples are initially hand polished 5 minutes with 0.25 μm diamond grit, followed by solvent rinses. The samples are then placed in a CrO₃/H₂SO₄ (125°C) solution for 20

minutes to remove non-diamond carbon. The samples are rinsed in DI water and then boiled in a 3:1 solution of HCl/HNO₃ for 20 minutes to remove any metals contamination. Samples subjected to this cleaning process typically show a good quality 1x1 LEED pattern at beam voltages as low as 50 volts with no annealing. Auger spectroscopy of the diamond surfaces as introduced to the chamber indicates that the surface is left O-terminated following the acid cleaning. In all cases atomic hydrogen for dosing was generated via a tungsten filament operating at a temperature of approximately 1500°C. Filament temperatures were measured with a hand held optical pyrometer. Atomic oxygen was generated via an iridium filament at 1100°C. VLSI grade hydrogen and oxygen gasses were used with no further purification. No attempt was made to quantify the percentage of atomic species generated by the filaments. EELS data were collected with a Perkin-Elmer single pass cylindrical mirror analyzer. The elastic peak was set at approximately 150 eV for all spectra to maximize surface sensitivity. Differentiation of the spectra was performed digitally using a Savitsky-Golay differentiation and smoothing routine.

3. RESULTS AND DISCUSSION

Figure 1 shows derivative EELS spectra obtained from annealing of a hydrogen terminated sample. The hydrogen dosed samples remained in a 2x1 configuration after exposure to the atomic hydrogen, with each dangling bond now terminated by a hydrogen. The unannealed sample shows large peaks at approximately 8 eV, 23 eV, and 33 eV away from the elastic peak. Upon annealing of the hydrogen terminated surface the 23 eV peak gradually diminishes in intensity relative to the 33 eV peak. The 8 eV peak grows in intensity relative to the other peaks and we observe the appearance of a new peak approximately 5 eV from the elastic peak

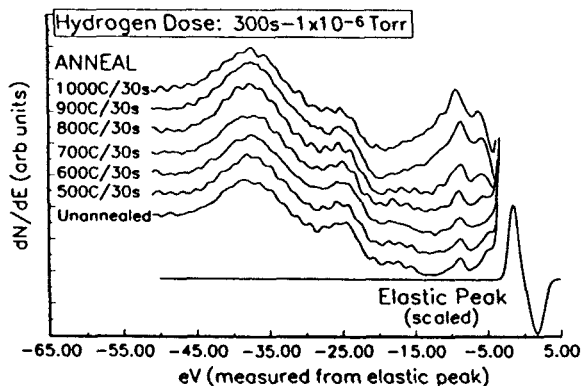


Figure 1. Electron energy loss spectra from diamond (2x1):H surface.

following the anneal at 700°C (Fig 1). The 5 eV peak grows in magnitude with subsequent anneals at 800°C and 900°C. The temperature at which the 5 eV feature first appears corresponds very well with the onset of hydrogen desorption from the surface measured in earlier thermal desorption experiments[2]. The differentiation process emphasizes changes in the peak structure, however peak positions quoted in the text refer to the undifferentiated spectra for consistency with previous literature. Figure 2 shows a comparison of differentiated and undifferentiated spectra. The evolution of EELS structure for oxygen

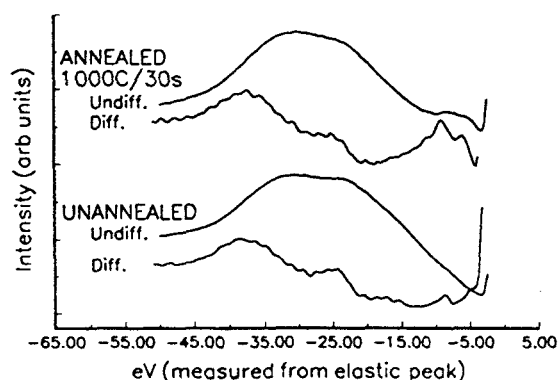


Figure 2. Comparison of differentiated and undifferentiated spectra from hydrogen-dosed sample.

terminated surfaces is more complex as can be seen in Figure 3. The oxygen dosed samples also exhibited a peak at 5 eV away from the elastic peak after annealing. The peak appeared at approximately 600°C, which again corresponds quite well with thermal desorption data[2]. However from Figure 3 one can see that the peak at approximately 8 eV undergoes more complex transformations. Following the anneal at 1000°C all of the oxygen has desorbed from the surface and the surface is left in a 2x1 configuration with 1 dangling bond per carbon atom. If the surface is then exposed to atomic hydrogen Figure 3 shows that the peaks at both 5 eV and 8 eV are suppressed.

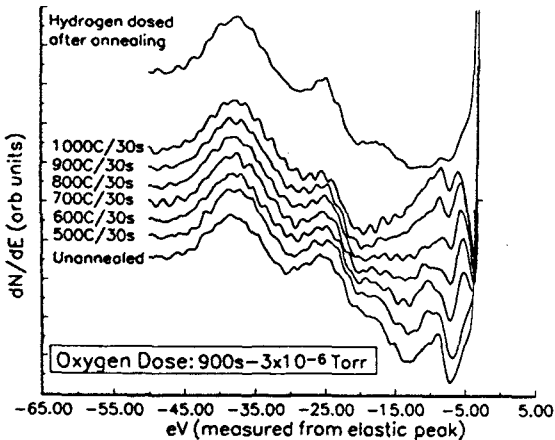


Figure 3. Electron energy loss spectra from diamond (1x1):O surface.

For comparison purposes EELS spectra were obtained from pyrolytic graphite samples using the same apparatus and geometry. Results from graphite surfaces are shown in Figure 4 along with spectra from hydrogen dosed samples. In the case of graphite the most prominent feature is a loss peak at approximately 6 eV. From the plot one can see that this feature is clearly at a different energy than the 5 eV loss feature seen on diamond surfaces.

The peak at 33 eV is associated with a bulk plasmon in diamond [3], and we do not see much change in this feature as a function of

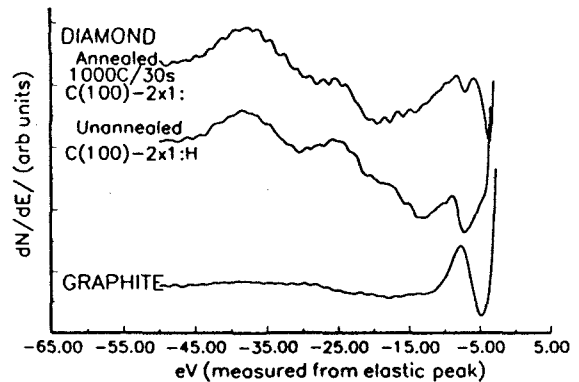


Figure 4. Comparison of EELS spectra from clean graphite and hydrogen-dosed diamond samples.

surface structure or termination. The peak at 23 eV has been correlated with plasmon and/or interband excitations and the peak at 8-10 eV with interband transitions[3]. The peak at 23 eV diminishes upon annealing for both H-termination and O-termination even though the surface structure remains in a 2x1 configuration throughout the process for hydrogenated surfaces and reconstructs from a 1x1 to a 2x1 structure in the case of oxygenated surfaces. It is not surprising that both desorption series converge to the same EELS spectra since equivalent 2x1 reconstructed surfaces are obtained via each path. Apparently the presence of dangling bonds serves to suppress or shift the frequency of the surface plasmon mode. Zangwill has pointed out that the zero point energy of the plasmon oscillator system increases as the electron density increases[4]. With dangling bonds on the surface we have effectively increased the electron density and we expect the plasmon frequency to shift to higher energies. With the resolution available in the present arrangement it is difficult to observe this shift but what may be happening is that the surface plasmon energy shifts towards the bulk plasmon and cannot be resolved. The behavior of the peak at 8-10 eV is more difficult to explain. This peak has been associated with a transition

from the valence band to the conduction band[3]. The behavior of the peak is also more complicated and distinct differences are observed between samples with oxygen termination and hydrogen termination. The evolution of surface structure accompanying oxygen desorption is more involved than the case for hydrogen. CO desorbs from oxygenated surfaces causing a loss of carbon and then the surface reconstructs.

We also observe the appearance of a peak at approximately 5 eV from the elastic peak after annealing both oxygen and hydrogen terminated surfaces. A similar feature has been observed following annealing of as deposited and oxygenated polycrystalline diamond[5]. The as deposited material was presumed to be hydrogen terminated. The 5 eV feature has been associated with band gap excitation[3]. Alternative explanations include surface states induced by dangling bonds or plasmon losses from π bonding as the surface reconstructs. The 5 eV loss feature disappears after the surface is dosed with atomic hydrogen. We do not expect band-gap excitation to disappear with hydrogen dosing. However the dangling bonds would be filled and/or π bonds lifted from the surface dimers. Several facts point to dangling bonds as the source of the loss peak at 5 eV. High resolution electron energy loss spectroscopy of (111) and (100) surfaces shows the presence of a C=C double bond on the (111) surface but not on the (100) surface[6]. The C=C double bond is seen on the (111) surface after hydrogenation, so the addition of atomic hydrogen does not necessarily break all of the double bonds on the surface. Double bonds may also exist on the (100) surface but cannot be resolved by the HREELS measurement. Recent quantum chemical calculations show the dimer bond on the (100) surface does not contain a significant π component[7]. Finally, EELS spectra from graphite surfaces taken under the same conditions show the π plasmon on graphite shifted by approximately 1 eV from the 5 eV loss feature observed on diamond.

4.0 SUMMARY

Electron energy loss spectroscopy has been used to study hydrogen and oxygen terminated diamond surfaces and graphite. Both terminated diamond surfaces exhibit similar loss spectra with major peaks at 33, 23, and 8 eV. Annealing of the samples gave rise to a new loss feature at 5 eV thought to be a result of the appearance of dangling bonds on the surface.

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