

An Auger Electron Spectroscopy (AES) and X-Ray Photoelectron Spectroscopy (XPS) Study of CVD and Natural diamonds

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Introduction and Perspective

Diamond is a material with many extreme properties [1]. Diamond materials are expected to find increasing use in optical and electronic applications in which heat is a consideration and as a result, oxidation and phase transformation (graphitization) are a concern. Diamond oxidation and phase transformation are connected phenomena that are not well understood. Research of diamond oxidation has been limited. Of the work that does exist, three technical approaches have emerged. The first is work involving chemisorption of specific oxides on powder diamond surfaces [2,3], the second set of work involves primarily one research group fortunate enough to study bulk diamond surface reactivity [4] and the third set of research is thermal decomposition analysis and microstructural characterization of CVD diamond surfaces [5-10].

Oxidation of diamond involves a heterogeneous gasification process. Oxygen, water vapor, and carbon dioxide are but a few of the species that react with diamond surfaces, yielding CO(g) and CO₂ (g). Of interest are the sites for active oxidation on the surface and the possibility of surface reconstruction from an sp³ to an sp² bond character. Identifying surface active sites, activity of specific crystallographic facets, and the extent to which surface conversion is involved in the oxidation process is key to the fabrication and design of diamond materials.

Auger electron spectroscopy (AES) and X-Ray Photoelectron Spectroscopy (XPS) have been the two most common characterization techniques to obtain surface composition, elemental distribution and atomic bonding prevalent at surface. AES is highly sensitive for surface or near surface analysis (4 to 40Å) of materials composed of light elements. The spatial resolution for elemental analysis could be as high as 20 Å. While

AES can provide limited chemical state information, XPS gives binding state information from relatively large areas.

Previous AES and XPS studies have been carried out on the clean and hydrogenated diamond surfaces under the driving force of vapor deposition of diamond films [11-13]. Our work extends this effort in examining oxygenated surfaces and the benefit of this is a closer approximation of actual working conditions for these materials. We expected to see that surface reconstruction of diamond is an aspect of the oxidation process and that oxidation on specific surfaces {111} is more closely approximated by that of graphite.

Materials and Experimental

CVD diamond films ET100 manufactured by Norton Diamond Film, Inc. and type 2A natural diamonds with specific cut are the subjects of the current research effort. HOPG graphite is the reference material used for comparison. Although the CVD diamond to be investigated is of high quality approaching that of bulk diamond in crystallite size (60-100 μm) and well defined crystallite orientation (growth orientation is <110> while {111} are the surface facets), impurities such as Si, Al, and hydrogen are found enriched at the grain boundary [14]. Therefore, investigation on high purity natural diamonds with [111], [110], and [100] cuts leads to understand how impurity and heterogeneity influence the surface chemistry, a fundamentals aspect of oxidation behavior.

The experiments to date were performed using PHI 660 Scanning Auger Microprobe (SAM) at Oak Ridge National Laboratory. The accelerating voltage was 2 kV. PHI 680 SAM will be used for the remaining AES analysis including elemental mapping and Auger Spectra collecting. X-Ray Photoelectron Spectra will be obtained using a PHI 5600 X-Ray Photoelectron Spectroscope.

Preliminary Results and Discussion

Preliminary experiments were conducted to determine if the ET100 film could be analyzed by AES or whether electron charging would be too severe to permit such an analysis. The "as-grown" or "rough" side of the sample was analyzed: (a) as-received, (b) after 10 s sputtering with Ar ions, and (c) after 60 s sputtering conditions. The spectra of (a) and (c) are collected in Figure 1. Charging was observed when analyzing the as-received film which increased as the partially-conducting surface contamination was removed by ion sputtering. The sputtering rate was estimated to be approximately 200 Å/min. However, charging was restricted to low energies and the spectra above 100 eV were intact and peak shapes remain unchanged. These results indicate that the impurity elements can be identified, there amount estimated, and some analysis performed on the using peak shape as related to the different structure types, e.g., diamond, amorphous carbon, graphite, etc. Nevertheless, oxidation state information regarding the carbon types would be very difficult, it not possible, because the gross effects of charging on peak shift would tend to mask any subtle peak-shifts due to changes in oxidation state. Such changes in oxidation state are better studied using XPS where X-Rays are used instead of electrons to generate the spectra.

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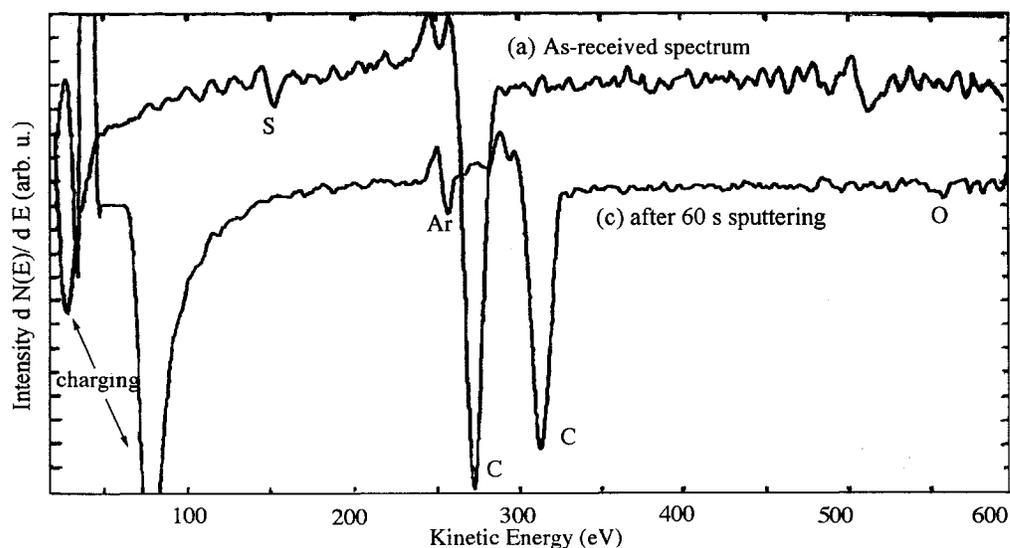


Figure 1. Auger spectra of diamond film ET100: (a) as-received, and (c) after 60 s sputtering.