Diamond & Related Materials 84 (2018) 86–94

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Chemical and semiconducting properties of NO_2-activated H-terminated diamond

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ARTICLE INFO

Keywords:
Diamond
Hydrogen-termination
Molecular adsorption
Nitrogen dioxide

ABSTRACT

The H-terminated surface of diamond when activated with NO_2 produces a surface conduction layer that has been used to make field effect transistors (FETs). Previous reports have suggested that during NO_2 exposure (NO_2-activation), NO_2^- forms on the diamond surface and generates positive carriers (holes) in the diamond, making the diamond surface conductive. We report here on X-ray-photoelectron-spectroscopy (XPS) surface characterization of single crystal diamonds and on infrared absorption of diamond powder. After activation, XPS showed the presence of N atoms on the diamond surface, but infrared absorption found no evidence of NO_2^-, but instead NO_3^- is present on the diamond surface.

Two wet chemistry techniques determined the concentration of NO_3^- per milligram of diamond powder. With the powder's surface area measured by the BET technique, the surface NO_3^- concentration was measured to be between 6.2×10^{13} and $8.2 \times 10^{13}\,cm^{-2}$. This is in the same range as the carrier densities, 3×10^{13} to $9 \times 10^{13}\,cm^{-2}$, determined by Hall mobility and surface conductivity measurements of single crystal diamonds. Using similar techniques, the concentration of NO_2^- was determined to be $< 10^{12}\,cm^{-2}$.

Both the surface conductance and the surface H atoms are stable in dry nitrogen, with or without NO_2-activation, but the surface conductance, the concentrations of H atoms both with and without activation and NO_3^- decrease when exposed to laboratory air over a period of hours to days. Infrared absorption measurements showed the reduction of surface NO_3^- and H atoms during laboratory air exposure, but gave no indication of what reactions are responsible for their loss in laboratory air.

1. Introduction

When the surface of diamond is covered with H atoms (H-terminated) the diamond becomes conductive when exposed to air [1]. This conductivity is further enhanced when covered with a layer of a high-work-function material (activation) by transfer doping [2,3]. Impressive field effect transistors (FETs) have been made, using this conductive layer with current densities > 1 A/mm [4,5], a wide operational temperature range, −263 (10 K) to 400 °C [4], high-voltage operation > 1 kV [4,6], and high maximum frequency of oscillation, f_{max}, ~100 GHz [7,8]. Of all the high-work-function activation compounds, MoO_3 [9,10], V_2O_3 [9,11] Al_2O_3 [4], and others, the gas, NO_2, gives one of the lowest surface resistances ~700 Ω sq^{-1} [12]. However, during FET fabrication, the surface resistance increases by nearly an order of magnitude to ~5 kΩ sq^{-1}. Still, to date NO_2-activated diamond FETs exhibit the highest drain current ~ 1.3 A/mm [5,8]. This article discusses the chemistry of NO_2-diamond activation and how it impacts the surface conductance.

NO_2 was first identified as being capable of activating diamond at concentrations as low as 5 to 10 parts per billion (ppb) [13,14]. Natural concentrations of NO_2 in air is from 20 to 60 ppb [15], and along with other atmospheric components cause the H-terminated diamond surface to become conductive over tens of minutes. Unsurprisingly, atmospheric activation is inconsistent and unstable in time as other atmospheric components (NH_3, organic amines etc.) will deactivate diamond or irreversibly react with the diamond surface, increasing the surface resistance to > 10 kΩ sq^{-1}. Kasu et al. suggested two mechanisms for NO_2-activation. In the first mechanism, NO_2 pulls electrons out of the diamond to form the conductive hole layer and NO_2^- [16,17]. In the second mechanism, some unknown reaction occurs on the diamond surface, forming a negative surface charge, not NO_2^-, and hole conduction in the diamond [18]. We favor the latter of the two models.

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https://doi.org/10.1016/j.diamond.2018.03.002
Received 12 January 2018; Received in revised form 28 February 2018; Accepted 5 March 2018
Available online 06 March 2018
0925-9635/

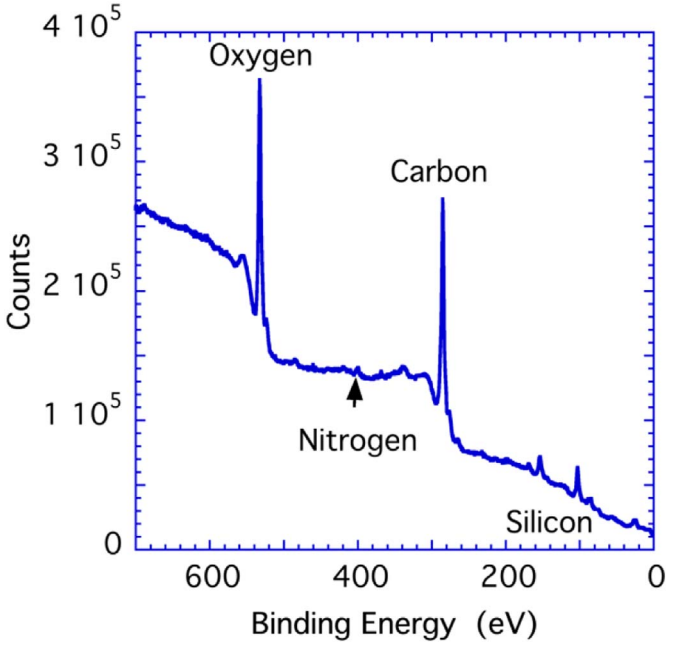

Fig. 1. X-ray photoelectron spectroscopy (XPS) of a single crystal (100) H-terminated NO_2-activated diamond. The electron intensity peaks are labeled with their corresponding elements. The silicon peak is believed from impurities incorporated into the diamond during growth.

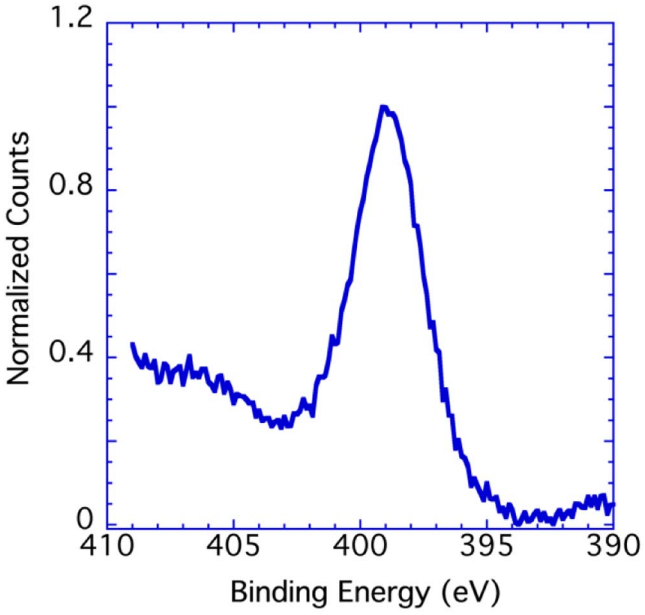

Fig. 2. XPS over the binding energies assigned to nitrogen. The integrated area under the peak associated with N is 1.7% of the combined areas of O, N and C. Carbon area is 68.6% and O is 29.7%.

Using x-ray-photoelectron-spectroscopy (XPS), Fourier-transform-infrared-spectroscopy (FTIR), wet chemical analysis for NO_2^- and NO_3^-, and electrospray mass spectrometry (ESMS), we found no evidence of NO_2^-, but instead found concentrations of NO_3^- matching the surface hole concentrations, 3×10^{13} to $9 \times 10^{13}\,cm^{-2}$ as calculated from Hall mobility and surface conductivity. Additionally, the NO_2 reacts with the hydrogen atoms on the H-terminated diamond surface, removing between 25 and 75% of them. While it is believed that the presence of NO_3^- is a necessary condition for diamond hole conduction, it is unknown what impact the removal of H atoms has on the conduction or what replaces it in the areas where hydrogen is removed.

2. Experimental procedure and characterization

Several characterization tools have been applied to characterize the effect of NO_2 on H-terminated diamond.

2.1. XPS

XPS of H-terminated, NO_2-activated (100) diamond is shown in Figs. 1 and 2. The diamond was etched in molten $NaNO_3$, H-terminated and NO_2 activated as described by Wade et al. [19]. These results are similar to those of Kasu [18] with O and C atoms covering most of the surface, but no indication of N atoms. However, on closer examination of our diamond there is a weak N signal, Fig. 2. From the ratio of the areas, using a Mg anode target and the sensitivity factors for the Perkin Elmer model 5500, the concentrations of C:O:N respectively, M_i, were 68.6%, 29.7% and 1.7%. Neglecting the O concentration and assuming all the N atoms are on the diamond surface, the concentration of N atoms in monolayers, Θ_N, is estimated by [20].

$$\Theta_N = \frac{M_N}{M_C} \times \sum_{n=0}^{\infty} \exp\left[\frac{-n*d_{Dia}}{\lambda_{Dia}*\cos(\varphi)}\right] = \frac{M_N}{M_C}\left[1 - \exp\left[\frac{-d_{Dia}}{\lambda_{Dia}*\cos(\varphi)}\right]\right]^{-1}.$$

M_N and M_C are the concentrations of N and C atoms; d_{Dia} is the spacing between two (100) planes, 0.357 nm; take off angle, φ, is 45°; and λ_{Dia} is the electron attenuation length, EAL, of C1s electrons, ~1.74 nm at an electron energy of ~970 eV [21]. The estimated N coverage is 0.098 monolayer or $1.5 \times 10^{14}\,cm^{-2}$.

After XPS characterization, the sample's resistance was $7\,k\Omega\,sq^{-1}$ with a Hall mobility of $30\,cm^2\,V^{-1}\,s^{-1}$ giving an estimated carrier density of $3.0 \times 10^{13}\,cm^{-2}$. Assuming each N atom represents a negatively charged molecule that generates a hole, the XPS-estimated N surface density is within an order of magnitude of the carrier density. The peak associated with O is likely from absorbed H_2O and CO_2 and chemically bounded OH and CO. All of which appear in the infrared spectrum discussed below. Although, H_2O and CO_2 individually have been shown not to contribute to surface conduction [8], they may increase conductance in combination with other components.

The XPS measured binding energies are 283.9 eV for C and 399.1 eV for N. The binding energy for C is consistent with a H-terminated diamond surface [22]. However, the binding energy for N is consistent with cyanides, CN, and not for the binding energies of nitrites, NO_2^-, 404–405 eV or nitrates, NO_3^-, 407–408 eV [23]. Since we see only N in the form of nitrates as discussed below using FTIR, we speculated that XPS emission from nitrates is shifted by a negative potential locally on the surface where the nitrates are absorbed compared to the bulk of the diamond.

2.2. Infrared absorption by FTIR

XPS is a powerful technique, but does not have the ability to accurately determine surface concentrations and molecular structure at low surface concentration levels, $1 \times 10^{12}\,cm^{-2}$. Another approach, infrared absorption with FTIR of diamond powder was used. It has sensitivity to surface concentrations of $< 1 \times 10^{12}\,cm^{-2}$ depending upon the diamond powder's surface area per gram and the infrared optical cross section of the surface component. Diamond powder, 0 to 0.25, formed from high-pressure high-temperature (HPHT) diamonds, washed with 1 to 1 HCl and H_2O_2, heated to 525 °C in air for > 15 h, and stored in dry N_2, was used as the starting material. Figs. 3 and 4 show a wide distribution in particle size. H-termination was accomplished by first evenly dispersing 60 to 100 mg of powder in a 2.5 cm circle centered on a 2.25 × 2.25 × 0.025-inch Al_2O_3 plate. H-