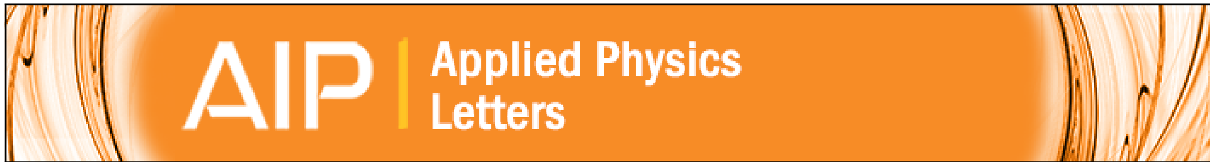

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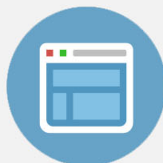
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n-type conductivity in ultrananocrystalline diamond films

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Hall effect measurements have been carried out to determine the carrier density and mobilities in ultrananocrystalline diamond films grown with added nitrogen. The results show clear *n*-type conductivity with very low thermal activation energy. Mobility values of 1.5 $cm^2 V^{-1} s^{-1}$ are found for a sheet carrier concentration of $2\times10^{17} cm^{-2}$. These measurements indicate that ultrananocrystalline films grown with high nitrogen levels in the growth gas mixture can have bulk carrier concentrations of up to 10^{21}, which is very high for diamond films. The *n*-type nature of this material was also confirmed by Seebeck effect measurements. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1785288]

Diamond has a number of extreme properties, such as its wide band gap and high breakdown field strength, which make it ideal for high performance electronics. However, to date, problems with doping diamond *n*-type—in part due to its high atomic density have hindered its development as a device material. *p*-type doping can be achieved with substitutional incorporation of boron, yielding an activation energy of 0.37 eV and, hence, fewer than 1% of the holes are activated at room temperature.[1] Hydrogen-induced surface conductivity can also be utilized to generate holes with an extremely low activation energy,[2,3] and high-performance devices have been demonstrated using this type of layer.[4,5] *n*-type doping has been much more elusive, with success in substitutional phosphorus doping achieved by relatively few laboratories;[6] an activation energy of 0.6 eV also makes phosphorus an unsuitable dopant for many applications. However, *p*-*n* junctions have been demonstrated utilizing the boron–phosphorus interface.[7] A shallow donor species is still sought for diamond.

Ultrananocrystalline diamond (UNCD) is a unique form of diamond grown from an Ar/CH_4 gas phase,[8] where the conductivity of the material is strongly influenced by the addition of nitrogen into the source gases.[9] The material becomes conductive with an apparently low thermal activation energy. This is in stark contrast to the case in conventional diamond, where the activation energy of substitutional nitrogen is 1.7 eV.[10] In this letter, Hall effect measurements are reported, which characterize the nitrogenated UNCD conductivity as unequivocally *n*-type.

UNCD films were grown on highly insulating ($>10^9$ Ω) commercially available type-Ib HPHT 100 diamonds with various concentrations of nitrogen added to the gas phase. Au contacts were thermally evaporated in the van der Pauw configuration at a base pressure lower than 2×10^{-7} mbar. The ohmic nature of the contacts was confirmed by current–voltage measurements. The samples were then mounted into a cryostat and wire bonded with silver paint onto the gold contacts. Hall and resistivity measurements were performed in a Lakeshore 7504 Hall Measurement System with an Advanced Research Systems helium atmosphere-based cryostat. The magnetic field was swept between ±1 T under a constant excitation current, the magnitude depending on the sample resistivity. This procedure is essential when measuring samples with significant offset voltages.[11] Field sweeps were run at each temperature point for in excess of 2 h, throughout the 40–350 K temperature range.

Figure 1 shows two examples of Hall effect sweeps at a given temperature. Figure 1(a) shows the case for a standard *p*-type boron-doped polycrystalline diamond control sample. It can be seen that the Hall signal is periodic and 180° out of phase with the applied magnetic field, thus the sample is *p*-type. The actual Hall voltage is one-half of the magnitude of this oscillation. Figure 1(b) shows the case for a nitrogenated UNCD sample. It shows a similar effect, but with a voltage that is in phase with the applied magnetic field. This material is therefore *n* type due to the opposite direction of the force exerted by the magnetic field. The oscillation amplitude differences between Figs. 1(a) and 1(b) are due to the differences in carrier concentrations and excitation currents in each sample.

The conductivity and carrier concentrations of nitrogenated UNCD can be tuned by the amount of nitrogen added to the gas phase. Figure 2 displays the variations in sheet carrier concentrations with temperature of films grown with 10% and 20% nitrogen in the gas phase. It can be seen that the sheet carrier concentrations of both samples reduce with decreasing temperature. At room temperature, the 20% N_2 sample has a sheet carrier concentration of $\sim2\times10^{17} cm^{-2}$

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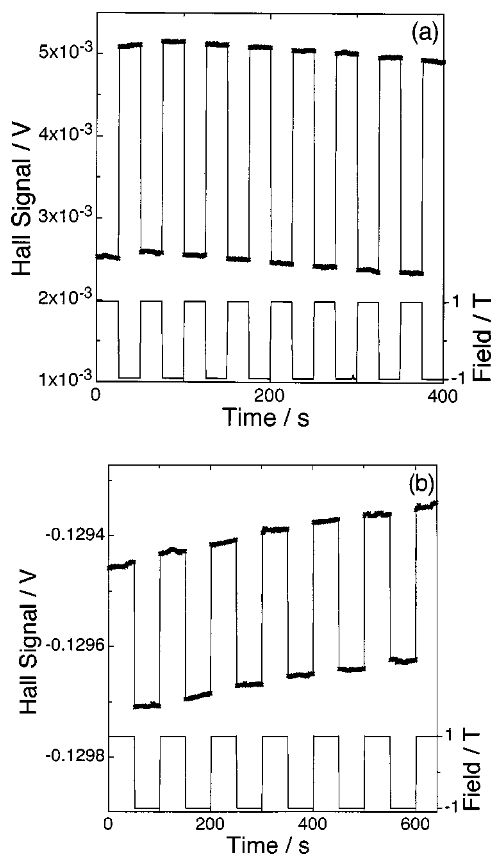

FIG. 1. (a) Hall effect measurements for boron-doped microcrystalline diamond, where the Hall voltage is plotted as a function of time as the magnetic field is switched in polarity and (b) Similar measurements for UNCD grown with nitrogen added to the gas mixture.

and the 10% N_2 sample $\sim 5\times 10^{15}$ cm^{-2}, samples grown with lower N_2 content in the plasma did not yield strong Hall signals. This is due to the drift in Hall offset voltage being greater than the hall voltage, a result of the large resistivity and low mobility values of those films. The films are between 2–3 μm thick, yielding bulk carrier concentrations of 10^{19}–10^{21} cm^{-3} which are extremely high for diamond at room temperature. These high carrier concentrations are also largely temperature insensitive, with the sheet carrier concentrations of the 20% N_2 sample varying from 1.8×10^{17} cm^{-2} at 300 K to 1.3×10^{17} cm^{-2} at 15 K. This shows that this sample displays an extremely low thermal activation energy. The 10% N_2 sample varies from 4.8×10^{15} cm^{-2} at 300 K to 2.2×10^{15} cm^{-2} at 50 K, a more significant variation, but still slight. The *n*-type nature of the films was also confirmed by the positive electromotive force generated at the hot probe with respect to the cold probe during Seebeck measurements,[12] and thus this material does not exhibit a sign anomaly despite its disordered nature.[13] The sign anomaly is more often found in amorphous materials with mobility values in the range $<10^{-1}$ cm^2 V^{-1} s^{-1}, such as amorphous silicon, and the correct signal is usually observed in microcrystalline silicon where the grain size can be as small as 3–5 nm, i.e., comparable with the material characterized here.[13]

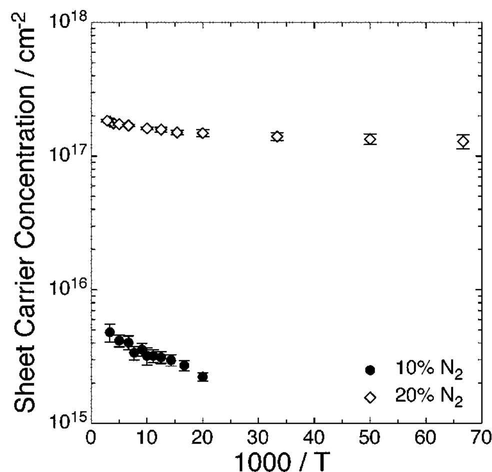

FIG. 2. Sheet carrier concentrations determined from Hall effect measurements in UNCD grown with nitrogen as a function of temperature.

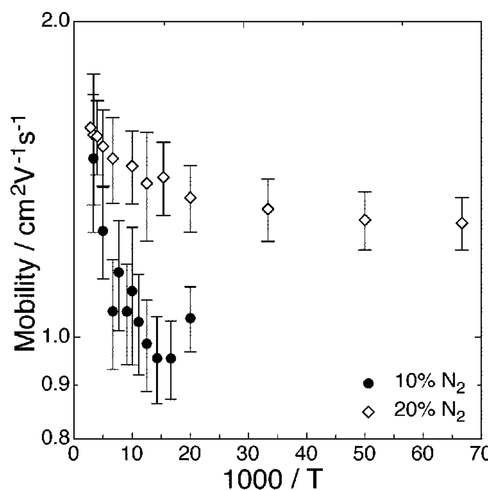

FIG. 3. Hall mobilities in nitrogen-doped UNCD as a function of temperature.

The variations in mobility against temperature and plasma nitrogen content are shown in Fig. 3. It can be seen that the room-temperature values of mobility are around 1.5 cm^2 V^{-1} s^{-1}, and are again rather insensitive to temperature. The 20% N_2 sample varies from 1.565 cm^2 V^{-1} s^{-1} at 300 K to 1.285 cm^2 V^{-1} s^{-1} at 15 K, whereas the 10% N_2 sample varies from 1.485 cm^2 V^{-1} s^{-1} at 300 K to 1.045 cm^2 V^{-1} s^{-1} at 50 K. Again, the reduction is more significant in the 10% N_2 sample, but the overall variation is slight. These values of mobility were derived from the sheet carrier concentration and resistivity values. The resistivity values of films grown with 0%–20% N_2 in the gas phase were measured previously, and it was found that the higher plasma nitrogen content films exhibited both lower resistivities and lower-temperature variations of the resistivities. The room-temperature values of sheet resistivity were 22 Ω/sq for the 20% N_2 film, 880 Ω/sq for the 10% N_2 film, 2.5×10^4 Ω/sq for the 5% N_2 film, and 1×10^5 Ω/sq for the 0% N_2 film. These are the lowest values of sheet resistivity reported for *n*-type diamond.[6]

UNCD appears to be an intriguing material. Nitrogen has been shown to reduce the resistivity of amorphous carbons such as "diamondlike carbon" and "tetrahedrally bonded carbon" (ta-C) in the past, but the resulting mobility values were generally in the 10^{-6} cm^2 V^{-1} s^{-1} range,[14,15] i.e., six orders of magnitude lower than this case and undetectable by the Hall effect. In single crystal and microcrystalline diamond, nitrogen is a substitutional donor with activation energy of 1.7 eV,[10] but can also form complexes (such as the

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$N-V$ center)[16] which generally result in deep traps or compensation of any conductivity. Type-Ib diamond contains substantial levels of nitrogen and is hence yellow, but the resistivity of this material is extremely high at room temperature, at least $1\times10^{9}\ \Omega/\mathrm{sq}$. Thus, the conductivity mechanism observed in this work cannot be thought of as due to a single shallow donor beneath the conduction-band minimum. In fact, the activation energy of these films decreases with added nitrogen in the gas phase, and is below 10 meV for nitrogen gas phase concentrations above 10%. Theoretical modeling has shown that nitrogen in the gas phase promotes π-bonded states within the grain boundaries, resulting in an impurity band near the Fermi energy.[17] The predicted density of states also shows the Fermi level to be situated close to the valance band for films grown without nitrogen. This has been confirmed by the Seebeck effect. As nitrogen is added, the Fermi level moves toward the conduction band, but the primary reason for the increase in conductivity is the high density of states within the band gap due to π bonding at the grain boundaries.[18] This density of states at the Fermi level increases with added nitrogen. In this way, nitrogenated UNCD has similarities to ta-C[19] but with the stark contrast of significantly higher mobility, presumably due to the higher crystallinity of this material. Near-edge x-ray absorption fine structure, electron energy-loss spectroscopy, x-ray diffraction and selective area electron diffraction measurements have shown there is no evidence of crystalline graphite within these films.[8]

Spectrally resolved photoconductivity, transmission, impedance, and electron spin resonance measurements are currently underway to explain this transport mechanism. The low activation energy of nitrogenated UNCD could be of critical importance in the fabrication of electronic devices for use at room temperature, and has been shown as a highly efficient electrochemical electrode. Heterostructure diodes with high rectification ratios and high temperature stability have recently been fabricated using this material.

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