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Electrical conductivity studies of chemical vapor deposited sulfur-incorporated nanocomposite carbon thin films

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The room-temperature electrical conductivity of sulfur-incorporated nanocomposite carbon (n-C:S) thin films synthesized by hot-filament chemical vapor deposition was investigated as a function of the sulfur concentration. The films were prepared using a 2% CH_4/H_2 gas mixture and H_2S as the dopant source. The n-C:S films exhibited an increase in conductivity by four orders of magnitude (up to 160 $\mathrm{S\,cm^{-1}}$) with an increase in sulfur content compared with those grown without sulfur (n-C). The films grown at the highest $[H_2S]$ possess the highest carrier concentration ($\sim 5 \times 10^{19}/\mathrm{cm}^3$) and the lowest carrier mobility (0.005 $\mathrm{cm^2\ V^{-1}\,s^{-1}}$). These findings are discussed in terms of the *multiple roles of sulfur* atoms in the films: (i) induction of structural defects and their corresponding midgap states, (ii) enhancement of the spatial connectivity of the sp^2-bonded carbon network, and (iii) electrical activity of only a small fraction of the sulfur atoms. [DOI: 10.1063/1.1491600]

The coexistence of several superlative material properties in diamond make it a very promising material, but important electronic applications have remained limited due to the difficulty of making semiconducting n-type thin films of sufficiently high electrical conductivity. The synthesis of diamond or diamond-like carbon thin films with high n-type conductivity has been so far difficult to achieve.[1–6] Although some earlier work has demonstrated the induction of shallow donor levels in diamond, the room-temperature conductivities were still too small to enable their application in conventional electronic devices.[4] This problem was recently overcome in nitrogen-doped ultrananocrystalline diamond (UNCD) grown by microwave plasma chemical vapor deposition (CVD).[7]

Electrical conductivity studies of carbon-based materials have proved to be a powerful tool in investigating defects and/or impurities in such films. Currently, these materials are of much interest due to their many potential applications, such as in field emission displays (FEDs).[8] It is believed that potential n-type dopants of diamond may enhance the electron field emission properties of disordered and nanocrystalline carbon films by providing electrons close to the conduction band[7,9,10] and/or helping to control the film microstructure by either introducing specific types of defects or induce synthesis-specific nanostructured carbon materials. There is a great deal of interest in sulfur doping due to experimental and theoretical findings that it is a promising donor dopant in diamond.[11]

Our recent work has focused on the incorporation of impurities into nanocrystalline carbon films, in particular, the incorporation of sulfur via the addition of H_2S gas to the CH_4/H_2 gas mixture. We reported that sulfur-incorporated nanocrystalline carbon thin films (denoted by n-C:S from here on) exhibit striking field emission properties that could be exploited in cold cathodes for FEDs.[12] By introducing sulfur, we have gained control of the microstructural properties of the films in such a way that we can tailor the formation of nanosized quasifilamentary sp^2-bonded carbon (sp^2 C) conducting channels that produce local field enhancement and are capable of withstanding high emitting currents.[13] Sulfur atoms also induce changes in the electronic structure by the introduction of midgap states within the fundamental optical gap of the material, as demonstrated recently.[14] In this letter, the answer to some important open questions about these films is attempted: (i) What is the electrical resistivity of the films in general? (ii) Is there any evidence of n-type doping activity due to sulfur incorporation? (iii) How are the sulfur atoms distributed? The focus of the present work therefore is to report the room-temperature electrical conductivity of n-C:S grown under different conditions (changing both the substrate temperature and hydrogen sulfide concentration) and to correlate these results with corresponding morphological and microstructural variations.

The n-C:S thin films studied here were synthesized in a custom-built hot filament CVD (HFCVD) reactor on polished Mo substrates, which is described in detail elsewhere.[12] A 2% $CH_4:H_2$ gas mixture with a total flow of 100 sccm was directed through a rhenium (Re) filament heated to 2500 °C. Hydrogen sulfide was used as the source of sulfur atoms and was varied from 100 to 500 ppm. All of the films were deposited at substrate temperatures of 900 °C. The films thicknesses were 0.5–1.0 μm as measured mechanically using a Tencor surface profilometer (Alpha Step 100).

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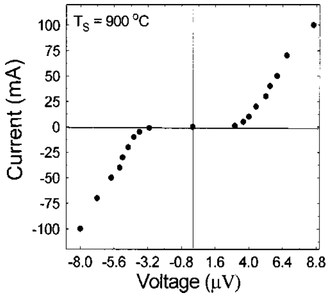

FIG. 1. Representative $I-V$ relationship of sulfur-incorporated nanocomposite carbon showing ohmic behavior.

For the electrical resistivity and Hall measurements, a custom-built Van der Pauw system composed of a Keithley 224 programmable current source unit and a Keithley digital voltmeter (196 DMM) were used. The electrical conductivity was measured using the four-probe method in a metal (silver paint)–diamond–metal configuration. These measurements permitted us to determine the electrical conductivity ($\sigma = 1/\rho$), carrier density (n_e), Hall mobility (μ_H), and carrier type. Hall measurements were taken at a magnetic field of 0.6 T. The amount of sulfur introduced into the films ranged from 0.3 to 1.5 at. %, quantified by x-ray photoelectron spectroscopy (XPS). The surface morphology of the films was revealed by scanning electron microscopy using a JEOL electron microscope (model 35 CF). Visible ($\lambda_L = 514.5$ nm) Raman spectroscopy (RS) was used to analyze the structural bonding in the films.

It has been found previously that the behavior of the electrical contacts depends on a number of factors such as the surface morphology, material pretreatment, doping, and the architecture of the device or of the electrode itself.[15] In order to assess the electrodes and the configuration (to avoid or minimize the diamond–metal interface effect involved in electrical activity), room-temperature $I-V$ measurements were performed. They reflected almost ohmic behavior of these contacts (see Fig. 1) in contrast to sputtered gold contacts, which were also tested.

Figure 2 shows scanning electron microscopy (SEM) images of *n*-C:S films grown at the indicated $[H_2S]$ in gas phase (an interval of 200 ppm is chosen for space conservation) to assess surface morphological variations. These films were grown at substrate temperature of 900 °C. Qualitatively, their microstructure is dominated by nanosize crystallites. Similar morphological changes have been reported for nitrogen-doped microwave plasma CVD diamond films.[12] Notice that, although there are morphological changes apparent in Fig. 2, the nature of the films remain nanostructured and the sizes of these crystallites varied from a few hundred nm to a few tens of nm with an increase in $[H_2S]$. In other words, the dispersed nanocrystallites start diffusing with distinct grain boundaries (GBs) and, if imaged three dimensionally, they appear either ball or cauliflower like.[12] In fact there are several ways of changing the shape or growth habit of the diamond particles or crystallites: variation of the methane concentration and/or deposition temperature,[16] the addition of oxygen,[17] and use of impuritities such as B, P, N,[18] and now S,[12] in the chamber during the CVD process. The range of H_2S studied here along with 2% $[CH_4]$ was enough to induce a change in morphology from well-defined crystallite growth (faceted) to nanocrystalline or ballas like.

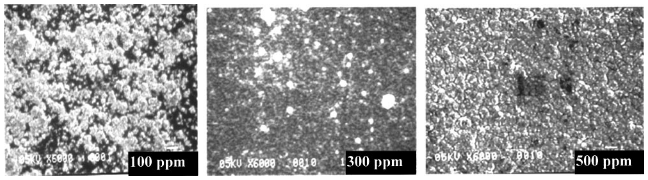

FIG. 2. Scanning electron micrographs exhibiting the changes in surface topology of sulfur-incorporated nanocomposite carbon thin films deposited at the temperatures indicated with 400 ppm of H_2S in the gas phase during the CVD process.

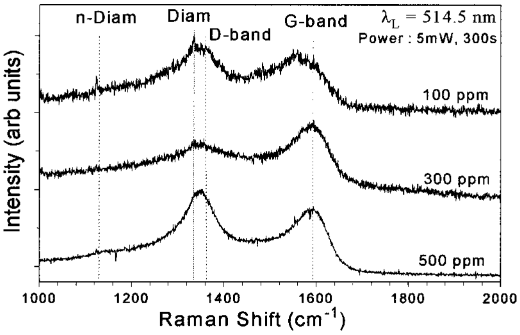

FIG. 3. Raman spectra of sulfur-incorporated nanocomposite carbon (*n*-C:S) thin films depicting characteristic diamond, nanocrystalline diamond, and disordered carbon signatures. The dotted lines are the characteristics of various carbon-based reference materials. All of the films were deposited at T_s of 900 °C.

The Raman spectra of the *n*-C:S thin films is used to assess changes in the structural bonding configurations. They are shown in Fig. 3, as a function of the $[H_2S]$ indicated (an interval of 200 ppm is chosen for space conservation) in the gas phase. Upon qualitative inspection, the film grown with 100 ppm shows a 1332 cm^{-1} peak (a fingerprint of diamond or sp^3-bonded C). Figure 3 also shows broad features at 1150, 1340, and 1580 cm^{-1}, typical of nanocrystalline diamond (n-D), and disordered carbon dominated by microcrystalline graphitic inclusions,[19] denoted by the D and *G* bands, respectively. These latter features predominate with respect to the increase in sulfur concentration. While the film grown with 100 ppm is quite similar to the intrinsic material (n-C), the diamond peak starts to disappear right at 300 ppm of $[H_2S]$. Relative heights of the Raman peaks (D and *G* bands) differ in general. The difference among the Raman spectra can be explained by sulfur addition. Under the specific growth conditions considered in this study, sulfur tends to introduce disorder and defects considerably, similar to nitrogen incorporation, which induces graphitization of carbon films.[7,18] The defect density grows to a critical point at which defects form a network and leave behind nanoscale islands of tetragonally bonded carbon surrounded by trigonally bonded carbon (analogous to percolation phenomena).[20]

There are strong correlations between the microstructural changes deduced from the Raman spectra and the changes observed in electrical properties of these sulfur-incorporated nanocomposite carbon thin films. The room-temperature electrical conductivity (see Fig. 4) increased systematically four orders of magnitude from 0.03 (for no sulfur) to ~160 S cm^{-1} (for the highest $[H_2S]$ employed in the present study). This trend is similar to that found for

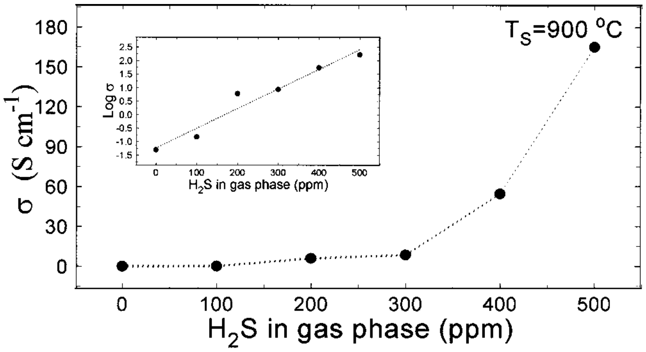

FIG. 4. Electrical conductivity (σ) data plot obtained at room temperature (298 K) of sulfur-incorporated nanocomposite carbon thin films as a function of the hydrogen sulfide concentration in the gas phase. All of the films were deposited at T_s of 900 °C.

nitrogen-doped nanocrystalline diamond.[7] All the films showed negative charge type carriers. The inset in Fig. 4 shows the electrical conductivity data on a log scale. The mobilities remained in the 0.1–0.005 $cm^2 V^{-1} s^{-1}$ range, which is quite low compared to either single crystal (1700 $cm^2 V^{-1} s^{-1}$) or polycrystalline diamond (1–30 $cm^2 V^{-1} s^{-1}$),[6] or even N-doped nanocrystalline diamond material.[7] These low carrier mobility values correlate with the high defect density and the corresponding midgap states due to sulfur addition and with the half width at half maximum (HWHM) of the diamond peak (fitted) obtained from the Raman spectra, as shown in Fig. 5.[13] The carrier density of these films varied from 5.10×10^{17} to 6.25×10^{19} cm^{-3} for films grown with no sulfur and with an increase in sulfur addition, respectively. The latter carrier density is around two orders of magnitude higher than that for the undoped films.

The above results indicate that there are about one or two negative charge carriers per 100 sulfur atoms. Therefore, most sulfur atoms remain electrically inactive, as expected from theoretical calculations.[21] This behavior is similar to that of other disordered semiconductors, like hydrogenated amorphous silicon, where a large excess of impurity atoms is required in order to obtain reasonable electrical activity.[21] The excess sulfur atoms here act as impurities within nanocrystalline carbon, and they are known to have a tendency to aggregate at grain boundaries.[7] This particular aspect has been demonstrated theoretically by tight binding molecular dynamics (TBMD) calculations for the case of nitrogen doping.[7] Whether there is a small percent of sulfur atoms actually acting as donor dopants is still the subject of investigation. The 1–2 at. % sulfur figure is only an upper bound. Conductivity may also arise from the enhanced spatial connectivity of sp^2-bonded carbon (sp^2 C).[13] However, the conductivities decrease with a decrease in [H_2S], although the material remains nanostructured with networked sp^2 C channels (see Fig. 4).[13] This finding is indicative of some sulfur electrical activity. Taken together, the results discussed above point to *multiple roles of sulfur* that contribute to the enhanced electrical conductivity in nanocomposite carbon films.

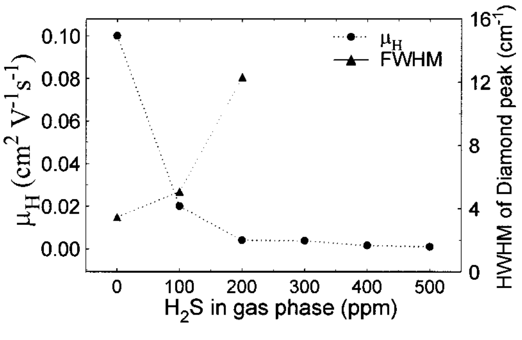

FIG. 5. Dependences of the Hall mobility (μ_H) and full width at half-maximum (FWHM) of the diamond Raman peak in *n*-C:S thin films at room temperature as a function of the hydrogen sulfide concentration grown at $T_s = 900$ °C.

In conclusion, sulfur-incorporated nanocomposite carbon thin films were synthesized using the HFCVD technique with a $CH_4/H_2/H_2S$ gas mixture. The surface morphology, Raman spectra, and electrical properties of the films are greatly affected by the addition of sulfur during the CVD process. A systematic increase in room-temperature electrical conductivity with an increase in the hydrogen sulfide concentration in the gas phase was found. Under the high doping concentration (S/C ratio) employed here, there are observable effects over the conductivity that can be related to enhanced electronic defect states, improved spatial connectivity of trigonally bonded carbon, and the electrical activity of a small percentage of sulfur atoms.

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