

# Resistivity of chemical vapor deposited diamond films

M. I. Landstrass and K. V. Ravi<sup>(\*)</sup>

Crystallume, 125 Constitution Drive, Menlo Park, California 94025

(Received 28 April 1989; accepted for publication 7 July 1989)

Diamond films grown by plasma chemical vapor deposition techniques display a fairly low resistivity ( $\sim 10^6 \Omega \text{ cm}$ ). Heat treating the films causes an increase in the resistivity by up to six orders of magnitude. The low resistivity of the as-grown films is postulated to be due to hydrogen passivation of traps in the films. Annealing causes dehydrogenation resulting in the electrical activation of deep traps with an attendant increase in the resistivity. This mechanism has been confirmed by an observed reduction of the resistivity of the heat-treated films when they are subjected to a plasma hydrogen treatment.

Diamond exhibits several remarkable properties that makes it a highly desirable material for passive and active electronic device applications.<sup>1</sup> The ability to synthesize thin diamond films utilizing plasma-enhanced chemical vapor deposition (CVD) techniques has enhanced the prospects for diamond-based electronics.<sup>2</sup> Diamond thin films can be synthesized by plasma-enhanced CVD techniques utilizing mixtures of methane and hydrogen as the gas specie. It has been demonstrated that a high concentration of hydrogen, typically in excess of 98% by volume, in the gas mix is required to promote the formation of diamond bonds, as opposed to the equilibrium form of carbon, graphite.<sup>3-5</sup> Several plasma synthesis approaches have been utilized for fabricating polycrystalline diamond films.<sup>4,6,7</sup>

For the use of these films in passive and active electronics, the physical properties that have the most significance are the thermal conductivity and the transport properties such as the resistivity, the carrier lifetime, and the mobility. The thermal conductivity of PECVD diamond films has been measured to range up to  $14 \text{ W/cm K}$ <sup>8,9</sup> demonstrating that this property is approaching that of natural diamond crystals ( $20 \text{ W/cm K}$ ). It has been shown that diamond films synthesized by the use of microwave-assisted plasmas display a low resistivity with evidence for space-charge-limited currents in the presence of an exponential distribution of traps.<sup>10</sup> High electrical resistivity diamond films, however, have not been reliably synthesized to date.

In this letter we present the first results demonstrating that the electrical resistivity of CVD diamond films is governed by the presence of dissolved hydrogen in the films. As-grown diamond films typically display low resistivities of the order of  $10^6 \Omega \text{ cm}$  as a result of hydrogen passivation of defect states in the films. When the films are heat treated the resistivity is found to increase by several orders of magnitude due to removal of hydrogen from the films or due to a shift of the hydrogen from an electrically active to a nonelectrically active site in the film.

Diamond films  $\sim 2-4 \mu\text{m}$  in thickness were grown on 10-cm-diam polished silicon wafers using both a dc glow discharge approach and microwave-assisted plasmas utilizing mixtures of methane and hydrogen as the gas specie.

Electrical contacts to the films were made by depositing circular dots of chromium followed by gold with a sintered aluminum contact to the back of the silicon wafer. Both room-temperature and temperature-dependent current-voltage ( $I-V$ ) characteristics of the diamond films were obtained. The films were annealed to temperatures up to  $800^\circ\text{C}$  for up to an hour in flowing nitrogen. The  $I-V$  characteristics of the annealed films were measured at room temperature.

The films displayed typical Raman spectra of diamond with a strong shift at 1333 wave numbers due to diamond bonding. The spectra of some of the films exhibited small

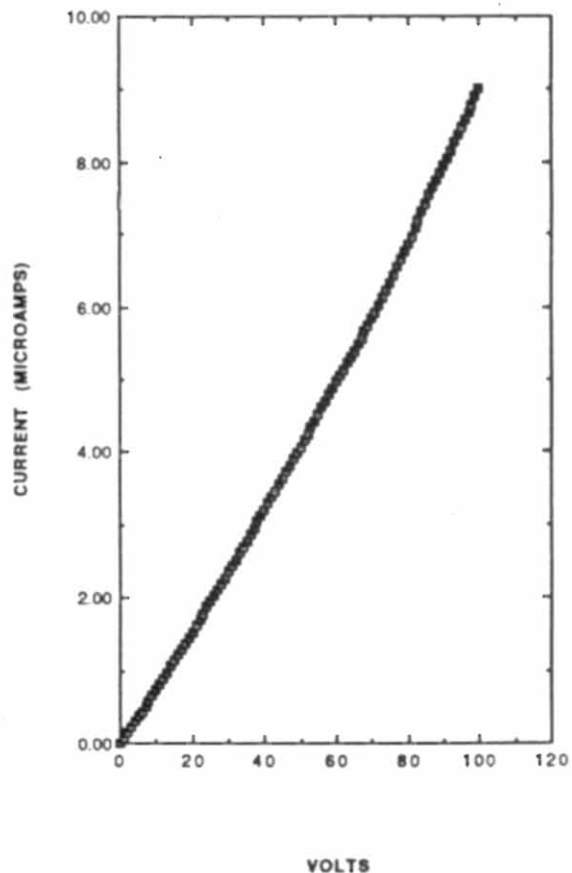


FIG. 1. Room-temperature  $I-V$  characteristic of as-grown diamond film on silicon.

<sup>(\*)</sup> Now at Lockheed Missiles and Space Company, Palo Alto Research Laboratory, 5251 Hanover Street, Palo Alto, CA 94304.

peaks at around 1550 wave numbers indicating the presence of some amounts of nondiamond phases in the films. The results presented in this letter were not influenced by small changes in the Raman spectra.

Figures 1 and 2 show typical room-temperature  $I$ - $V$  curves of an as-deposited diamond film and of a film subjected to heat treatment at 350 °C in air for 30 min. The two curves in Fig. 2 are for positive and negative polarities. The effect of annealing is found to be very significant with the resistivity of the diamond increasing by up to six orders of magnitude ( $\sim 10^{13} \Omega \text{ cm}$ ) and evidence of trap-dominated conduction being observed in the annealed films. Since resistivity changes in the films have been observed to occur at annealing temperatures as low as 100 °C, the most probable cause for the observed changes is related to the movement of hydrogen within or out of the film. To test this hypothesis an annealed film was rehydrogenated by placing the film in a hydrogen plasma for 4 h at a temperature of 400 °C. Upon measuring the  $I$ - $V$  characteristics of the rehydrogenated film, its resistivity and current-voltage behavior was found to be essentially identical to that of the as-grown film as shown in Fig. 3. Low-temperature annealing was observed to result in an initial decrease in the resistivity of the films

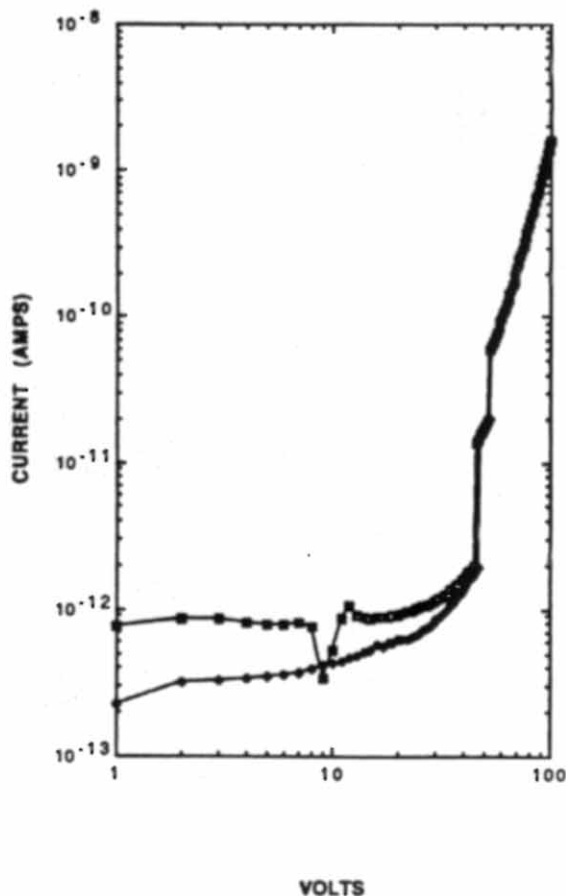


FIG. 2.  $I$ - $V$  characteristics of a diamond film following annealing at 350 °C for 30 min in air. The two plots shown are for positive and negative polarities. Their essential similarity indicates that the observed effects are bulk effects in the diamond film rather than contact related artifacts.

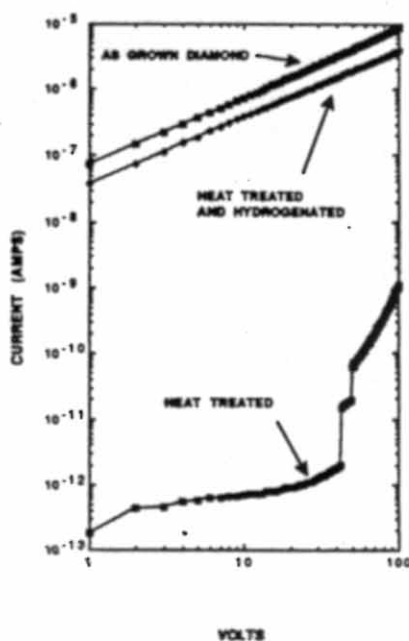


FIG. 3.  $I$ - $V$  characteristics of a diamond film in the as-synthesized condition, following heat treatment at 600 °C for 30 min and following rehydrogenation at 400 °C in a hydrogen plasma.

followed by a monotonic increase in the resistivity at higher annealing temperatures (Fig. 4).

It has been shown, for the first time, that current conduction in polycrystalline diamond films is governed by dissolved hydrogen. This result is not surprising in view of the

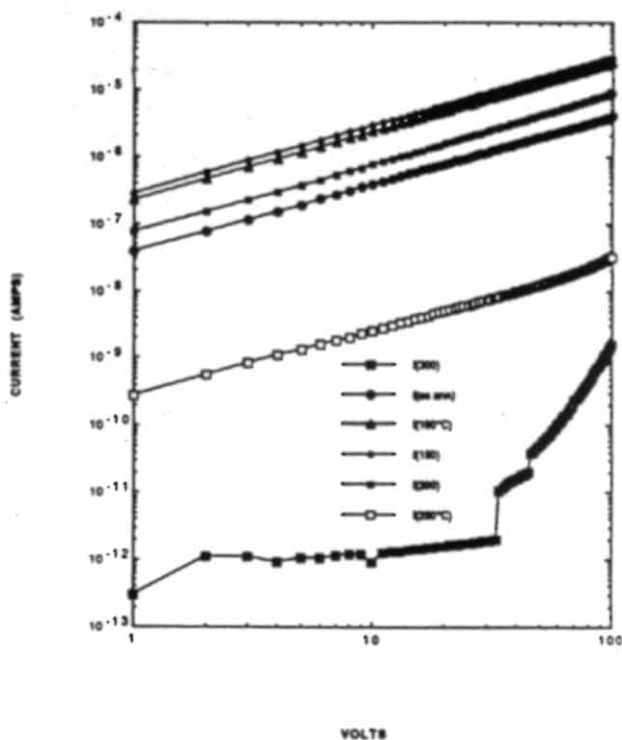


FIG. 4. Room-temperature  $I$ - $V$  characteristics of a diamond film as a function of annealing temperature. The unannealed condition is represented by the film exposed to a hydrogen plasma for 4 h at 400 °C.

fact that the electrical effects of hydrogen in other semiconductors have been well documented.<sup>11</sup> Hydrogen passivation of dangling bonds in amorphous silicon,<sup>12</sup> grain boundaries in polycrystalline silicon,<sup>13</sup> donor and acceptor impurities in silicon,<sup>14</sup> and shallow impurities in gallium phosphide<sup>15</sup> have been demonstrated. In this work we have shown that hydrogen, which is present in its atomic form in large quantities in the plasma ambient used to synthesize diamond films, has a profound impact on current conduction in the films. The *I-V* characteristics of annealed films display trap-limited behavior with two steeply rising current steps always being observed in the films heat treated at high temperatures. These steps mark the onset of the deviation from ohmic behavior observed at low applied fields and are postulated to occur when the injected charge from the contacts fills hole traps (deep donors) in the films. The appearance of the current step terminating the ohmic region indicates a trap level at or just below the Fermi level which pins the Fermi level and gives rise to the observed high resistivity. The second step indicates a second donor level just above the Fermi level. The trap density can be estimated from the relationship<sup>16</sup>:

$$V = Q/C = ND^2/\epsilon,$$

where *Q* is the trap charge, *C* is the capacitance, *N* is the trap density, and *D* and  $\epsilon$  are the thickness and the dielectric constant of the film. The trap density has been estimated to be  $\sim 1.5 \times 10^{15}/\text{cm}^3$ . Hydrogenation electrically neutralizes the traps and the resistivity in the hydrogenated films is governed by shallow acceptor levels.

The effects of hydrogen have been found to be similar for diamond films synthesized using dc glow discharge techniques as well by the use of microwave-assisted plasmas. These results suggest that as-grown diamond films are unstable with respect to their carrier transport properties, and that the causes for this instability are related to hydrogen

passivation of defect states. The hydrogen can evolve from these films at relatively low temperatures and the films can be stabilized at fairly high resistivity levels of the order of  $10^{13} \Omega \text{ cm}$  by annealing.

This work has been supported by Strategic Defense Initiative Organization/Innovative Science and Technology through the Office of Naval Research.

<sup>1</sup>K. V. Ravi and M. I. Landstrass, *Proceedings of the Fourth International High Frequency Power Conversion Conference*, Naples, FL (Intertec Communications, Ventura, 1989), p. 103.

<sup>2</sup>B. V. Deragin, L. L. Builov, V. M. Zubkov, A. A. Kochergina, and D. V. Fedoseev, *Sov. Phys. Crystallogr.* **14**, 449 (1969).

<sup>3</sup>B. V. Spitsyn, L. L. Bouilov, and B. V. Derjaguin, *J. Cryst. Growth* **52**, 219 (1981).

<sup>4</sup>S. Matsumoto, Y. Sato, M. Kamo, and N. Setaka, *Jpn. J. Appl. Phys.* **21**, L183 (1982).

<sup>5</sup>D. V. Fedoseev, V. P. Varnin, and B. V. Deryagin, *Russ. Chem. Rev.* **53**, 435 (1984).

<sup>6</sup>K. Kobashi, K. Nishimura, Y. Kawate, and T. Horuchi, *Phys. Rev. B* **38**, 4063 (1988).

<sup>7</sup>A. Sawabe and T. Inuzuka, *Thin Solid Films* **137**, 89 (1986).

<sup>8</sup>A. Ono, T. Baba, H. Funamoto, and A. Nishikawa, *Jpn. J. Appl. Phys.* **25**, L808 (1986).

<sup>9</sup>J. A. Herb, K. V. Ravi, and P. A. Denning, *First International Symposium on Diamond and Diamond-Like Films* (The Electrochemical Society, Los Angeles, in press).

<sup>10</sup>K. Srikanth, S. Ashok, A. Badzian, T. Badzian, and R. Messier, *Thin Solid Films* **164**, 187 (1988).

<sup>11</sup>S. J. Pearton, J. W. Corbett, and T. S. Shi, *Appl. Phys. A* **43**, 153 (1987).

<sup>12</sup>A. Madan, in *Silicon Processing for Photovoltaics*, edited by C. P. Khattak and K. V. Ravi (North-Holland, Amsterdam, 1985), p. 331.

<sup>13</sup>J. I. Hanoka, C. H. Seager, D. J. Sharp, and J. K. G. Panitz, *Appl. Phys. Lett.* **42**, 618 (1983).

<sup>14</sup>A. J. Tavendale and S. J. Pearton, *J. Appl. Phys.* **54**, 1357 (1983).

<sup>15</sup>M. Singh and J. Weber, *Appl. Phys. Lett.* **54**, 424 (1989).

<sup>16</sup>M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970), Chaps. 2, 4, and 5.