Journal of Electronic Materials, Vol. 21, No. 6, 1992

Electrical Conductivity and Photoluminescence of Diamond Films Grown by Downstream Microwave Plasma CVD

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Electrical conductivity measurements and photoluminescence (PL) were used to study the effects that sample distance from the plasma during growth has on the carrier transport properties of undoped CVD diamond. The films were grown by downstream microwave plasma chemical vapor deposition at distances from 0.5 to 2.0 cm from the edge of plasma glow. Electrical conductivity measurements were performed between room temperature and 1000° C and then complimented with Raman spectroscopy and PL studies in an attempt to gain a better understanding of the CVD growth process and the resulting electrical and optical properties of the diamond films. Room temperature electrical conductivity was found to vary by over 5 orders of magnitude with increasing growth distance from the plasma, while only moderate changes were observed in the luminescence spectra.

Key words: Diamond, electrical conductivity, photoluminescence

I. INTRODUCTION

There are many applications for highly electrically insulating materials that will remain stable at extreme temperatures, such as the insulator in high temperature thermoelectric power conversion devices. Diamond appears to be a good candidate for such high temperature applications due to its intrinsically high electrical resistivity and very high thermal conductivity. Chemical vapor deposited (CVD) diamond thin-films are thus an attractive alternative to alumina, which is the material currently used in such devices.

The quality of CVD diamond films is greatly improving yet their electrical resistivities are still several orders of magnitude lower than that of natural II-A diamond.[1] However this and other reports[2–4] have shown that the resistivity of the as grown diamond films may be greatly altered, without appreciable change in diamond quality as determined by Raman spectroscopy, by various post deposition treatments. Landstrass and Ravi[4] and Albin and Watkins[3] showed that the resistivity of both bulk and CVD diamond could be decreased by exposing the samples to a hydrogen plasma. Nakahata and coworkers[2] showed that this effect could be reversed and the resistivities increased to near that of natural diamond by either a post deposition anneal in oxygen or an oxygen-containing plasma. Adams *et al.*[1] in a study of the electrical resistivity as a function of temperature, found that the as-grown films initially showed a high electrical conductivity, but after heating to 1000° C and then cooling to room temperature they became very resistive (see Fig. 1).

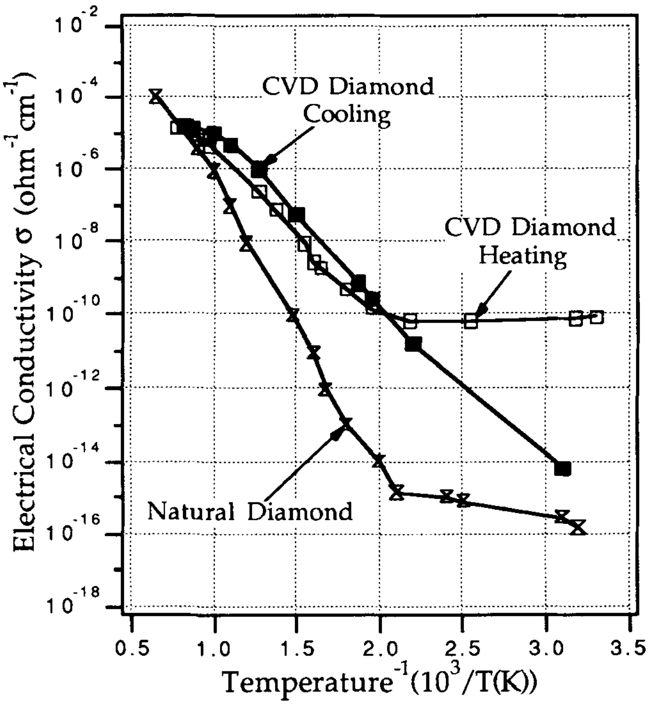

Fig. 1 — Electrical conductivity vs temperature of CVD diamond film and natural type IIa diamond showing that the room temperature conductivity of the CVD film decreases by several orders of magnitude after initial heating.[1]

Some of the above researchers have speculated and it is the belief of the current authors that the low resistivities associated with the as-grown, or hydrogenated diamond films is due to hydrogen passivation of defects in the diamond lattice that would otherwise act as electrical traps. The purpose of the current research was to study the effects that deposition distance in downstream microwave plasma

(Received January 17, 1992)

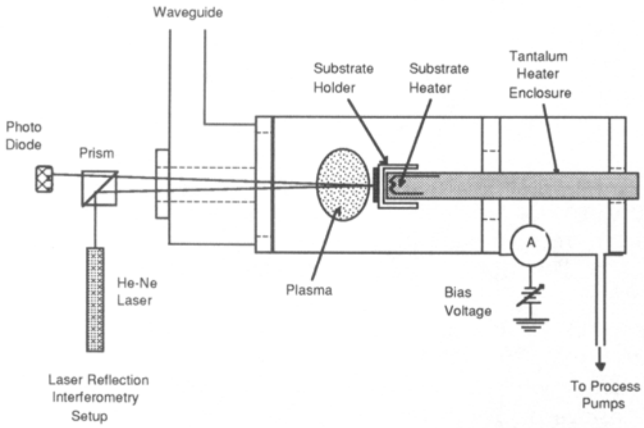

Fig. 2 — Schematic of microwave plasma CVD system with laser reflection interferometry apparatus to measure film thickness in-situ.

CVD has on the electrical properties of the as-grown diamond films in hopes of gaining a better understanding of the deposition process. Diamond films were grown at various distances downstream of the plasma and were analyzed using electrical resistivity measurements as a function of temperature. Raman spectroscopy and photoluminescence (PL) were also performed on the samples to draw a correlation between the optical and electrical properties of the CVD films.

The GR1 peak in the photoluminescence spectra at approximately 1.673 eV is an optically active center that has been found to exist in both natural and synthetic diamonds. The GR1 defect can be produced in diamond by radiative damage that subsequently gives rise to interstitials and vacancies in the diamond lattice.[5–8] It has thus been speculated that the GR1 band is associated with neutral vacancies in natural diamond. Many diamond films grown by vapor phase techniques exhibit a PL emission line at 1.681 eV which is a shift of 8 meV from the GR1 of natural diamond. This shift may indicate that the center originates from a slightly different defect center than the vacancy of natural diamond. Some studies have shown that the introduction of Si during growth increases the 1.681 eV peak significantly.[9,10] Explanations for this result were that the Si atoms were incorporated into the diamond octahedral lattice sites and formed a radiative center. Another study on Si-implanted natural diamond showed that the 1.68 eV center was due to defects containing two interstitial Si atoms.[11] The PL measurements in the current research were intended to determine whether the defects associated with the 1.68 eV band, contribute significantly to the electrical conductivity behavior of CVD diamond films.

II. EXPERIMENTAL

Samples were grown in an ASTeX microwave plasma CVD reactor (Fig. 2). The power supply used was an ASTeX S-1000, 2.45 GHz microwave supply with a rectangular waveguide that is coupled to the cylindrical growth cavity. The substrate holder is a fully retractable, differentially pumped tantalum heater that may be used to control the substrate temperature independently of the plasma power. The plasma forms at a stable position in the center of the cavity and the substrate position relative to the plasma may be varied between 0(immersed) and 8 cm. The tantalum heater consists of a Ta filament encased in a boron nitride insert inside of a differentially pumped, isolated 0.04 inch thick tantalum can.

Four samples were grown on 1 inch diameter mirror finish Si(100) wafers that were pretreated in-situ, prior to growth using a bias enhanced nucleation technique that is described elsewhere.[12,13] The samples were grown at distances of 0.5, 1.0, 1.5, and 2.0 cm downstream from the edge of the visible glow discharge of the plasma. The deposition pressure, plasma power, and substrate temperature were held constant at 25 Torr, 600 W, and 700° C, respectively, for all four samples. The methane concentration in hydrogen was 1%, at a total flow rate of 1000 sccm. Gas flows were monitored and controlled by MKS mass flow controllers and the substrate temperature was monitored by an IR pyrometer normal to the substrate. All samples were grown to a thickness of approximately 2 ± 0.1 μm. Sample thicknesses were monitored in-situ using laser reflectance interferometry, shown in Fig. 2, which is described in greater detail elsewhere.[12]

Each of the four samples were cleaved into four pie-shaped pieces for subsequent analysis. One section was used for electrical conductivity measurements as a function of temperature (room temperature to 1000° C) and another used for Raman spectroscopy and photoluminescence (PL) studies as described in further detail below. The remaining sections were utilized for scanning electron microscopy (SEM) or stored for future analysis. Raman spectroscopy and PL were performed on the samples both before and after the conductivity vs temperature measurements to observe any bulk changes that may have occured in the diamond films as a result of exposure to the high temperatures.

The electrical conductivities of the films were measured using an experimental apparatus that was specifically designed and built to measure very high resistivity insulators up to greater than 1200° C. The sample holder and oven are shown in Figure 3. The holder was made out of 0.998 pure alumina and all the wiring feedthroughs and connections were made in such a way as to minimize leakage currents. A dc two point probe method was used to measure the resistivity of the samples perpendicular through the plane of the samples. The apparatus was first tested on single crystal sapphire and the results were reported elsewhere.[14] It is believed that with this apparatus conductivities can be accurately measured to as low as 10^{-16} to 10^{-17} Ω^{-1} cm^{-1}.

Initially, a guard ring and volume guard configuration were used but the same initial test results were obtained without them, thus they were no

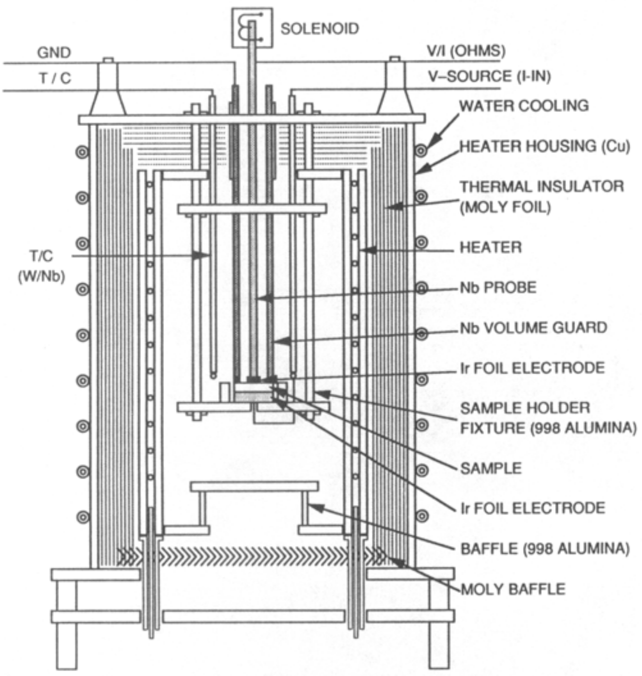

Fig. 3 — Electrical conductivity measurement apparatus capable of measuring to temperatures as high as 1200° C.

longer used in subsequent measurements. Occasionally, a sample would be measured both with and without the guard ring and volume guard as a check.

The top center niobium electrode rod rested (with slight pressure) on the small circular piece of iridium foil (typically 5 mm in diam, depending on the size of the sample) that rested on top of the sample. The bottom electrode (on which the substrate rested) was a circular piece of iridium foil 12 mm in diam. The samples were measured from room temperature up to 1000–1200° C and then back down to room temperature. The vacuum throughout the measurement was maintained at 10^{-5}–10^{-6} Torr to minimize surface leakage due to adsorbed water vapor and other atmospheric contaminants.

The photoluminescence and micro-Raman spectroscopy were carried out at room temperature using an ISA U-1000 scanning monochrometer. The samples were excited with the 514.5 nm line of an Argon-ion laser, which was focused to a spot on the sample of about 5 μm in diameter, and a power of approximately 20 mW. Focusing was facilitated by the use of an Olympus BH-2 microscope. The Raman spectra were taken in the region 1000–1800 cm^{-1}, and the photoluminescence spectra were taken in the region 400–7000 cm^{-1}.

III. RESULTS AND DISCUSSION

Figure 4 shows SEMs of the four samples grown at 0.5, 1.0, 1.5, and 2.0 cm downstream from the plasma. The micrographs show that the films are uniformly thick with no pinholes and that there is very little difference in morphology as a function of growth distance from the plasma. The Raman spectra from the 4 films, Fig. 5, also confirm that growth distance relative to the plasma has little effect on the bulk optical quality of the films. The full widths at half max (FWHM) of the diamond 1332 cm^{-1} peaks varied only between 8 and 9 cm^{-1} in a random manner.

Figure 6 shows the PL spectra for the four films. A common method of determining the relative density of defects associated with a given peak is to look at the area ratios of the peak of interest to that of the diamond peak at 1332 cm^{-1}. The absolute density of the associated defects may not be determined without proper knowledge of the relative cross sections, but to observe relative changes in defect densities between several films this technique is acceptable. In this case, the ratios of the integrated area under the 1.68 eV band to that of the diamond peak were calculated for the four films and plotted as a function of growth distance from the plasma in Fig. 7. The plot shows only a factor of two change in peak area ratios over the four films with the highest corresponding to the film grown furthest from the plasma. It will be shown that this is insignificant in comparison to the observed changes in electrical conductivity.

Figure 8 shows the plots of electrical conductivity as a function of inverse temperature for the four different films and natural type IIa diamond for comparison. With the exception of the sample grown closest to the plasma, the initial room temperature conductivity of the films decreases by over 5 orders of magnitude with increasing growth distance from the plasma. To insure that this trend was not due to a measurement error, identical measurements were performed on each of two quarters cleaved from the original 1 inch wafers, discussed in the experimental section. Measurements between the two sets of samples agreed to within a factor of two with each other, which is very acceptable given the several orders of magnitude range of the data. Raman spectroscopy was performed on the samples after the conductivity measurements to insure that bulk graphitization or any other major changes to the films did not occur as a result of the heating process. Figure 9 shows the Raman spectra of the 4 films both before and after the conductivity vs temperature measurements and depicts very little resulting changes in film quality. It should also be noted that the relative amounts of graphite or non-diamond component is nearly identical for all four films, both before and after the high temperature process. Thus the dramatic changes in conductivity observed in Fig. 8 cannot be attributed to changes in concentration of non-diamond component in the films.

The possible anomaly associated with the sample grown at 0.5 cm is unclear. It is possible, however, that distortions in the plasma caused by the sample proximity may be partially responsible. When the substrate is further downstream, the plasma is spherical, however, when the substrate is brought closer, the plasma distorts slightly into an ellipsoid. This distortion may affect the defect passivation during CVD of diamond, although a much more

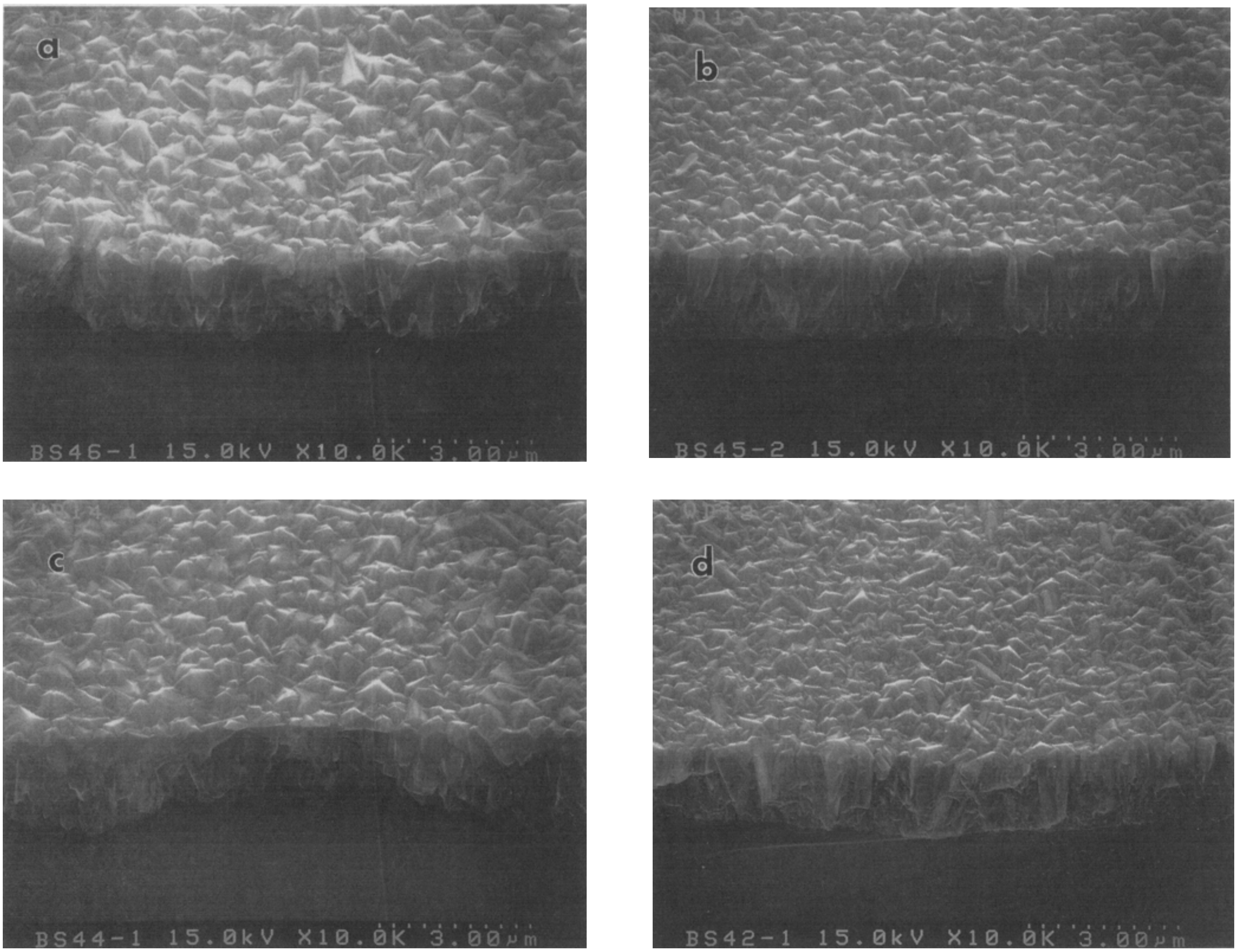

Fig. 4 — SEMs of 2 μm thick samples grown grown at (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 cm downstream from the edge of the plasma, showing little change in growth morphology as a function of distance from the plasma.

thorough study is required in order to fully understand this phenomena.

Since the 1.68 eV peak shows only a factor of 2 change in relative intensity as a function of distance from the plasma (Fig. 7) it is unlikely that it is responsible for the greater than 5 order of magnitude variation in conductivity over the same distance range. This is not to suggest that the centers associated with the 1.68 eV band do not effect electrical conductivity but that under the above experimental conditions they represent only a minor contribution.

If it is believed that the high conductivity at low temperature is due to the temporary passivation of electrical traps by atomic hydrogen, as has been suggested by other researchers,[2-4] then as a result of the data, it appears to be easier to incorporate hydrogen into the films at closer distances to the plasma. One might quickly argue that this is due to a rapid decay in the concentration of atomic hydrogen as a function of distance from the plasma. Atomic hydrogen, however, requires a three body collision in order to recombine with another to form H_2 and is not expected to undergo a 5 order of magnitude decrease in concentration over a distance of 1 or 2 cm. The temperature of the hydrogen gas may also play a significant role in its incorporation into the diamond lattice. While the substrate temperature was kept constant at increasing distances from the plasma, the temperature of the gas is expected to decrease significantly. Another possible explanation might be that the resulting hydrogen content in the films is a function of the density of either hydrogen ions (H^+) or activated hydrogen (H^*) near the growth surface, both of which should show a strong exponential decay as a function of distance from the plasma. At this time it is impossible to determine which of the two mechanisms should dominate.

Another important aspect of the conductivity vs temperature trend is the apparent change in activation energies. At lower temperatures (< 500 K) the activation energies for conduction are much lower than at higher temperatures. Below 500 K the ac-

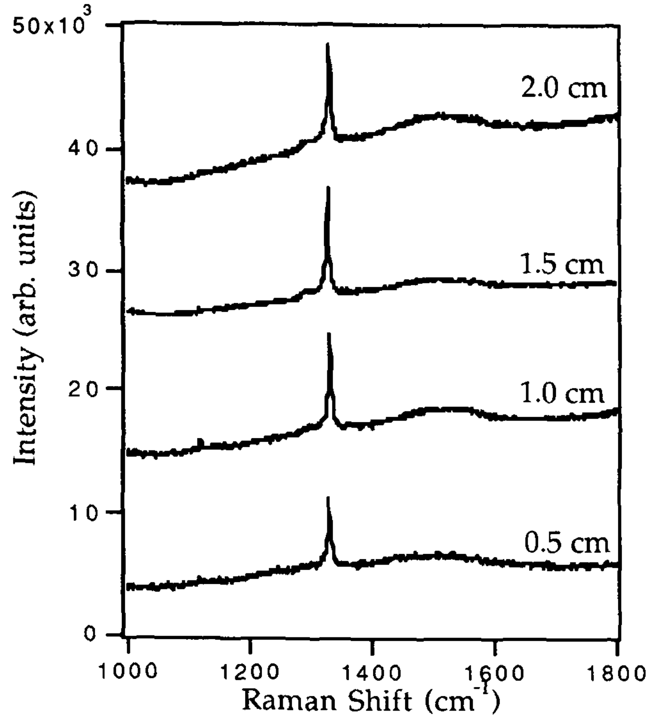

Fig. 5 — Raman Spectra of samples grown at 0.5, 1.0, 1.5, and 2.0 cm from the edge of the plasma, showing that the bulk quality of the diamond films was not greatly affected by variations in growth distance from the plasma.

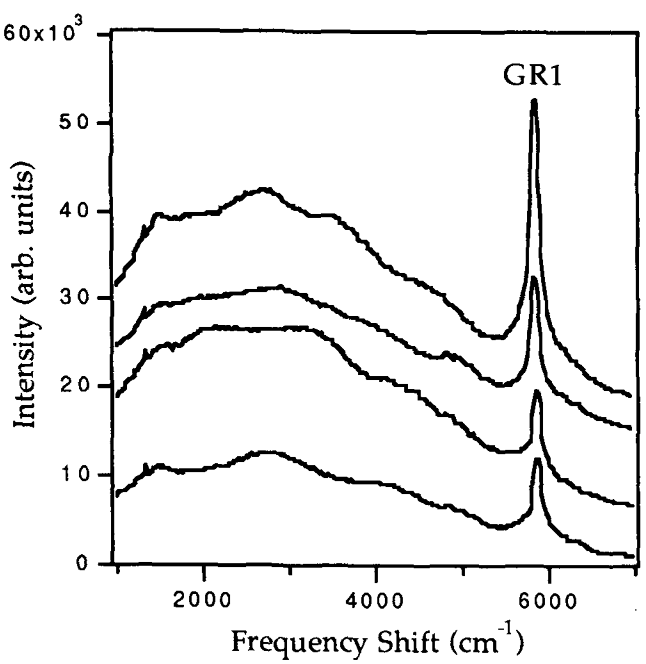

Fig. 6 — Photoluminescence spectra as a function of distance from the plasma showing almost a factor of 2 increase in the ratio of GR1 to diamond-1332 peaks from the film grown at 0.5 cm to that grown at 2.0 cm.

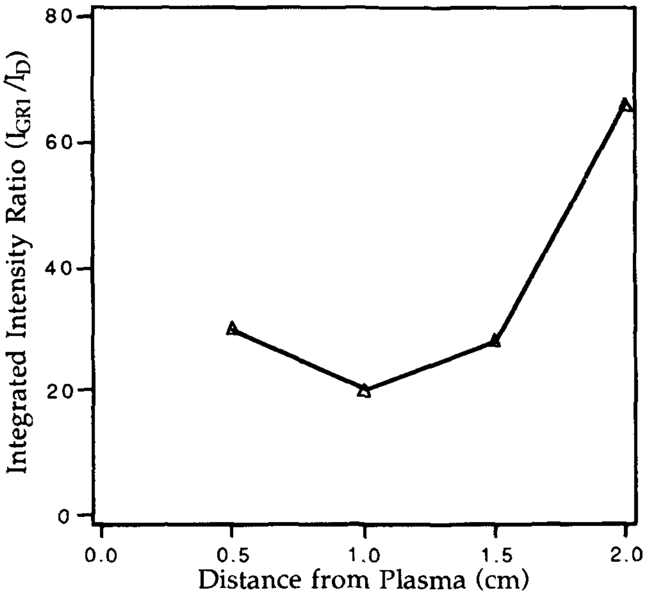

Fig. 7 — Plot of the ratio of the integrated intensity of the GR1 peak to that of the diamond 1332 cm^{-1} as a function of growth distance from the plasma.

tivation energy ranges from close to 0-eV to 0.5-eV. Above this transition temperature, three of the four films behave similarly, with an activation energy of approximately 1.1-eV, with the sample grown at 1.0 cm from the plasma being lower at 0.6-eV. The activation energy for the natural diamond is higher than that of the CVD films at approximately 1.6 eV, which is believed to correspond to either active vacancies or the nitrogen donor level.[15] The transition

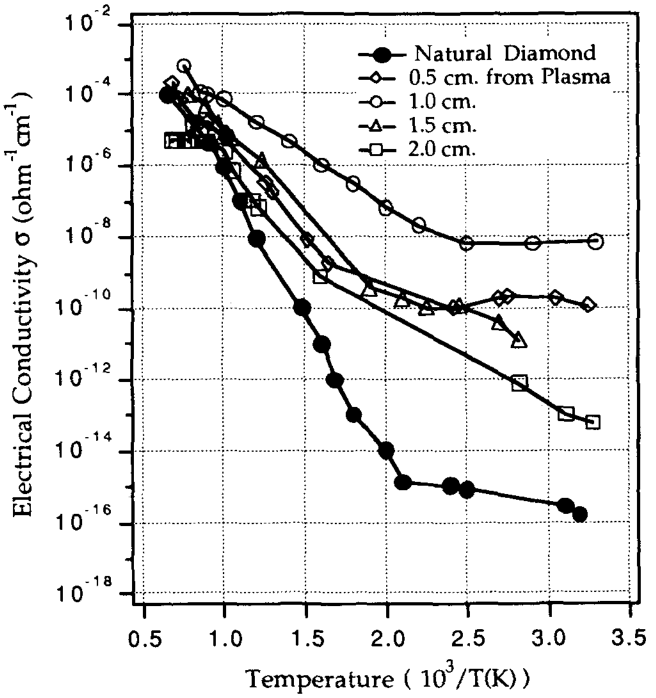

Fig. 8 — Electrical conductivity as a function of temperature for films grown at 0.5, 1.0, 1.5, and 2.0 cm from the plasma as compared to that of natural type IIa diamond.

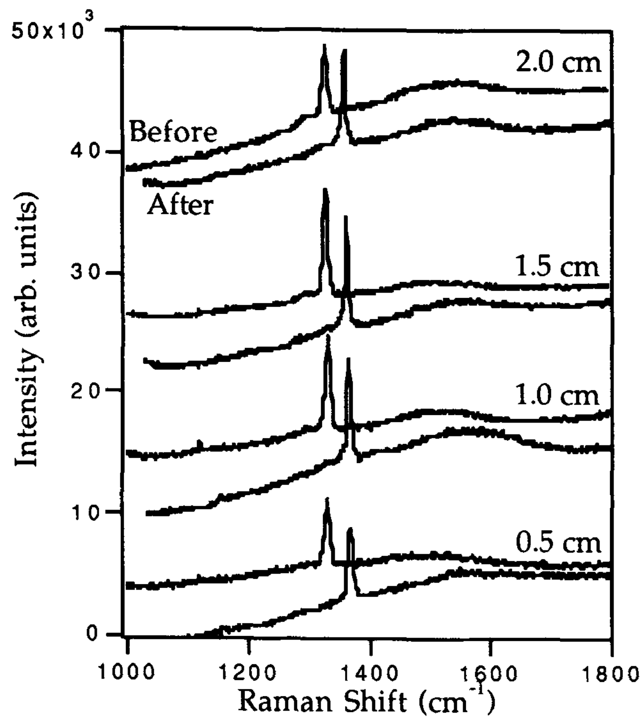

Fig. 9 — Raman Spectra of the samples both before and after (shifted by 40 cm^{-1}) the conductivity measurements show that the bulk quality of the films was not greatly altered by the heating process.

from the lower activation energy below 500 K to the higher energy above is speculated to be a result of the increased out-diffusion of the atomic hydrogen. As the hydrogen leaves the trap sites, carrier transport becomes more difficult, thus leading to a higher activation energy for conduction. Future work will involve thermal desorption studies of the hydrogen in the films and the resulting conductivities upon cooling.

IV. SUMMARY

Films were grown by microwave plasma CVD at distance ranging from 0.5–2.0 cm downstream of the plasma. The Raman spectra and SEM indicated very little observable change in quality or growth morphology as a function of growth distance from the plasma. PL measurements indicated that the density of defects corresponding to the 1.68 eV band increased by only a factor of 2 over the four films studied, while interestingly the low temperature electrical conductivities unexpectedly varied by over 5 orders of magnitude for the same films. It can thus be concluded that the defects associated with the 1.68 eV band did not significantly affect the carrier transport under the present conditions. The 5 order of magnitude variation in conductivity as a function of growth distance from the plasma suggests that hydrogen incorporation into the film may be more difficult at further distances from the plasma. The activation energies for conduction underwent a transition at a temperature of approximately 500 K. The activation energies below this temperature were less than 0.6-eV while those above were closer to that of natural type IIa diamond at approximately 1.1-eV. It was speculated that this transition above 500 K occurs because the hydrogen in the lattice becomes mobile and then no longer occupies the various trap sites. Additional work is needed to confirm this.

ACKNOWLEDGMENTS

This research was financially supported in part by SDIO/IST through ONR and the Kobe Steel, Ltd. Professorship at NCSU.

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