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Hydrogen Passivation of Electrically Active Defects in Diamond

M.I.Landstrass
Crystallume
125 Constitution Drive
Menlo Park, CA.94025

and

K.V.Ravi
Lockheed Palo Alto Research Laboratory
1335 Hanover Street
Palo Alto CA. 94304

Abstract

Subjecting natural diamond single crystals to the action of atomic hydrogen in a hydrogen plasma is shown to result in the passivation of interband states in the crystal resulting in a marked reduction in the resistivity to about 10^5 ohm cm from the expecetd high resistivity of ~ 10^{16} ohm cm. When the hydrogenated crystals are heat treated in a neutral ambient the hydrogen can be expelled form the crystals, restoring the high resistivity. The behavior of natural diamond crystals, with respect to the effects of hydrogen are shown to be sililar to the behavior of diamond thin films synthesized by plasma enhanced CVD techniques.

With the advent of the plasma enhanced CVD technique for the synthesis of diamond films at relatively low pressures (~ 5 to 100 torr) and temperatures (~ 600 - 1000°C) there is increasing interest in the physical properties of these films and their potential utility in a variety of applications. In particular the very attractive electronic properties of diamond (high band gap, high electrical resistivity), coupled with its extremely high thermal conductivity and ruggedness, has potential applications in high temperature, high speed and radiation hard electronics. [1]

Natural diamond has been reported to exhibit electrical resistivities of the order of 10^{16} Ohm cm. We have shown that CVD diamond films display relatively low resistivities, of the order of 10^6 Ohm cm, in the as synthesized condition as a result of hydrogen passivation of deep traps in the films. The resistivity of these films can be increased by

several orders of magnitude by annealing the films in neutral ambients to expell the hydrogen.[2] In the case of CVD diamond films, hydrogen passivation is a natural consequence of the synthesis process since the presence of atomic hydrogen, in the plasma ambient, is a necessary requirement for the promotion of diamond (Sp^3) bonding and the suppression of graphitic (Sp^2) bonding in these films.[3,4]

Natural diamond does not contain any hydrogen. Consequently, if the observed high resistivity of natural diamond is a result of the presence of traps resident deep in the band gap of the material, then hydrogen passivation of these traps should lead to a reduction of the resistivity of the crystals just as in the case of hydrogenated films synthesized by CVD techniques. In this paper we present experimental results which demonstrate that natural diamond crystals can, indeed, be hydrogen passivated and that current conduction in these crystals is strongly influenced by the presence of hydrogen.

Type IIA natural diamond crystals approximately 1 mm square by 0.5 mm thick were electrically probed to determine their resistivity. As a result of the very low conductivity of these crystals and their relative thickness, an accurate measurement of the resistivity was not feasible. The resistivity was estimated to be well in excess of 10^{15} Ohm cm. The crystals were then cleaned in solvents and placed in a DC plasma reactor with two parallel plate electrodes spaced approximately an inch apart. The diamond crystal was placed on the bottom electrode, hydrogen gas admitted into the reactor and a plasma generated by the application of ~ 300V across the electrodes. The reactor was externally heated to a temperature of 400°C. The crystal was subjected to the hydrogen plasma for a period of four hours. To compare the results of hydrogenation of the diamond crystal with a plasma synthesized diamond film, a film synthesized using a microwave excited plasma was also characterized. Both the hydrogenated natural diamond crystal and the plasma synthesized diamond film were metallized with chromium and gold, their I-V characteristics measures and subsequently subjected to heat treatments in a flowing argon atmosphere to expel the hydrogen. The crystal and the film were characterized by measuring their resistivity as a function of processing conditions. The Raman spectra of the films were obtained by the use of a micro Raman set up.

Figure 1 shows Raman spectra of the natural diamond crystal and the CVD diamond film. The Raman peak at 1333 cm^{-1} characteristic of diamond (Sp^3) bonding is evident in both the spectra. Other than an increased level of the background signal, the polycrystalline diamond films do not display any other prominent Raman peaks

which might be attributed to non diamond bonded phases in the material. The increased background signal from the diamond films may be attributed to the polycrystalline nature of the film and perhaps to defects in the films. In all other respects the two spectra indicate the presence on only diamond bonded carbon in the structure.

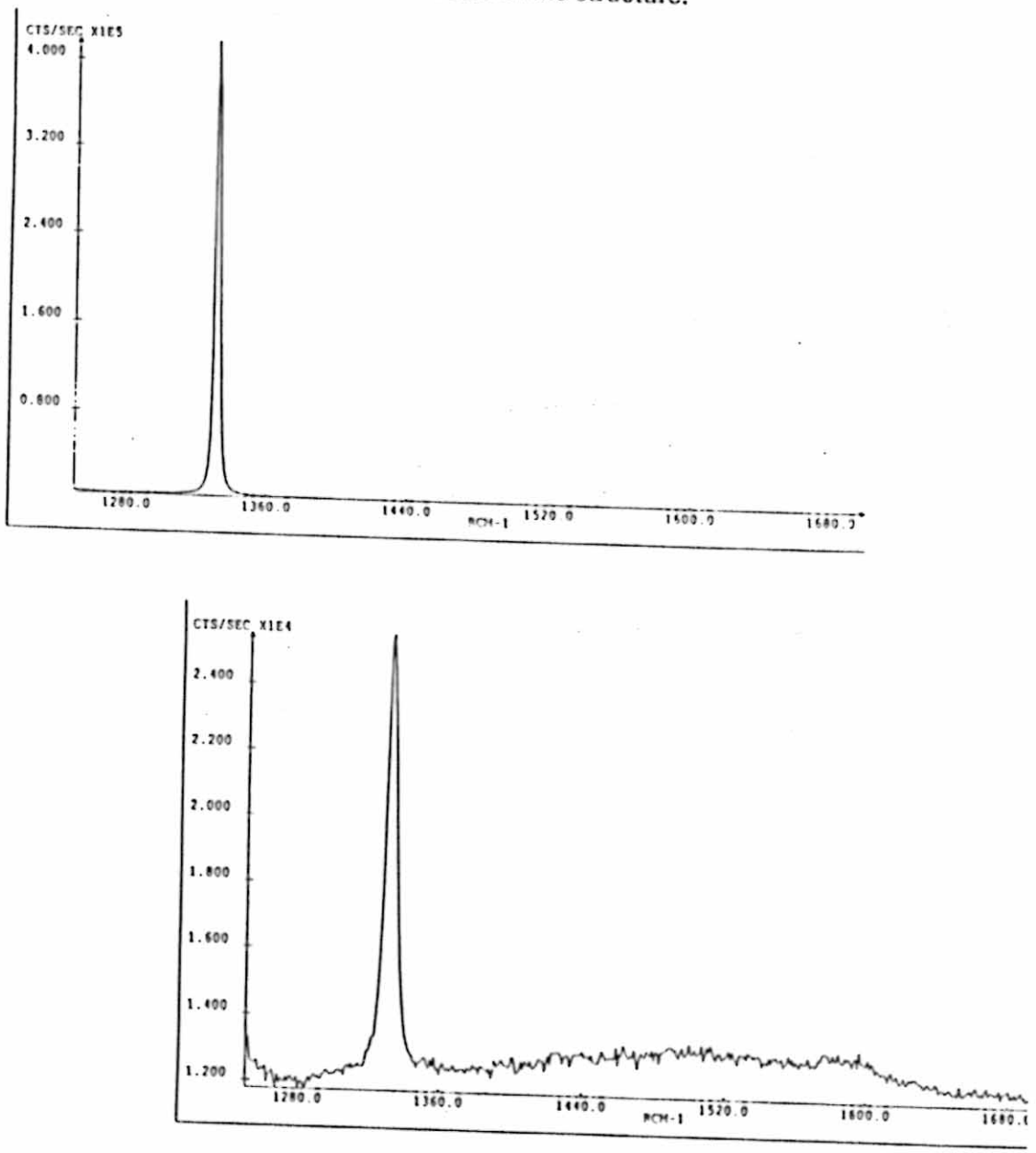

Figure 1. Raman spectra of a natural diamond single crystal (top) and a diamond film synthesized by the use of a microwave enhanced CVD process(bottom).

Figure 2 shows a series of I-V curves obtained from the natural diamond crystal, obtained as a function of processing conditions. Immediately following hydrogenation the

conductivity of the crystal is significantly increased and the I-V curves are ohmic in nature (top curve in figure 2). The resistivity of the crystal following hydrogen passivation has been estimated to be ~ 10^5 ohm cm. Heat treating the hydrogenated crystal in a flowing nitrogen ambient has the effect of enhancing the resistivity of the crystal,with a 780 °C, 2 hour heat treatment resulting in a resistivity of ~ 10^{14} ohm cm with indications of trap limited conduction behavior as evidenced by the two sharply rising current steps at about 5 volts and 35 volts respectively. The annealed films display trap limited behavior with the DC bias synthesized films displaying two steeply rising current steps separated by a small, finite voltage, behavior very similar to that displayed by the natural diamond crystals as shown in figure 2. Figure 3 shows two I-V curves of a diamond film synthesized by the use of a microwave excited plasma. The hydrogenated film has a low resistivity and the I-V behavior is ohmic, behavior very similar to that of hydrogenated natural diamond. Annealing the as synthesized film results in a marked increase in the resistivity attended by non linear I-V curves. The current- voltage behavior suggests the presence of a continuous density of states in the gap as opposed to discrete levels in films synthesized by DC plasmas and in the natural diamond single crystal. The typically higher growth rates of microwave plasma synthesized diamond films may lead to more inhomogeneous films with a wider distribution of defect states in the band gap whereas the slower growth rates of DC plasma synthesized films can lead to structures that are less random, with discrete energy levels in the gap.

The effects of atomic hydrogen in passivating interband states in various semiconductors has been well established. Defect states due to dangling bonds in amorphous silicon, grain boundaries in polycrystalline silicon and interband levels due to impurities have all been shown to be subject to hydrogen passivation [5-7]. For example, introducing high concentrations of gold into silicon results in a marked increase in the resistivity of the silicon [8]. Hydrogenation of the gold doped silicon has been shown to reduce the resistivity as a result of passivation of gold related deep levels.[9-10] In the case of natural diamond crystals and plasma CVD synthesized diamond films we postulate that the resistivity of the hydrogenated crystals and films is governed by shallow acceptor levels, whereas removal of the hydrogen by annealing electrically activates deep donors, pinning the Fermi level and giving rise to the observed high resistivity.

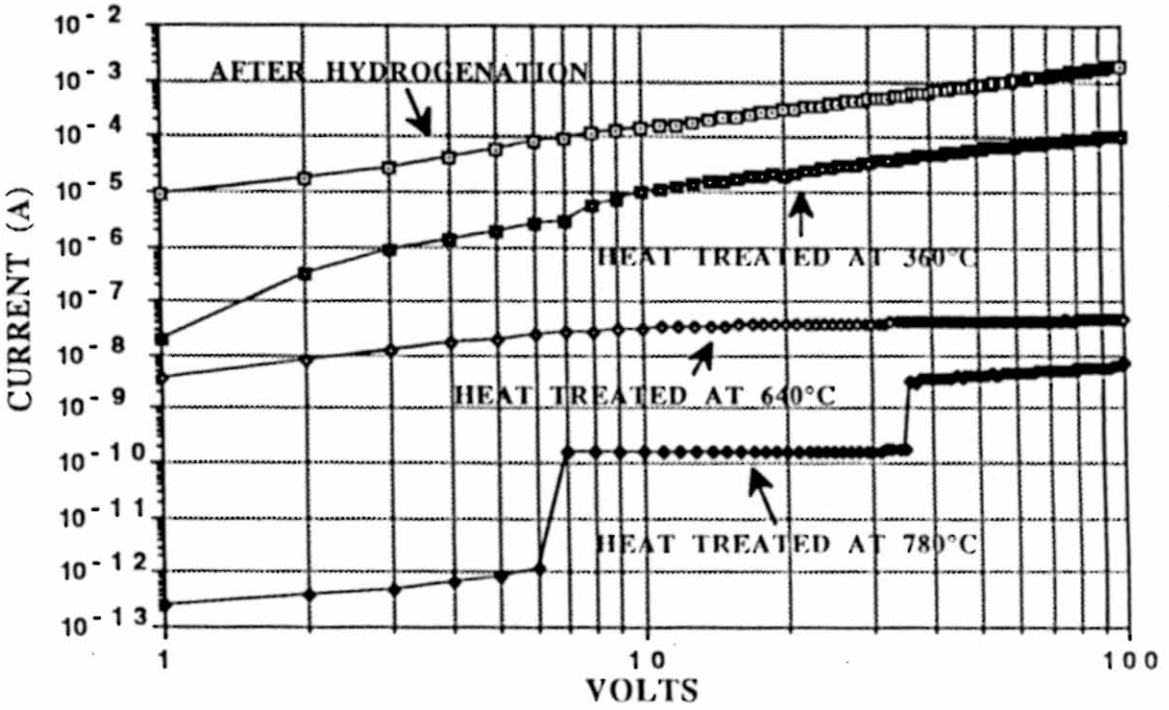

Figure 2. Room temperature current-voltage characteristics of a natural diamond single crystal as a function of hydrogen passivation and thermal treatments. Top curve shows the I-V behavior of the crystal following hydrogenation. Bottom curves show the effects of heat treatment of the hydrogenated crystal on current conduction.

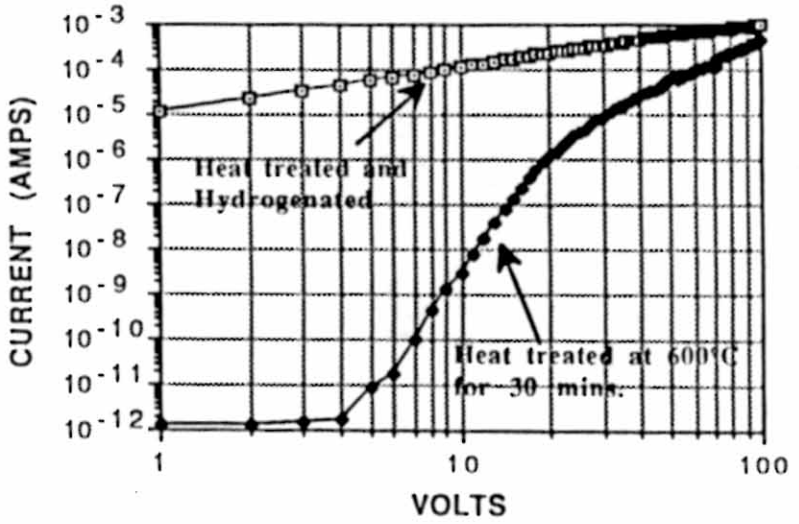

Figure 3. Room temparature I-V curves of a plasma CVD synthesized diamond film in the hydrogenated and in the heat treated condition.

We have shown, for the first time, that current conduction in naturally occurring diamond crystals can be strongly influenced by subjecting the crystals to atomic hydrogen generated in a hydrogen plasma. The hydrogen can be removed from the crystals by annealing at relatively low temperatures, restoring the high resistivity to the diamond crystals. The influence of hydrogen on current conduction is very similar for diamond films synthesized by plasma enhanced CVD techniques.

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