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Comparison of the hole mobility in undoped and boron-doped polycrystalline CVD diamond films

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Abstract The drift mobility of nonequilibrium holes injected in undoped polycrystalline diamond films was determined, by a transit-time technique, as ca. $10^{-3} \text{ cm}^2/(\text{V s})$. This hole mobility is three orders of magnitude lower than the “equilibrium” mobility in boron-doped diamond films [$0.1\text{--}1 \text{ cm}^2/(\text{V s})$], determined from the films’ dc conductivity. This difference is explained by the effect of a nonequilibrium charge carrier trapping during the carrier transport in polycrystalline diamond.

Key words Diamond · Drift mobility · Transit-time technique · Thin films · Trapping

Introduction

Born in 1987 [1], the electrochemistry of synthetic semiconductor diamond has become an important field of modern electrochemistry. On the one hand, boron-doped diamond thin-film electrodes proved to be very efficient in the electroreduction of hard-to-reduce substances (e.g., nitrate and nitrite ions to ammonia) [2] and very stable even in aggressive media like HF [3]. They have a wide potential window of negligible current in the background electrolytes and are thus very suitable for studying the kinetics of electrochemical reactions involving redox couples in solution [4]. Therefore, diamond films are anticipated to be used in the development of corrosion-stable electrodes for electrochemical engineering. On the other hand, electrochemical (in

particular, photoelectrochemical [5, 6] and impedance spectroscopy [7, 8]) techniques would give reliable information on the bulk and surface characteristics of diamond films.

We have shown recently that the electrochemical activity of boron-doped polycrystalline diamond thin-film electrodes correlates with the electrical characteristic of the films’ bulk – their conductivity (more precisely, the concentration of majority carriers, i.e., holes) [9]. In this work we used a combination of electrical (measurements of the kinetics of transient currents induced by the injection of nonequilibrium carriers in the film) and electrochemical techniques (the impedance spectroscopy of a diamond film/electrolyte solution interface), to determine another electrical characteristic of diamond, the hole mobility. A knowledge of the mobility magnitude and nature may be of use in the elucidation of possible effects of the charge carrier transport in diamond bulk and at interfaces on the electrochemical kinetics.

In this context, a distinction needs to be drawn between two kinds of samples: (1) undoped (dielectric) films which only acquire a detectable conductance upon injection of (nonequilibrium) charge carriers; (2) deliberately doped films possessing an appreciable conductance per se.

In what follows, we show that the difference between the two types of films depends on whether the charge carrier concentration is higher or lower than that of the traps in diamond. By convention, we shall refer to the measured mobility in these two cases as that for undoped and boron-doped diamond, respectively.

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Experimental

Samples

Undoped and boron-doped diamond films were chemical vapor deposited (CVD) on polished tungsten substrates from a hot-filament-activated methane + acetone + hydrogen gas mixture (the deposition techniques were described at length earlier [5]). The

majority of films were 2–14 μm thick. In our measurements of the kinetics of transient currents we used undoped films with a specific resistance of 10^9 – 10^{10} Ω cm, whereas in the determination of the films' conductance by the impedance spectroscopy measurements at electrolytic contacts, boron-doped films were used whose specific resistance was of the order of 10^4 Ω cm.

For the sake of comparison, we also performed the mobility measurements with a much thicker film (the no. O-4 free-standing 230 μm -thick film). It was deposited from a microwave-plasma-activated $\text{CH}_4 + \text{H}_2$ gas phase containing 0.5% of O_2 . Also, a synthetic diamond single crystal (no. S-1) grown by a traditional high P -high T techniques was examined. It has a plane-plate shape, approximately $4 \times 3 \times 0.6$ mm in size.

In addition to the electrochemical impedance measurements, the films were spot-checked by taking Raman and IR absorption spectra and by scanning electron microscopy (SEM) techniques. According to the Raman spectra (Fig. 1), the films have good crystallinity, with but a very small content of nondiamond carbon [5]. Indeed, the 1332 cm^{-1} peak is well pronounced, whereas no 1560 cm^{-1} maximum can be seen. In the boron-doped films, the uncompensated boron concentration found by the IR absorption measurements¹ agrees with that derived from Mott-Schottky plots (see below). The SEM studies revealed a faceted surface morphology, with the crystallites' average size of ca. 1 μm .

Samples were 1×1 cm in size. Electrical contact to the substrate was made with a silver-based paste. The area of electrical contact to the film surface (see below) was usually ca. 0.2 cm^2 .

The mobility measurements

Transport of the nonequilibrium charge carriers was studied by a transit-time method (for the principles and instrumentation, see, for example, [10]). We recorded the kinetics of transient currents in a sandwich-type structure "metal/diamond film/metal" (Fig. 2). These transients resulted from a unipolar drift, owing to the applied constant electric field, of the nonequilibrium charge carriers injected into the film. In particular, the tungsten substrate served as a collector electrode, the other (emitter) electrode being an evaporated semitransparent film of gold (for no. O-4 sample, aluminum) on top of diamond.

The nonequilibrium charge carriers used to be generated by light flashes. Unfortunately, the quantum yield of intrinsic charge carrier photogeneration in the CVD diamond films, at a wavelength of the laser light we used (337 nm), appeared to be too low (of the order of 10^{-4} [6]) to efficiently form a sheet of charge carriers in the near-surface region of the diamond samples. Therefore, we added a photoactive film of selenium to the sandwich structure (between the diamond surface and the semitransparent metal film), as a source of photogenerated charge carriers; these carriers were further injected from the selenium layer to the diamond film under study. Selenium was deposited by evaporation in vacuum (at a residual pressure of 8×10^{-5} Torr). Because the thickness of selenium layer (0.2–0.5 μm) was an order of magnitude lower than that of the thinnest diamond film, we neglected its effect on the field strength in diamond. Moreover, since the drift mobility of charge carriers in (vitreous) amorphous Se films is as high as $0.15\text{ cm}^2/(\text{V s})$ [11], the Se layer could not affect the mobility values measured in the dielectric films under study (see Table 1).

Under the action of the electric field applied to the sandwich, the photogenerated electron-hole pairs are separated in the selenium layer. Whether electrons or holes are then injected to the diamond film under study depends on the sign of the applied field. In particular, with the "plus" sign on Au (Al) and "minus" on W, holes were injected into diamond, whereas electrons were transported in the external circuit which contained a load resistor. A signal from the load was fed, via a preamplifier, to the input of a

¹ For the IR light (1282 cm^{-1}) absorption measurements, free-standing diamond films were prepared by depositing diamond onto a Si wafer and subsequently etching-off the substrate

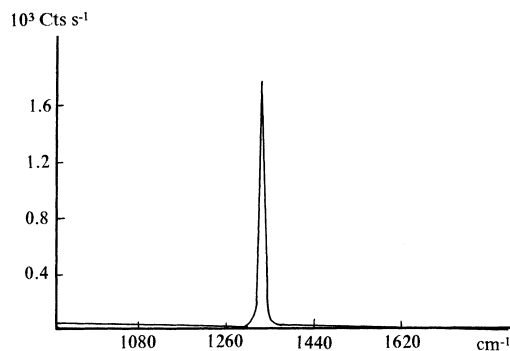


Fig. 1 Raman spectrum for a diamond film. Width of the 1332.4 cm^{-1} peak is 7.4 cm^{-1}

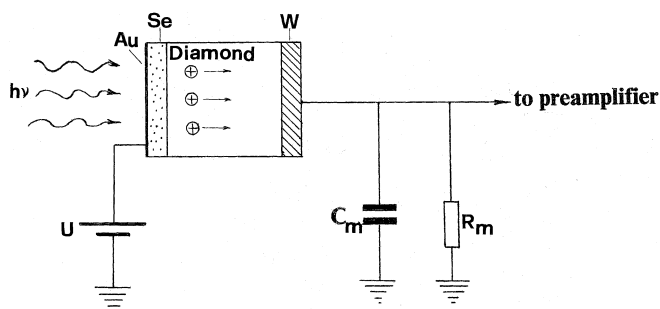


Fig. 2 Scheme of the set-up

measuring oscilloscope (Fig. 2). When the pulse duration t_{imp} is much less than the charge carrier transit time t_T , the problem of analyzing the transient current kinetics is alleviated. Charge carriers are injected into a film as a narrow sheet whose thickness is much less than that of the film. The full charge of injected carriers Q does not distort the electric field in the sample bulk, provided the inequality $Q \ll CU$ holds, where C is the film capacitance and U is the voltage applied to the film.²

To record the current transients, we used a set-up comprising an ILGI-503 nitrogen laser ($t_{\text{imp}} = 10\text{ ns}$ at the half-height of the pulse, wavelength 337.1 nm, power density not exceeding 1 kW/cm^2), a S9-8 storage oscilloscope provided with a Ya40-1102 pre-amplifier, a triggering electric pulse generator G5-54 for synchronizing the laser pulse and the oscilloscope, and a desk computer for the data acquisition and processing (all equipment produced in Russia). The measuring circuit time constant $t_m = R_m C_m$ was much less than t_T .³

All measurements were carried out at room temperature.

Results

A typical transient current curve in an undoped film is shown in Fig. 3. The curve comprises an initial decay section (A) related to the discharge of the measuring

² The total charge injected into the samples was less than 0.05 CU . In other words, the measurements were carried out at a small current. For example, for no. 475 sample, $C = 68\text{ pF}$ and U varied in the range of 30–100 V, whereas the injected charge was as small as 10^{-11} C (see below)

³ In particular, C_m was ca. 200 pF and R_m varied from 50 Ω to 10 k Ω ; thus, t_m did not exceed 10^{-5} s (compare the figures below)

Table 1 Values of the hole mobility and parameters used in the calculations

No. of sample	d (μm)	F (V/cm)	t_T (ms)	μ , in dielectric diamond, [$\text{cm}^2/(\text{V s})$]	σ (S/cm)	N_A (cm^{-3})	μ , in boron-doped diamond, [$\text{cm}^2/(\text{V s})$]
<i>Single crystal</i>							
Natural [13]							2100
Synthetic, S-1	640	6.3×10^3 3.15×10^3	1.4 3.0	7.3×10^{-3} 6.8×10^{-3}			
<i>Single crystal film</i>							
2 m [18]	10				0.6	2×10^{18}	800
<i>Polycrystalline films</i>							
475	26	1.4×10^4 1.9×10^4	0.3 0.16	6.2×10^{-4} 8.4×10^{-4}	7×10^{-10}		
508	8	0.75×10^4	0.055	19×10^{-4}	3×10^{-10}		
354	10	0.09×10^4	1.1	10×10^{-4}			
O-4	230	2.2×10^4	0.45	20×10^{-4}			
306	10				0.9×10^{-4}	5×10^{17}	1
559	6				0.5×10^{-4}	3×10^{18}	0.1
419	2.5				0.6×10^{-4}	0.6×10^{17}	6
420	2.3				1.2×10^{-4}	10^{17}	7
<i>a-C:H film</i>							
228 [14]	0.1	9×10^{-4}	4	3×10^{-8}			

circuit (possessing the time constant t_m) and the partial recombination of photogenerated electron-hole pairs in the Se layer; a plateau (B) followed by a relatively fast drop in the current (C); and a residual current section (D). The time t_T which is shown by an arrow in Fig. 3 marks the end of the constant current section B. It corresponds to the instant the leading front of the sheet of injected charge carriers arrives at the collecting electrode, thus covering distance d , the film thickness.

We calculated the drift mobility μ of nonequilibrium charge carriers by the formula

$$\mu = d/Ft_T \quad (1)$$

where $F = U/d$ is the electric field strength. The mobility values for undoped samples thus obtained are given in Table 1 (5th column), together with some characteristics of the samples under study.

The hole mobility in boron-doped films was calculated by the formula

$$\mu = \sigma/ep \quad (2)$$

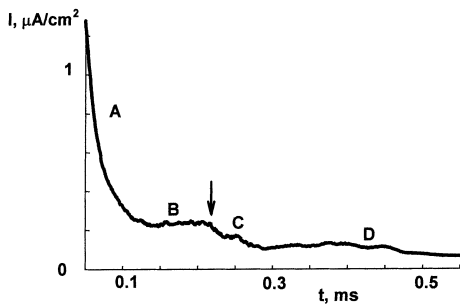


Fig. 3 Current transient upon the injection of electrons into an undoped diamond film. Sample no. 475. Electrical field $F = 1.4 \times 10^4$ V/cm. Arrow shows the transit time t_T

Here σ is the specific conductance of diamond, e is the electron charge, and p is the bulk concentration of the majority carriers (that is, holes in boron-doped diamond, a p-type semiconductor). The latter quantity was calculated as:

$$p = (N_A N_V / 2)^{0.5} \exp(-E_A / 2kT) \quad (3)$$

where N_A is the acceptor concentration, $N_V \cong 2 \times 10^{19} \text{ cm}^{-3}$ is the density-of-states for the valence band, and $E_A = 0.37 \text{ eV}$ is the acceptor (boron) ionization energy. Equation 3 holds true for a semiconductor containing a single dopant (an acceptor). In fact, diamond generally contains an admixture of nitrogen, a deep-lying donor; in other words, it is partly compensated. However, when the donor concentration N_D is less than both N_A and p , Eq. 3 is a reasonable approximation (thus giving actually the concentration of uncompensated acceptors in the sample, $N_A - N_D$). When this is not the case, the actual hole concentration appears less than that calculated by Eq. 1; therefore, the calculated “equilibrium” mobility given in Table 1 (8th column) is but the lower limit. The magnitudes of σ and N_A , which are also given in the table, had been previously determined [6, 7]. In the cited works, we obtained the films’ resistivity by extrapolating complex-plane plots of the impedance spectra, taken at diamond/electrolyte junctions, to an infinitely high frequency, whereas the uncompensated acceptor concentration was found from the slope of Mott-Schottky plots constructed for the same junctions.

Shown in Fig. 4 is a transient current curve for the case of hole injection in the same film as in Fig. 3. Note that both the shape of curve and the transit time (hence, the calculated mobility value) are similar to those for the electron injection curve (Fig. 3).

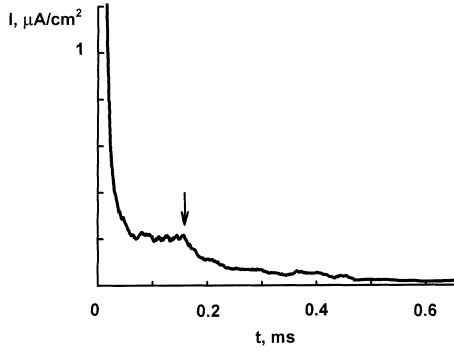


Fig. 4 Current transient upon the injection of holes into an undoped diamond film. Sample no. 475. Electrical field $F = 1.9 \times 10^4$ V/cm. Arrow shows the transit time t_T

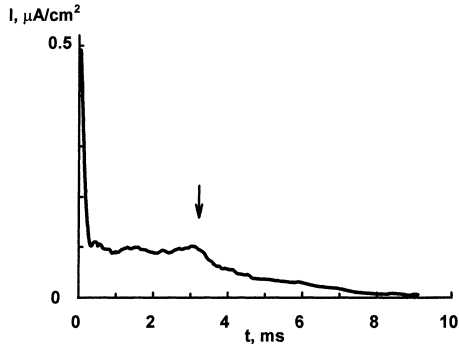


Fig. 5 Current transient upon the injection of electrons into undoped synthetic single crystal diamond. Sample no. S-1. Electrical field $F = 6.3 \times 10^3$ V/cm. Arrow shows the transit time t_T

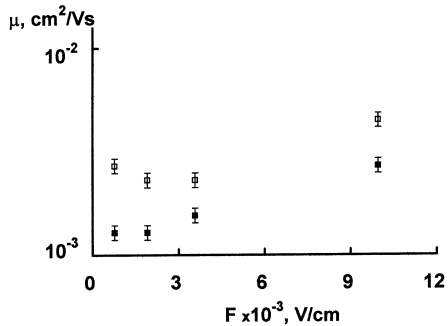


Fig. 6 Field dependence of the electron (□) and hole (■) mobility in undoped diamond. Sample no. 354

Figure 5 relates to the single-crystal diamond. Except for a longer transit time (due to the much higher sample thickness), it resembles the curves of Figs. 3 and 4. Again, the electron and hole mobilities appeared to be of the same order of magnitude for this sample: 3.8×10^{-3} and 7.0×10^{-3} $\text{cm}^2/(\text{V s})$, respectively.

The field dependence of the mobility, if any, remains low, as can be seen from Fig. 6, at least in the field range studied (i.e., 10^3 – 10^4 V/cm); we did not further investigate this dependence.

Discussion

The transient current curves (Figs. 3–5) have a pronounced constant current section. For this reason alone we conclude that the transport of a sheet of injected charge carriers in the diamond samples under study is a nondispersive drift. That the duration of the current decay section C is much smaller than that of the constant current section B (i.e., t_T) shows the negligibly small thickness of the injected sheet, as compared to the film thickness d . We estimated the diffusional broadening of the sheet during its transit across the film (that is, by the time t_T) using the formula $L = (Dt_T)^{1/2}$, where the diffusion coefficient D is linked to the mobility μ by the Einstein formula: $D = \mu kT/e$. Using the magnitudes of t_T and μ found in this work, we obtained $L \cong 10^{-4}$ cm, which is an order of magnitude less than d .

By integrating the transient current curve of Fig. 3 for t going from $t = 0$ to t_T , we found the injected hole charge: $Q \cong 1.5 \times 10^{-11}$ C. Then, allowing for the illuminated area of 0.21 cm^2 and the above-given sheet thickness L , we estimated the total injected hole concentration in the sheet at $5 \times 10^{12} \text{ cm}^{-3}$. (What part of the initially injected holes has been readily trapped or recombined, e.g., at the diamond/selenium interface, and thus eliminated from the transport process, is unknown. However, the interface recombination can affect but the amplitude of the measured signal, and not its characteristic time. Moreover, the contacts cannot have any significant impact on the propagation of the injected charge carriers, owing to the relatively large sample thickness.) This nonequilibrium free hole concentration in the immediate vicinity of the emitter appears to be an order of magnitude higher than the equilibrium (“dark”) hole concentration in the dielectric diamond films.

When the hole sheet reaches the collector, the holes recombine with electrons supplied from the external circuit. A further permanent flow of current, that was at all detectable, becomes impossible because practically no free charge carriers are present in the undoped diamond. The small residual current (section D of the curve, Fig. 3) is likely to be caused by arrival at the collector of holes being captured in the bulk of the diamond by traps (whose characteristic time exceeds t_T) and then released. It is notable that, owing to the unipolar nature of the induced current in diamond under the conditions of the described experiments (unlike, e.g., the case of photo-generation of electron-hole pairs in the photoconductivity techniques), the injected charge carriers are not subject to recombination, although the lifetime of electron-hole pairs in diamond films can be as low as 150 ns [12]; no carrier of other sign is present in the sample.⁴ However, the nonequilibrium charge carriers can be trapped. When the detrapping time is much higher than the transit time t_T for the main body of injected charge carriers, the trapping

⁴ The opposite sign carriers are accumulated in the collector electrode, thus keeping the sample on the whole electroneutral

does not affect the measured value of the mobility, although the magnitude of the measured signal decreases. When, however, the carriers undergo repeated trapping and releasing during their drift across the film, the effective mobility decreases.

The measured mobility in polycrystalline diamond (both undoped and boron-doped) appears to be much lower than the drift mobility reported for electrons and holes in the natural single-crystal diamond (2500 and 2100 cm²/(V s), respectively [13]). This is no surprise, since the intercrystallite boundaries and other crystal structure defects pose great difficulties for the transport of charge carriers. This is corroborated by a very low mobility value in the amorphous diamond-like carbon films recently measured by us [14]; a-C : H may be considered as a model of the highly disordered intercrystallite boundary material (see, e.g., [15]).

In this context, a rather low mobility value obtained for a single-crystal sample is surprising. In all probability, the HPHT synthetic crystal still contains a high concentration of lattice defects which deteriorate the charge carrier transport.

Note that in the polycrystalline diamond films with the boron concentration ranging from 10¹⁶ to 10²⁰ cm⁻³, that is, not too far different from those studied in this work, the Hall mobility was found as 1–10 cm²/(V s) [16, 17], which practically falls in the range of the “equilibrium” mobility values found in this work. At the same time, for some “high-quality films”, values as high as 4000 cm²/(V s), i.e., no lower than in single-crystal diamond, were reported [12]. In a recent study [18], we also obtained a rather high – 800 cm²/(V s) – mobility in single-crystal boron-doped epitaxial films grown on dielectric single-crystal diamond substrates (see Table 1).

Comparing the data of 5th and 8th columns of Table 1, we conclude that, with due reservation for the data scattering owing to some undetectable differences in the film preparation, the hole mobility in boron-doped (fairly conductive) films is by a factor of 10³ higher than that in undoped (dielectric) diamond. This difference is attributable to the difference in mechanism of charge carrier transport in these two kinds of films under the experimental conditions described.

We shall discuss the observed difference within the frame-work of the concept of charge carrier transport in trap-containing matter.⁵ Thus, we assume that crystal lattice defects act as traps for charge carriers in polycrystalline diamond. When no traps are present, for example, in defectless natural single-crystal diamond, the charge carrier transport can be characterized by a value of microscopic mobility μ_0 , that is, the velocity of charge carrier motion in an electric field, related to unit field strength [10]. Because the emptying of traps is an

activation process, for the mobility in a defect-containing material we can write:

$$\mu \cong \mu_0 \exp(-E_t/kT), \quad (4)$$

where E_t is the trap ionization energy, that is, the depth of the trap level relative to the level of conductance characterized by the microscopic mobility.

When measuring the mobility in dielectric samples which initially are practically free of charge carriers, the injected (nonequilibrium) charge carriers first become trapped because the traps were initially empty; thus, the above-described current transients involve charge carriers which undergo trapping and further releasing by the traps. (Note that the practically nondispersive character of the transport may indicate that the traps are distributed over a limited range of energy.) This mechanism is prevailing in the undoped diamond and is characterized by relatively low mobility values.

In moderately or heavily doped films, on the contrary, traps initially are entirely filled with holes; therefore, only free holes are involved in the current flow. This second conductance mechanism thus describes free hole transport in the valence band with much higher mobility. However, it can be realized only when the equilibrium hole concentration is sufficiently large, as compared with the trap concentration, that is, in diamond films with sufficiently high doping levels.

We mention once more that the mobility of equilibrium and injected (“nonequilibrium”) charge carriers has been measured with different samples: the former with reasonably conductive (boron-doped) diamond films, and the latter with insulating (undoped) ones. These conditions were imposed by the essential features of the methods used, namely: the transit-time experiments require samples with negligibly small initial conductance, which makes it possible to record the current transients at a high signal-to-noise ratio. On the other hand, Mott-Schottky plots can be obtained with fairly conductive films only, whose thickness d thus remains much larger than the space-charge region width. (The latter varies significantly, depending on the potential applied to the diamond/electrolyte solution junction.) Whether or not the admixture of boron directly affects the charge carrier mobility in diamond remains unclear.

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⁵ Among others, nitrogen interstitial atoms, nitrogen-vacancy complexes, and silicon impurities are believed to form defects in the dielectric CVD diamond films; in addition, boron-involving lattice defects can be traps in boron-doped films. Their characteristics were investigated, for example, in [19]

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