$1/f$ noise in semiconducting and just-metallic boron-implanted diamond

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$1/f$ noise and conductivity measurements have been made on boron-doped polycrystalline CVD diamond and boron-ion implanted single crystal (type IIa) diamond surface layers over the temperature range 200–430 K. The measured noise spectral densities follow a $1/f^{\gamma}$ frequency dependence, with the exponent γ close to unity. For all three samples the measured Hooge parameter is much larger than for metals. The ion-implanted surface layers are close to the metal-insulator transition and the noise magnitude is suppressed as the boron concentration approaches the critical concentration. For the temperature range covered, hopping conduction plays an important role in determining the noise power in insulating diamond containing a sufficiently high concentration ($>10^{18}$ cm^{-3}) of boron ions.

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The special properties of diamond have made it a desirable material for producing semiconducting devices. Reviews of developments in this area summarize the progress that has been made.[1,2]

Use of boron-ion implantation methods has demonstrated[3] that it is possible to explore the metal-insulator (MI) transition region in boron-doped diamond. Low-temperature conductivity measurements have revealed hopping conduction, involving boron acceptor centers, on the insulating side of the transition, with a change to metallic behavior occurring[3] at a critical boron concentration $n_C \approx 4.0 \times 10^{21}$ cm^{-3}.

This paper is concerned with low-frequency noise measurements made on boron-ion-implanted diamond both on the insulating side and the just-metallic side of the transition. For comparison purposes, measurements have also been made on semiconducting CVD diamond doped with boron. Diamond is a wide band-gap material (5.4 eV) and the boron acceptor levels lie 0.37 eV above the valence band. At ambient temperatures, a relatively small number of holes are present in the valence band.

Reviews of low-frequency $1/f$ noise phenomena and their occurrence in metals and semiconductors have been given by Dutta and Horn[4] and Weissman.[5] Recently, $1/f$ noise has been used to investigate charge dynamics in nonmetallic Ge:Ga (Ref. 6) and Si:B,[7] where hopping conduction is important at low temperatures.

We report on the measurements of $1/f$ noise in the diamond samples mentioned above as a function of temperature from 200 to 430 K over the frequency range 1–1000 Hz. The surfaces of two cut and polished high purity single crystal natural type IIa diamond samples, referred to as samples A and B, have been heavily implanted with boron atoms at liquid nitrogen temperatures, followed by annealing at temperatures up to 2000 K. This implantation-annealing scheme, known as cold-implantation rapid annealing (CIRA), has been developed by Prins,[8] and is highly reproducible. The concentrations of the implanted boron atoms have been measured as 0.6×10^{21} cm^{-3}$(n/n_C \sim 0.15)$ and 4.1×10^{21} cm^{-3}$(n/n_C \sim 1.03)$ for the samples A and B, respectively, using secondary ion mass spectroscopy (SIMS). The boron atoms are distributed in a reasonably uniform way in a layer 0.2-μm thick. Following the high-temperature annealing process, it is likely that most of the boron ions occupy substitutional acceptor sites in the diamond lattice.[3] The concentrations of vacancy and interstitial defects, that are produced in the implantation process, are greatly reduced by annealing.

A semiconducting free-standing CVD diamond film, referred to henceforth as sample C, was grown by means of a microwave plasma-enhanced process using a commercial reactor (Astex Inc., 5 kW–2.54 GHz) on a water-cooled polished tungsten plate. Boron atoms were doped *in situ*, using a flow of diborane during the CVD process. The boron dopant concentration is estimated as 10^{18} cm^{-3} with an uncertainty of 25%.

The resistance and $1/f$ noise were measured using standard dc four-point probe techniques. The electrodes were vacuum-deposited gold strips on the samples, to which leads were bonded by means of silver paint. The samples were then mounted on a variable temperature insert that was operated in a shielded chamber. Sample temperature was monitored using a shielded thermocouple and controlled by a heater, mounted on the same copper block as the samples and operated by batteries. Twelve 9 V alkaline batteries in series with a variable wire-wound buffer resistor formed the dc power supply for the resistance and noise measurements. The resistance of the buffer resistor was kept at least ten times larger than the sample resistance during measurement to minimize the effect of contact noise. The magnitude of the dc current through the sample being measured was the same for both the resistance and $1/f$ noise measurements in order to produce consistent results. The voltage drop across the sample was ac coupled to a preamplifier (SAR SR560) running on its rechargeable internal batteries. The amplified voltage signal was then transmitted to an HP3562A signal analyzer, which performed the fast Fourier transforms and which was set up to take the average of 10 sweeps. All the circuits, except the signal analyzer, were placed in a metal

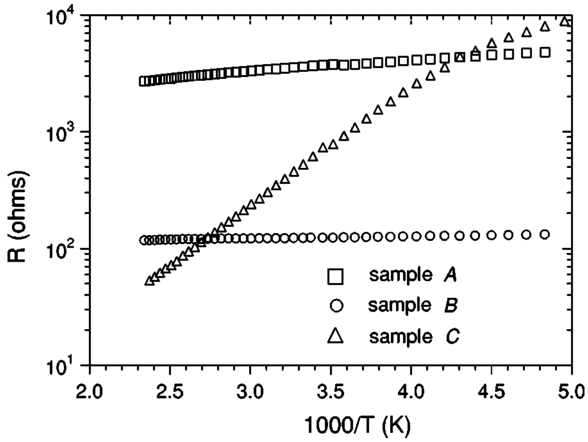

FIG. 1. Resistance versus $1000/T(200\text{ K} \leqslant T \leqslant 430\text{ K})$, for three boron-doped diamond samples. Sample $A(0.6\times10^{21}\text{ cm}^{-3})$, and sample $B(4.1\times10^{21}\text{ cm}^{-3})$ are boron-implanted single crystals. Sample $C(\sim1\times10^{18}\text{ cm}^{-3})$ is boron-doped polycrystalline CVD diamond.

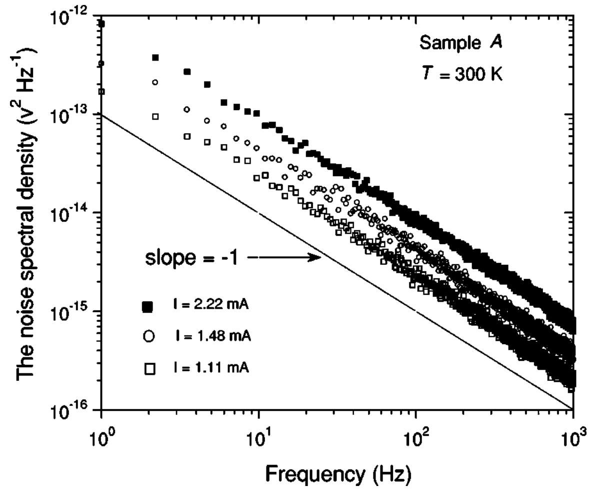

FIG. 2. The $1/f$ noise spectral density as a function of frequency and dc current for boron-implanted diamond sample A at room temperature.

box for shielding. The noise from the batteries was examined by measuring the noise generated by a wire-wound resistor, which replaced the sample in the circuit and had approximately the same resistance as a sample at room temperature. The background noise (the sample thermal noise plus preamplifier noise), which superposed on the $1/f$ noise spectrum, was negligible since it was found that it was three orders of magnitude less than the smallest $1/f$ noise level measured in this study. In addition to using the four-probe electrode configuration, the contact noise contribution to the measured $1/f$ noise was further checked using a method proposed by Leemann *et al.*[9] Both the voltage of the dc source and the resistance of the buffer resistor were decreased to half their previous values so that the voltage drop across the sample was the same, but the ratio of buffer resistance to sample resistance was halved. No change in the slope and in the magnitude of the noise power spectrum was observed.

Figure 1 shows the resistance R versus $1000/T$ for samples A,B, and C in the temperature range 200–430 K. The lead connections were the same as those used in the $1/f$ noise measurements. The resistance of sample C increases with decreasing temperature, with the mean thermal activation energy ε_a calculated to be 0.21 eV for $T>300$ K. This value of ε_a is smaller than the accepted value of $\varepsilon_a = 0.37$ eV for boron-doped diamonds because the upper temperature limit reached in our measurements is not high enough for thermal activation of charge carriers to dominate in electrical conductivity. Below 220 K, the resistance data of C show a more gradual increase down to 200 K, deviating from the thermally activated carrier conduction towards Mott hopping conduction[10,11] described by $\sigma=\sigma_0\exp[-(T_0/T)^{1/4}]$. The resistance variation of sample A with T is consistent with Mott hopping over the entire temperature range covered in these experiments. Efros-Shklovskii (ES) hopping behavior is observed at temperatures below 100 K.[3]

Sample B appears to be very close to the metal-insulator (MI) transition as its resistance variation with temperature is approximately flat. Low-temperature measurements have confirmed that $n\approx n_C$.[3] At $T=200$ K the electrical conductivities for the three samples are $\sigma_A=4.2\ (\Omega\text{ cm})^{-1}$, $\sigma_B=5.7\times10^2\ (\Omega\text{ cm})^{-1}$, and $\sigma_C=1.5\times10^{-2}\ (\Omega\text{ cm})^{-1}$.

$1/f$ noise due to resistance fluctuations may be described using the Hooge empirical expression[12]

$$S_v = \frac{\alpha V^2}{N f^{\gamma}}, \tag{1}$$

where V is the average dc voltage drop across the sample, N is the total number of charge carriers in a homogeneous sample, α is a dimensionless parameter, for $\gamma=1$, and f is the frequency. For metallic systems, the Hooge parameter is $\alpha \sim 2\times10^{-3}$.

The V^2 dependence of $1/f$ noise in our samples was verified for dc currents in a range 1–10 mA by fixing the buffer resistance and varying the voltage of the dc power source at three temperatures 200, 300, and 400 K. These results, after interpolation to other temperatures, have shown that the noise measured is due to resistance fluctuations. Figure 2 shows the frequency $(1\text{ Hz}<f<10^3\text{ Hz})$ and dc current magnitude dependence of the measured $1/f$ noise on a log-log scale for sample A at room temperature. The spectral slope is obtained by fitting a linear relation in a $\log S_v$ vs $\log f$ plot.

In Fig. 3, we have plotted the normalized noise power against temperature at a fixed frequency of 9.7 Hz. In this plot, the normalized noise power magnitudes for A and C have a very similar temperature dependence: a decreasing trend with the variation less than one order of magnitude $(200\text{ K}\leqslant T\leqslant 430\text{ K})$. Below 270 K, the noise power decreases with decreasing T. These data may be compared with the resistance data sets shown in Fig. 1, where the resistances of A and C decrease with increasing T, with a total variation of about three orders of magnitude for sample C and less than half an order of magnitude for A. A much weaker temperature dependence of $1/f$ noise than that of resistance has been observed in conventional metals and narrow bandgap semiconductors.[5,6] Kosub[13] has shown that for a percolation

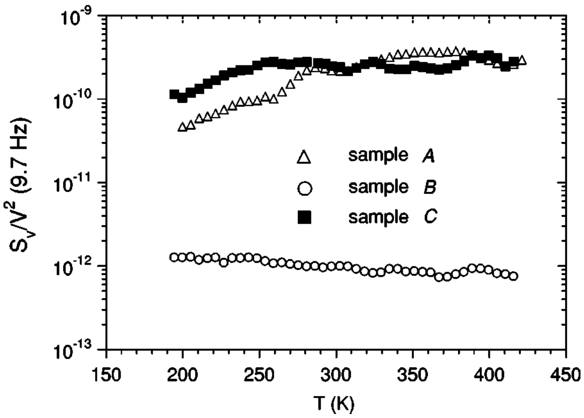

FIG. 3. The normalized noise power at 9.7 Hz as a function of temperature (200 K $\leqslant T \leqslant$ 430 K) for the three diamond samples. Insulating samples *A* and *C*, in which hopping conduction processes are important, show similar behavior with *T* while the just-metallic sample *B* shows quite different behavior.

network model nearest-neighbor hopping leads to *T*-independent noise power and, with certain assumptions, Mott and ES variable range hopping give inverse temperature dependences. The present results for sample *A* shown in Fig. 3 show a gradual decrease in noise power with decreasing *T* rather than an increase contrary to the percolation network predictions. While hopping conduction fluctuations appear to play an important role in the observed behavior for insulating samples *A* and *C* the just-metallic sample *B* shows quite different properties. The noise power is smaller by roughly two orders of magnitude with little temperature dependence over the range shown.

The Hooge α parameter in Eq. (1) has been customarily used to compare the $1/f$ noise level in different materials. We have estimated the values of α for *A* and *B*, based on the boron concentrations obtained from the SIMS profile, following the approach of Cohen *et al.*[14] If we assume that, following annealing, all boron centers are substitutional and that the factor *N* in Eq. (1) is equal to the boron concentration in these two samples, we calculate $\alpha_A = 1\times10^7$ and $\alpha_B = 2\times10^4$ at room temperature. For *C*, the number of activated boron centers in this sample is estimated as 1×10^{18} cm^{-3} and this gives $\alpha_C \approx 1\times10^5$. These three values of α are much larger than the α values for typical metals and semiconductors but are consistent with the observations made on disordered systems by Cohen *et al.*[14] who showed that α decreases as the *MI* transition is approached.

In Fig. 4, we have plotted γ against temperature for sample *A*. Our γ values lie in the range 0.95–1.27 for *A*. Similar results are obtained for *B* and *C*. γ values in this range, typical for $1/f$ noise, have been reported by a number of authors.[4,5,7]

One of the most plausible kinetic models for $1/f$ noise, the thermally activated fluctuator model that incorporates the

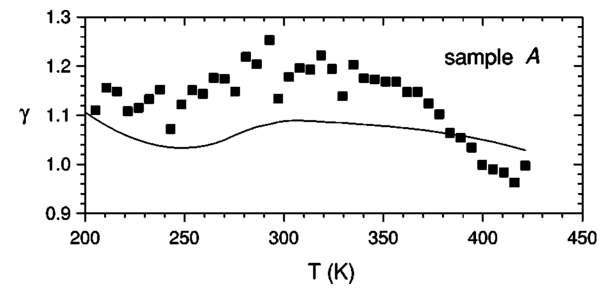

FIG. 4. The $1/f$ noise spectral slopes γ vs temperature (200 K $\leqslant T \leqslant$ 430 K) for boron-implanted diamond sample *A*. The solid curve is the prediction of the DDH model (Ref. 15) given in Eq. (2).

temperature of the system, has been presented by Dutta, Dimon, and Horn (DDH).[15] They obtain

$$\gamma = 1 + \left[1 - \left(\frac{\partial \ln S_v(f,T)}{V^2\, \partial \ln T}\right)\right]\ln\left(\frac{f_0}{f}\right) \qquad (2)$$

depending on the nature of the fluctuation center. We have assumed $f_0 \sim 10^{12}$ Hz. In this model a uniform distribution of activation energies leads to $\gamma=1$.

In using Eq. (2), the experimental data shown in Fig. 2 are replotted on a natural log scale and then fitted by using cubic splines, which give the necessary smooth numerical derivatives. The full curve in Fig. 4 was obtained in this way in good agreement with the γ values obtained for *A* over the temperature range. Similar results were obtained for *B* and *C*. The γ values show a decreasing trend for $T > 280$ K. This may be linked to a change from interacting to noninteracting hopping behavior[7] in the case of sample *A*. The change from Mott to ES hopping occurs at around 100 K for this dopant concentration. The source of the decreasing trend for samples *B* and *C* is not clear.

In conclusion, we have measured the $1/f$ noise as a function of temperature in a CVD semiconducting diamond sample and in surface layers of two boron-ion-implanted single crystal type II*a* diamond samples. For all three specimens, the measured noise spectral density follows a $1/f$ frequency dependence in the temperature range 200–430 K. The noise level in the diamond sample that is close to the metal-insulator transition is lower than for the other samples and is almost temperature-independent. The $1/f$ noise levels observed in a CVD polycrystalline diamond sample and in the insulating boron-ion implanted sample appear to be primarily linked to hopping conduction processes.

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