Superconductivity and low temperature electrical transport in B-doped CVD nanocrystalline diamond

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Abstract

In this work, we report on superconductivity (SC) found in thin B-doped nanocrystalline diamond films, prepared by the PE-CVD technique. The thickness of the films varies from about 100 to 400 nm, the films are grown on low-alkaline glass at substrate temperatures of about 500–700 °C. The SIMS measurements show that films can be heavily doped with boron in concentrations in the range of $3 \times 10^{21}$ cm\textsuperscript{-3}. The Raman spectra show Fano resonances, confirming the substitutional B-incorporation. The low temperature magnetotransport measurements reveal a positive magnetoresistance. The SC transition is observed at about $T_c = 1.66$ K. A simple theory exploiting the concept of weak localization accounting for this transition is proposed.

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1. Introduction

Recent interests in diamond superconductivity (SC) [1,2] and the still unresolved SC mechanism [2–6] brought interests for studying diamond films prepared by the CVD method, with a promising rise of critical temperatures for the superconductive transition $T_c$ above 10 K. Interestingly, in all heavily B-doped diamond films showing the SC transitions, the temperature dependence of conductivity is observed, different from that one would expect for ordinary SC metals. Local disorder induced by boron doping and/or limited grain sizes are therefore of interest for further studies of the transport mechanism in B-doped diamond. Besides the observation of SC in single crystal diamond layers, the SC has also been found also in predominantly (1 1 1) oriented polycrystalline diamond films [6]. A further reduction in grain sizes, towards e.g. so called nanocrystalline CVD diamond [7] leads to a transition to more disordered systems including also an increased proportion of the grain boundary conduction [8,9]. Due to their inherent disordered character, these systems are however interesting for studying the SC mechanism. This was the main motivation of our work, presented at the first SC meeting in Tsukuba. As we show below, indeed, a heavy boron doping of B-NCD leads to an SC transition at about 1.66 K for films with carrier concentrations of about of $1.7 \times 10^{21}$ cm\textsuperscript{-3}, as determined by the Hall measurement. The magnetoresistance (MR) measurements made on such films show a positive MR, characteristic for a localization of the electron-wave function onto a boron atom, and suggesting a transport in B-dopant impurity band [3].

2. Growth and experimental set-ups

A typical morphology of films deposited onto Corning glass substrate is shown in Fig. 1. Boron-doped nanocrystalline diamond films (B-NCD) were prepared in a home made microwave plasma-enhanced chemical vapour deposition (PE-CVD) apparatus at CEA in Paris, enabling application of high microwave powers (typically 2 kW) at relatively low pressures (20 mbar). A1 × l in Corning 1737...
glass plates were used as substrates. The substrate temperature during PE-CVD growth was typically 550 °C, as measured by a calibrated two-colour pyrometer. The selected growth conditions, together with high diamond nucleation densities (above 10¹¹ cm⁻²) proved to be essential for the preparation of relatively very thin (from about 60 nm) fully closed nanocrystalline diamond films. The nucleation treatment for obtaining such high nucleation densities consisted of a controlled impact of 10 nm size diamond powder using an ultrasonic vibration table before PE-CVD growth. B-NCD films of thickness ranging from 60 to 500 nm were then prepared, depending on the growth time used. The growth rate was 0.05 μm/h for a 0.5% CH₄ dilution in H₂. TMB was used as a B-doping source with B:C ratios ranging from 100 to 3000 parts per million (ppm). The films prepared from 3000 ppm B:C ratio contained about 3–4×10²¹ cm⁻³ B atoms, as determined from the SIMS analysis (based on the precision of the absolute SIMS calibration). Due to the columnar crystal growth type, the resulting NCD films had grain sizes depending of the film thickness. Typically, for 60 nm film thickness, the grain size was about 30–60 nm as determined from SEM and XRD, while for films of about 500 nm, the grain sizes were about one order of magnitude larger. The samples were then cut into squares ≈7 × 7 mm and provided at the corners with small (∼150 μm) triangular evaporated Au/Ti pads. The samples were connected to the measuring terminals in a liquid helium (LHe)// Oxford cryostat by means of ≈50 μm thick silver wires attached to the contact pads by a silver paste. The MR set-up was used as described elsewhere [8,9].

Fig. 1. AFM morphology micrograph of a 100 nm thick B-doped nanocrystalline film prepared onto a Corning 1737 substrate.

Fig. 2. Raman spectra of 3000 ppm B-doped nanocrystalline diamond sample. The position of 1332 cm⁻¹ central zone peak is indicated by arrow. The inset shows the SIMS B-concentration data for 3000 and 100 ppm B-doped sample.
3. Experimental results and discussion

The Raman spectrum for 3000 ppm B-doped sample is shown in Fig. 2, together with the SIMS B-atom concentration profile. By analysing the Raman spectrum, one can resolve a Fano-resonance peak, typical for heavily B-doped diamond films with B-concentrations above the Mott’s metal-insulator transition (MIT). The Fano resonance in diamond films was explained by Bustarret as a resonance of central zone phonon peak with the continuum of electronic states [10]. Upon boron doping, the Raman peaks at 1332 cm\(^{-1}\) shifts to lower energy and soften, what has been observed clearly for our heavily B-doped films. The Fano resonance confirms thus the substitutional incorporation of boron in the bulk of CVD diamond grain. Surprisingly the sp\(^2\)-related Raman peak is not observed in any significant manner in the measured spectra for 3000 ppm B-doped sample in Fig. 2. However, the sp\(^2\) related peak is clearly observed in our samples for lower doping levels [11].

Fig. 3(a) shows MR data at LHe temperatures for both SC and non-SC B-doped samples and in Fig. 3(b) the electrical conductivity data measured in a wide temperature range are plotted. Based on the SIMS estimation, the Hall carrier concentration measurement and data shown in Fig. 3, the B-concentration for the 800 ppm and 3000 samples lies above the MIT threshold which was reported in several papers to be about \(2 \times 10^{20} \text{cm}^{-3}\) [10]. The 3000 ppm B-doped samples had carrier concentration of about \(1.6 \times 10^{21} \text{cm}^{-3}\). Interestingly, the samples in Fig. 3 show a decreasing conductivity towards low temperatures. The conductivity data in the Arhenius coordinates cannot be fitted with single activation energy. The small \(E_A\) values (below kT) and the fact that the \(N_c\) is above the MIT practically exclude the thermally activated mechanism of the conductivity. The conductivity data thus resemble a typical behaviour of conductivity in disordered metal. However, the MR data for the 3000 ppm B-doped SC sample in Fig. 3 show a weak positive MR, which is for the SC sample too small (few %) to support the picture of the hopping-like conductance modified by the wave-function shrinkage effect. We thus assume that the transport takes place within highly disordered metallic-like impurity band.

Fig. 4 shows the electrical resistivity measurements for 3000 ppm B-doped sample, measured at LHe temperatures. At about 1.66 K, the resistivity drops below the detection threshold of our setup (~\(10^{-9} \Omega\)). The inset of Fig. 4 reveals the cancellation of superconductive transition above a critical magnetic field. In order to describe the superconducting state of B-NCD films together with its transport properties above \(T_C\) consistently, we have used the model of highly disordered Mott’s metal as a starting point. Recalling that in a system with an appreciable intrinsic disorder at low temperatures the decisive role is played by the effect of weak localization, the essence of which is the constitution of relatively stable coherent electron (hole)-wave interference patterns [9,11]. The extent

![Fig. 3](image1)

Fig. 3. The dependence of the resistivity on the magnetic field for 3000 ppm doped (superconductive) and 800 ppm doped (non-superconductive) (a). Fig. (b) shows the electrical conductivity data.

![Fig. 4](image2)

Fig. 4. The electrical resistance for 3000 ppm B-doped sample measured at liquid helium temperatures. The arrow indicated the superconductivity transition at 1.66 K, where the resistivity drops below detection limit.
of these patterns, called weakly localized orbits (WLO), is controlled by temperature and external magnetic field by Aharonov–Bohm's phase-breaking process. Within such an extent (typically ~10^{-7} m) the WLO can be considered as a fully coherent non-dissipative subsystem which traps a conductive electron (hole). As we claim, just these properties can account for the observed decrease of conductivity with decreasing temperature (because of depletion of free carriers) and for the transition of the B-NCD into the superconducting state as well. Indeed, with decreasing temperature the number and extent of WLO must increase till they touch each other. It can be further shown by a simple estimate [11] that below a certain temperature, which is very near to the experimentally observed $T_c$, the spins of neighbouring WLO buried in a diamond lattice should flip into the anti-parallel state changing thus the fermionic nature of the subsystem into bosonic. Resulting network of overlapping paired WLO containing trapped carriers can provide, as we believe, a plausible picture of an unconventional superconductor which fits very well B-NCD.

4. Conclusions

Here, we present clear evidence that SC can be observed also in nanocrystalline diamond films, when heavily doped with boron. The superconductive transition for the B-NCD film with a carrier concentration of $1.7 \times 10^{21} \text{cm}^{-3}$ is 1.66 K.

The MR data show a weak positive MR for all B-doped NCD films measured, which together with the Fano resonances observed point towards the localization of the electron wave-function onto the B-atoms, substitutionally incorporated in the bulk of B-NCD films.

All the films above the MIT transition show transport behaviour which is not typical of ordinary metals, witnessing an impurity band-type of conduction, as treated by Baskaran [3].

For the description of superconducting transition and magnetotransport properties observed in B-NCD above $T_c$ as well, an original model based on the concept of weakly localized orbit has been proposed. A detail exposition of this model involving quantitative arguments will be presented elsewhere.

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