STM/STS study of superconducting diamond

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Abstract

We present a scanning tunneling microscopy/spectroscopy (STM/STS) study of synthetic polycrystalline boron-doped diamond in the temperature range 0.5–4.3 K. At 4.3 K the sample-surface was very non-uniform and tunneling I(V) spectra were typical for p-type semiconductors. After cooling below the superconducting transition temperature, we detected and measured the superconducting gap of diamonds. At temperatures around 0.5 K the energy gap was around 0.8 and 1 mV (for two different samples).

Keywords: Superconductivity; Diamond; Scanning tunneling microscopy

1. Introduction

Superconductivity in heavily boron-doped polycrystalline diamond at 2.2 K was recently reported [1]. Study of this phenomenon is of interest both from a practical point-of-view and for furthering our understanding of the physics of superconductivity. Currently, there are two different theoretical interpretations for the existence of superconductivity in diamond. One is by analogy with MgB\textsubscript{2}, and explains the superconductivity of diamond by invoking a strong hole–phonon coupling [2], while the alternative theory takes into account a resonating valence bond mechanism of the impurity band [3]. However, there have been few experimental studies concerning superconductivity in diamond although there have been measurements of magnetic susceptibility, electrical resistivity [1] and heat capacity [4] of diamonds around the superconducting transition. Superconductivity of diamond in thin film form [5] with transition temperatures up to 7.4 K has also been reported.

2. Experimental

The main purpose of this work was to detect and measure the value of the superconducting energy gap by means of scanning tunneling spectroscopy/microscopy (STS/STM). We studied two samples of boron-doped diamond fabricated by two different methods in IHPP RAS. The first sample (marked #1) is similar to that described in the first paper about diamond superconductivity [1] and is a polycrystalline B-doped diamond synthesized by reacting B\textsubscript{4}C and graphite under 8–9 GPa pressure and at 2500–2800 K. After fabrication the surface layer was removed by mechanical polishing so that the resulting sample had a thickness of about 1 mm and a diameter of \~{}3 mm. The mass was approximately 19 mg. The second smaller sample (\#2) (about 2 \times{} 2 \times{} 1 mm) was synthesized from a powdered mixture of boron and graphite under the same conditions, and the preparation procedure has been already briefly described [4]. In order to remove all nondiamond phases both samples were etched in acid. Following this procedure the samples had visibly rough structures on their surfaces.

To define the superconducting transition temperature of the diamond samples we measured their magnetic susceptibilities in the range 1.8–10 K using a DC-SQUID (“MPMS” system) magnetometer operating at low magnetic...
field. Our results (Fig. 1) are consistent with data reported previously [1,4]. As shown in Fig. 1, sample #1 has a transition temperature at about 2.3 K, while the second sample probably consists of two phases with different transition temperatures at about 4.3 and 2.3 K.

In this work we used two different STM systems: one for the temperature range 1.8–4.5 K, the other for measurement at lower temperatures down to 0.5 K. Both systems contain STMs operating under ultrahigh vacuum conditions. The former setup [6] uses a cryogenic pump, and allows choice of scanning area over the entirety of the sample’s surface with tip position viewing through an optical system. Thus, a relatively flat area of the surface can be chosen. For measurement at 0.5 K, we used an ultra high vacuum STM system (UNISOKU, USM-1300SD2) with pumping of liquid helium-3. Pt–Ir wire was used as STM tip in both cases.

3. Results and discussion

It is known that the diamond surface is oxidized quite easily under atmospheric conditions [7] and this causes some problems in the study of diamonds using STM. We did not apply any additional surface cleaning procedures except etching and washing in an organic solvent. On one occasion we attempted to clean the surface by irradiation with Ar ion (ion energy ~2 keV) but this resulted in a metallic layer on the surface (judging from the linear tunneling $I(V)$ spectra). It is likely that the surface layer of the diamond was converted to graphite and this is in agreement with similar work of another group [8]. According to experience, however, it is possible to obtain STM images of diamonds even coated with a thin oxide layer [7].

As expected, the surface of the diamond samples at the micrometer scale were very irregular and it was required

![Fig. 1. Magnetic susceptibility of diamond samples measured using DC-SQUID magnetometry in a field of 4 Gauss. Upper curves are field cooled (FC), lower curves—zero field cooled (ZFC): (a) sample #1, transition temperature ~2.3 K; (b) sample #2, superconductivity appears at ~4.2 K.](image1.png)

![Fig. 2. Tunneling spectra (STS) observed on the surface of p-type diamond: (a) $T = 4.3$ K, two different points on the surface; (b) curves acquired while cooling the STM head from 3 to 2 K (sample #1).](image2.png)
that we search for a sufficiently smooth scanning area in order to obtain reproducible results. Since the boron-doped diamond is a p-type semiconductor, we applied a positive bias voltage to the sample while the tip was grounded. Some of the resulting current–voltage tunneling curves are presented in Fig. 2. At 4.3 K, they are typical for p-type semiconductors (similar $I(V)$ dependencies were reported earlier for thin films [9]) as well as for bulk single crystals of p-type synthetic diamond [10]. During scanning we recorded two arrays simultaneously: topography and spectroscopic data. Under this regime the feedback system maintained a constant tunneling current while scanning with a positive bias applied to the sample. At each measurement point (we recorded images of $128 \times 128$ or $256 \times 256$ pixels) the output feedback was frozen, the bias was changed to a negative value and the tunneling current was recorded. These images give us information about electronic structure at the surface of the samples. Typical images of topography and negative bias current at the

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**Fig. 3.** STM images of the diamond surface, image is about $10 \text{nm} \times 10 \text{nm}$, $T = 4.3$ K. Left image (a) is topography recorded at bias $V_t = 2.5$ V. The right image (b) represents the values of tunneling current measured at negative bias ($-3$ V). Dark areas relate to negative current, bright areas are mostly the noise level of current.

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**Fig. 4.** Tunneling current–voltage dependencies (STS) of the surface of diamond in the superconducting state at 0.5 K for (a) sample #1 and (b) sample #2.
nanometer scale are shown in Fig. 3. Dark areas in the current image represent regions with high values of the negative tunneling current (level “b” in $I(V)$ curve, Fig. 2(a)), bright tones in the image relate to almost zero current (point “a” in Fig. 2(a)). These images give information about the electronic uniformity of the structure of polycrystalline diamond samples and this structure is not surprising because of the fabrication procedure. However, a reliable interpretation of these results is difficult because of the oxide layer on the surface. We can speak authoritatively only about differences in the qualitative structure of the surfaces of our samples. Tunneling spectra acquired while cooling should also be interpreted with great care but to clarify this point we will continue measurements. Because of cooling-induced thermal drift the STM tip is likely to be shifted so that we cannot be sure that these curves (Fig. 2(a),(b)) were acquired at the same point. However, the shapes of these dependencies are typical for our samples—at 4.3 K the main part of the $I(V)$ curves were similar to that presented in Fig. 2(a) whereas while cooling the STM head down to 2 K the major part of the observed dependencies were similar to Fig. 2(b).

To detect the superconducting gap on the diamond surface we measured the tunneling current–voltage dependencies at low temperature (0.5 K). Two of these dependencies are presented in Fig. 4. The oxide layer on the surface exhibits a Schottky-like junction which has a specific nonlinear response of the current to the applied voltage. With this background it is difficult to detect the superconducting gap, but the thickness of the oxide layer varies from point to point. At points with a thick oxide layer we could not obtain a reproducible $I(V)$ spectrum together with the topography. Conversely, in other areas we observed an almost linear $I(V)$ spectrum with a gap around zero bias in addition to a reproducible topography image. We used such areas for measurements of the superconducting gap although some noise was inevitable (Fig. 4(a), sample #1). Occasionally, we could find a much smoother region with low noise, such as that presented in Fig. 4(b) (sample #2). This $I(V)$ spectrum is the result of averaging nine dependencies acquired along one scan line of length around 10 nanometers. If we take into account the relatively high noise and Schottky barrier on the surface then we can estimate the value of the gap with some approximation. From our experiments, this statistical estimation gives us values of the superconducting gap around 0.8 and 1 mV for samples #1 and #2, respectively. These values are slightly higher than results obtained by Sidorov [11] (0.4–0.7 mV at 1.1 K) but they are in reasonable agreement.

4. Conclusions

In this work we have studied bulk polycrystalline samples of p-type synthetic diamonds using scanning tunneling microscopy/spectroscopy at temperatures down to 0.5 K to detect the superconducting gap. We found that the surface of the samples were very irregular although the tunneling $I(V)$ spectra are typical for p-type semiconductors at 4.3 K and exhibit rectification. We also observed that cooling to the superconducting state causes changes to the shape of the $I(V)$ spectra. At temperatures (0.5 K) well below the superconducting transition we observed an energy gap around zero level bias voltage. We estimate the value of the gap to be about 0.8 and 1 mV for samples #1 and #2, respectively, at $T = 0.5$ K.

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