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Thermoelectric transport properties of boron-doped nanocrystalline diamond foils

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ABSTRACT

Natural diamond is known for its outstanding thermal conductivity and electrical insulation. However, synthetic production allows for doping and tailoring microstructural and transport properties. Despite some motivation in the literature and the ongoing search for abundant and non-toxic thermoelectric materials, the first experimental study on a set of eight substrate-free boron-doped nanocrystalline diamond foils is presented herein. All transport coefficients were determined in the same direction within the same foils over a broad temperature range up to 900 °C. It is found that nanostructuring reduces the thermal conductivity by two orders of magnitude, but the mobility decreases significantly to around 1 $cm^2 V^{-1} s^{-1}$, too. Although degenerate transport can be concluded from the temperature dependence of the Seebeck coefficient, charge carriers notably scatter at grain boundaries where sp^2-carbon modifications and amorphous boron-rich phases form during synthesis. A detailed analysis of doping efficiency yields an acceptor fraction of only 8–18 at%, meaning that during synthesis excess boron thermodynamically prefers electrically inactive sites. Decent power factors above 10^{-4} W $m^{-1} K^{-2}$ at 900 °C are found despite the low mobility, and a Jonker-type analysis grants a deeper insight into this issue. Together with the high thermal conductivity, the thermoelectric figure of merit zT does not exceed 0.01 at 900 °C.

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1. Introduction

Nature uses harsh conditions to create diamond, i.e., high temperature and high pressure. This process results in a material with outstanding properties such as the highest thermal conductivity, one of the widest band gaps, highest hardness, smallest molar volume, strongest bonds, lowest diffusion coefficients and therefore excellent stability at high temperature and against chemical or mechanical wear.

No matter how desirable the latter properties may make diamond for a broad variety of applications, its high thermal conductivity and electrical resistivity seem to disallow its application in the field of thermoelectric power generation. But then, in turn, synthetic processes like chemical vapor deposition (CVD) provide parameters to tailor the material's chemistry, microstructure and overall transport properties. Many established thermoelectric materials (Bi_2Te_3, PbTe, SiGe) are toxic and not abundantly available as required for

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their use in industrial mass products. The production of CVD-diamond does not depend on rare or toxic raw materials, as only hydrogen, methane and electric energy are needed. Cheap dopant precursors with low toxicity are readily available and only needed in small amounts. The production volume is fully scalable by adjusting the number and size of coating machines.

In thermoelectrics, the general necessity of tailoring the Seebeck coefficient α, the electrical conductivity σ and the thermal conductivity κ as independently as possible can easily be seen from their relation with the dimensionless figure of merit zT given in Eq. (1):

$$zT = \frac{\alpha^2 \cdot \sigma}{\kappa} \cdot T \quad (1)$$

All transport properties in turn are functions of the absolute temperature T. The numerator $\alpha^2\sigma$ is commonly referred to as the power factor. An increase in the figure of merit can be achieved, e.g., via the optimization of the charge carrier concentration and the microstructure, where the latter has gained attention in the last two decades with the ascent of nanostructured and nanocomposite materials for enhancing the Seebeck coefficient and reducing the thermal conductivity [1–4].

In addition to the possibility of nanostructuring, some strong motivation to investigate the thermoelectric properties of CVD diamond can be found in the literature, which will be assessed in the following section. For a consistent experimental study, a set of eight foils was deposited with varying boron concentration in two different hot filament CVD (HFCVD) reactors. The chemical composition and the microstructure were characterized using glow discharge optical emission spectroscopy (GDOES), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Thermoelectric transport coefficients were measured perpendicularly to the growth direction (in the plane of the foils) between room temperature and 900 °C. From these data, the charge carrier concentration, the mobility and the doping efficiency are calculated. A Jonker-type analysis reveals the influence of the mobility on the power factor. Since our study investigates all transport properties in the same direction within the same specimens, it is the first to assess the overall thermoelectric figure of merit. Besides this, the single transport coefficients and their temperature dependence could be of interest for researchers applying nanocrystalline diamond as a surface coating with outstanding mechanical properties [5].

2. Thermoelectric transport in CVD diamond

In 1987, Revin measured a decent power factor of $10^{-5}\,W\,m^{-1}\,K^{-2}$ in single-crystalline, synthetic, nominally undoped p-type diamond and attributed this result to the very high carrier mobility, recognizing the potential application of diamond as a thermoelectric material [6]. Triggered by the aforementioned developments in nanotechnology and the discovery of ultrananocrystalline diamond (UNCD), Gruen suggested the investigation of UNCD and related carbon composites with regard to their thermoelectric properties [7]. Another stimulus comes from the high Debye temperature of diamond, raising the question whether the phonon drag effect could be used at temperatures well above room temperature. This effect was experimentally shown in high quality crystals with doping concentrations lower than $10^{17}\,cm^{-3}$ [8,9]. A calculation for a nanocomposite of diamond and graphite predicted very large zT values [10], whereas other sources find the application of the phonon drag effect unlikely due to the high charge carrier concentration needed for thermoelectrics [11,12].

Most easily, doping of diamond is achieved with boron due to its negative formation energy and its size [13]. Boron forms a deep acceptor level at 0.37 eV above the valence band edge, which decreases to about 0.1 eV with increasing dopant concentration [14,15]. Astonishingly, only very few reports on Seebeck coefficients in boron-doped CVD-diamond can be found in the literature, and no reports show data below 250 K or above 350 K [7,16–18]. A recent theoretical approach [19] calculates Seebeck coefficients from experimental Hall and resistivity data in a p-type CVD-single-crystal [20]. Mainly older sources use the Seebeck effect in order to confirm p-type conduction [14,21–23]. The scarcity of experimental data may be explained with the high thermal conductivity of diamond leading to experimental difficulties as mentioned by Revin [6] and by Horiuchi et al. [18].

From the viewpoint of thermoelectrics, the reduction of thermal conductivity in diamond is a key aspect, demanding grain sizes well below the micrometer range. In the 1990s, much emphasis was laid on perfecting CVD films to increase their thermal conductivity for heat spreading applications [24,25]. The columnar microstructure in these films was found responsible for a large anisotropy and thickness dependence of the thermal conductivity: Thinner films with much smaller average grain size show much lower thermal conductivity, especially perpendicularly to the growth direction [26]. Such a columnar structure is not found in the case of UNCD due to its homogeneous growth within the thickness range reported [27,28]. The resulting thermal conductivity may be very low, e.g., $2\,W\,m^{-1}\,K^{-1}$ [7], but the implications on other transport properties remain unclarified.

Since the introduction of grain boundaries will affect the charge carrier transport, several effects and contributions should be mentioned. In and around the grain boundaries, carbon will largely adopt sp^2-hybridized bonds, generating additional states in the band structure [29]. With decreasing grain size, e.g., UNCD of 3–5 nm synthesized in a plasma containing nitrogen, the sp^2-content increases to up to 15 at% [30]. This leads to the consideration of the grain boundaries as a matrix phase in a composite of amorphous carbon and *trans*-polyacetylene-like structures and to the assumption that, in this case, the matrix possibly contributes significantly to electrical conduction [30]. Despite this contribution, quite low mobilities around $1\,cm^2\,V^{-1}\,s^{-1}$ are found in UNCD [31], opposing the potential idea that sp^2-carbon grain boundaries may benefit charge carrier transport as compared to the transport within the grain: the hole mobility in single-crystalline diamond is well above $1000\,cm^2\,V^{-1}\,s^{-1}$ [32]. In the case of doping high-pressure, high-temperature diamond with boron, the dopant tends to accumulate in the grain boundaries, and it has been hypothesized that superconductivity arises from intergranular boron-rich material [33]. In particular, segregation of boron is expected when its amount exceeds

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