World’s First Thermoelectric Generator Made of Tailored Carbon Allotropes

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Carbon and carbon-based compounds are today’s mostly used sources of energy. By burning them, their chemically stored energy can be transformed to mechanical energy and further on to electrical energy. These transformation steps entail huge thermal losses. Thermoelectric generators (TEGs) are devices that allow the direct conversion of thermal gradients into electrical energy through a smart combination of n- and p-conducting materials and are therefore an appealing approach to tackle thermal losses. However, the materials in today’s TEGs, e.g., Bi$_2$Te$_3$, show limited thermal stability and often are toxic or not abundantly available which only allow for niche applications like military and aerospace equipment. Herein, the fabrication of the first, fully functional all-carbon TEG is shown. The used carbon materials, made by chemical vapor deposition (CVD) processes, are both, nontoxic and abundant, and potentially paves the way for the large-scale use of TEGs. Not only the thermal losses of conventional combustion processes but also thermal gradients established by solar thermal systems are potential fields of application. The assay is anticipated to spark further interest in carbon-based thermoelectric materials. Such materials can be produced on a large scale and combined to a fully functional thermoelectric device.

The performance of a thermoelectric device is given by the figure of merit (ZT) of the materials it is made of (see Equation (1)).

$$ZT = \frac{\alpha^2 \sigma}{\lambda} \frac{T}{T} = \frac{\text{power factor}}{\lambda} \frac{T}{T}$$

\[ \text{(1)} \]

\(\alpha, \sigma, \lambda, \) and \(T\) denote the Seebeck coefficient (SC), electrical conductivity (EC), thermal conductivity (TC), and absolute temperature, respectively.\[1]\] The power factor is calculated by the product of SC squared and EC. It is used to determine the usefulness of a thermoelectric generator (TEG) or thermoelectric material without considering its efficiency. Thus, to achieve a decent ZT value, a high power factor is needed to gain a high electrical power output and a low TC is required to reach an adequate and stable thermal gradient alongside the material. However, the interdependent tuning of these variables is challenging.\[2\] In the past decades, research has shown that semiconductor and skutterudite materials are most promising to accomplish decent ZT values and electron- and hole- (n- and p-type) conducting properties can be tailored.\[3,7\]

Carbon, as one of the building blocks for life on Earth, can form a vast number of chemical compounds. The different carbon allotropes clearly show that in addition to the four valence electrons and small atomic radius of carbon, hybridization states have a major influence on the properties of carbon-based materials, like diamond and graphite. Naturally occurring diamond is known to be an electrical insulator and exhibits the highest hardness of any known natural material, whereas graphite shows semiconductive behavior and a reduced mechanical strength. These characteristics can be ascribed to the sp$^2$- or sp$^3$-hybridized carbon atoms of diamond respectively (the stacked graphene layers of) graphite. Being an electrical insulator with high TC, diamond seems to be unsuited for use as a thermoelectric material which requests the opposite properties. Synthetic fabrication by means of CVD, however, allows modifying the properties and specifically tailoring them to certain applications. Doping, e.g., can provoke EC, and adjusting the crystallinity to nanoscale grain sizes drastically lowers the TC.\[8,9\]

For the fabrication of our TEG that is shown in Figure 1a, we chose three kinds of CVD-derived carbon materials: undoped, microcrystalline diamond (UDD) as heat spreader, BDD as p-type material, and NDG nanowalls as n-type conductor.

The heat-spreading UDD was grown on a 3 mm-thick graphite disk with a diameter of 56 mm. Prior to deposition the disk was dipped in a dispersion of nanodiamonds (Carboonde Anandate) mixed with ethanol in a ratio of 1:20. During deposition in a microwave-plasma-CVD (MWCVD) reactor (AX 6350 by ASTeX), the pressure within the chamber was kept at 160 mbar and microwave power at 4000 W. Constant gas flows of 193 sccm hydrogen and 7 sccm methane were set throughout the deposition time of 200 h.

To obtain a free-standing diamond plate, the graphite substrate was removed by particle blasting with SiC.

The second diamond material, namely BDD, was grown on a dip-seeded 6" silicon wafer. Seeding solution was the
nanodiamond ethanol dispersion with a ratio of 1:100. Deposition took place in a hot-filament CVD (HFCVD) reactor (CemeCon WTMCC800DIA-8) at a chamber pressure of 6 mbar. During the deposition time of 190 h gas flows of 1000 sccm hydrogen, 20 sccm methane, and 0.4 sccm dopant precursor trimethyl borate (TMB) were applied.

The diamond film was removed from the silicon wafer by cutting a defined breaking line with a Nd:YAG laser (Rofin Starline 100D) with a wavelength of 1064 nm. Due to internal stresses in the diamond the film delaminates with the help of an ultrasonic treatment. The detailed description of the diamond foil manufacturing process can be found in the study by Lodes et al.\[10\].

The n-conducting NDG material was produced using the same MWCVD reactor as mentioned earlier but the deposition parameters were changed. Chamber pressure was 133 mbar and microwave power 3500 W. A flow of 10 sccm hydrogen and 5 sccm methane was combined with 100 sccm nitrogen as dopant. Deposition time was 96 h and the graphite substrate was removed from the grown film by subsequent SiC particle blasting.

Prior to the brazing of the TEG the three prepared carbon materials were laser cut into the desired rectangular shapes. To add up the thermoelectric power of the p- and n-type material, five p–n-couples, consisting each of a BDD foil and an NDG platelet, were arranged in a zigzag series connection (Figure 1a). The UDD plates have two functions. On the one hand, they serve as a mechanical framework for the p–n-couples, and on the other hand, they act as heat spreaders.

The colored part of the TEG and the magnified view illustrate the arrangement and stacking of the three different carbon materials. Silver–titanium (AgTi) active solder foil (BrazeTec CB2) in between the overlapping areas of the TEG materials was used to braze the materials together in a vacuum furnace at 1020 °C. The solder acted as the binder to achieve mechanical stability as well as the electrical connection of the BDD and NDG.

However, with the use of the AgTi solder, no true p–n-junctions were formed between the BDD and NDG, as the titanium forms a carbide with the carbon materials, and it is reported that this leads to ohmic contacts\[11,12\] hence no Schottky barrier. Therefore, no rectifying behavior was observed at the individual p–n-couples or the assembled TEG.

Copper contacts were brazed onto the two ends of the TEG for electrical connection. A graphite holder ensured the accurate positioning of all parts during brazing. Small tungsten weights provided a constant pressure on each joint. Brazing itself took place in a vacuum furnace (MUT) that was evacuated to a pressure of 5 × 10⁻⁵ mbar. The furnace was heated with a rate of 10 °C min⁻¹ up to 1020 °C and kept at that peak temperature for 15 min to ensure a homogenous brazing.

The thermoelectric transport coefficients of the freestanding BDD and NDG foils were measured in plane, as this is the

Figure 1. a) Carbon allotropes TEG and b–d) top-view SEM micrographs of the used carbon materials. a) Zigzag arrangement of the five p–n-couples brazed onto UDD heat spreaders. The schematic cross section (not to scale) shows the stacking of the carbon materials and the active AgTi solder. b) Heat-spreading microcrystalline UDD. c) p-conducting BDD with smaller and twinned microcrystals, compared with the UDD. d) Porous morphology of the n-conducting NDG. The TEM inset shows that the NDG platelets consist of nanowalls.
relevant transport direction in the TEG. The SC and the EC were measured simultaneously using a ZEM-3 (Ulvac-Riko, Inc.). The TC of NDG and BDD was determined in an LFA 457 Microflash (Netzsch-Gerätebau GmbH). These temperature-dependent values were measured partly up to 900 °C. Detailed information on measurement setups, sample geometries, and data evaluation can be found in the study by Engenhorst et al. [8]

To determine the output characteristics of the whole TEG module, its two heat-spreading UDD plates were placed on a heated and a cooled stage, respectively (Figure 2a). Thereby a temperature gradient was established within the BDD and NDG platelets that form the thermoelectrically active part of the TEG. The temperature of the cooled stage was kept constant, whereas the power of the heated stage was varied, which allowed for the adjustment of the temperature difference in the TEG. This difference as well as the mean TEG temperature was calculated from the temperatures measured directly at the UDD heat spreaders. The induced thermoelectric voltage was gauged using a voltmeter (Fluke 289).

Via an ammeter and a potentiometer added to the test setup, we were able to meter the voltage and current simultaneously at different electrical loads (Figure 2a). This enables the determination of the TEGs’ maximum power point (MPP).

To obtain a high TC and provide mechanical stability, the 1 mm-thick microcrystalline diamond plates were produced (Figure 1b). These plates show crystal sizes of up to 250 μm. The boron-doped diamond (BDD) material was fabricated as a 50 μm-thick freestanding foil. Figure 1c shows a top-view scanning electron microscopy (SEM) image on the growth side of this BDD foil with the mixed morphology of twinned micro- and nanocrystallites. As n-type doping of diamond has not been solved yet, we prepared nitrogen-doped graphene (NDG) nanowalls as our n-conducting material (Figure 1d). The addition of nitrogen gas during the CVD favors the growth of NDG and provokes n-type conduction. The porous morphology clearly differs from the compact crystalline diamond materials’ appearance. The inset in Figure 1d shows a transmission electron microscopy (TEM) cross section of these nanowalls.

As mentioned, SC, EC, and TC are necessary to determine the ZT value of a thermoelectric active material. The graphs in Figure 3a show the dependencies of the SCs of BDD and NDG on the measurement temperature. BDD shows a positive SC that linearly increases with temperature. The values range from 100 μV K⁻¹ at 50 °C to 320 μV K⁻¹ at 900 °C mean sample temperature. Due to its n-type conduction, NDG shows a negative SC. Absolute values also exhibit a linear, however, flatter increase. A linearly extended fit line indicates that it might reach values of about −60 μV K⁻¹ at 900 °C. The EC of BDD (Figure 3b) gradually increases with increasing temperature within a range between 3 × 10⁻³ and 9 × 10⁻³ Sm⁻¹. Our temperature-dependent EC measurements of NDG up to 400 °C resulted in nearly constant values of roughly 2.5 × 10⁻⁴ Sm⁻¹. However, the here-shown polynomial fit indicates a decline of the EC for elevated temperatures, which is in accordance with results published by Zhao et al. [13] In Figure 3c, the TC of BDD and

Figure 2. a) Schematic measurement setup and b,c) TEG output characteristics. a) A heated and a cooled stage are used to establish a temperature gradient within the TEG. The applied load can be varied with a potentiometer and the resulting output is measured with an ammeter and voltmeter. b) OCV versus temperature. c) Power output curve recorded at 200 K temperature difference between \( T_{\text{hot}} \) and \( T_{\text{cold}} \).
NDG is shown. Due to phonon scattering at crystallite boundaries, the TC of microcrystalline BDD is considerably lower than the one of single-crystalline diamond (2000 W m\(^{-1}\)K\(^{-1}\))\(^{[14,15]}\) yet still two orders of magnitude higher than the TC of NDG. The low TC of NDG results from cavities within the bulk material and ineffective thermal coupling among the graphene nanowalls.\(^{[9]}\) Using the obtained fit functions of the measured transport coefficients, temperature-dependent \(ZT\) curves were calculated for BDD and NDG, respectively (Figure 3d). Both materials show similar behavior, yet the \(ZT\) increase for BDD shifts to higher temperatures. This is mainly caused by the relatively large difference in TC. Admittedly, these \(ZT\) values are still low compared with, e.g., Bi\(_2\)Te\(_3\), which reaches a maximum \(ZT\) of 1.0 at \(\approx\)100 °C\(^{[5,17]}\). However, SC and EC and consequently the power factor of BDD (0.9 mW m\(^{-1}\)K\(^{-1}\)) at 900 °C are already competitive with conventional thermoelectric materials.\(^{[16]}\) Solely the high TC of our BDD is currently disadvantageous for efficient thermoelectric conversion, but TC as low as 1 W m\(^{-1}\)K\(^{-1}\) was reported for ultrananocrystalline diamond.\(^{[13]}\) The \(ZT\) of NDG, in contrast, mainly suffers from a poor SC. Published results show that the thermoelectric properties of BDD\(^{[8,15,18]}\) and NDG\(^{[9,15,19]}\) can be set in a wide range by tuning the deposition parameters. These evidences imply that the \(ZT\) of both materials can be further increased.

Figure 2b shows the dependency of the temperature difference on the TEGs open-circuit voltage (OCV). With a larger temperature difference, the OCV increases. The nonlinear behavior can be explained by the increasing mean TEG temperature and the temperature-dependent SCs of our materials. With our test setup, we measured an OCV of up to 125 mV at a temperature difference of 200 K. From the SC measurements of the single materials, we know that \(\approx\)160 mV is theoretically achievable at this temperature. Thermal losses, however, lead to lower actual temperatures at the thermoelectrically active materials and cause this reduced OCV.

The graphs depicted in Figure 2c show the data recorded at a temperature difference of 200 K. Current and voltage show a linear characteristic that leads to the parabolic shape of the power output curve. As typical for TEGs, the MPP is located at half OCV, which in our case is 118 μW at 63 mV. This power output is quite low; nevertheless, it would be enough to constantly power about 50 wrist watches (\(\approx\)2.5 μW/watch).

In conclusion, our here-shown TEG based on carbon allotrope materials can be seen as a technical feasibility study. By combining undoped diamond plates, thermoelectrically active foils of BDD, and NDG nanowalls, a fully functional device could be fabricated. To transfer this concept from a laboratory demonstration to real-world applications, we see two potential strategies. First, efficiency needs to be increased by improving the materials’ \(ZT\) values. The difficulty hereby is to combine a high SC, a high EC, and a low TC all in one material, as it has proven tricky to alter the thermoelectric properties independently. Yet, new pulsed CVD processes have shown first promising results. Second, with our current state material, we see applications in areas where mainly the PF is relevant. Suchlike TEGs, e.g., could be integrated into the absorber architecture in thermosolar power stations.\(^{[20]}\) The solar power could thereby be partially converted.
to electrical energy while being transferred to the working fluid. Here, the high TC of diamond is helpful to evenly distribute the solar power. Further, the excellent thermal stability of these machine-made materials favors these high-temperature applications. We hope our here-shown results are examples of out-of-the-box thinking, that inspires research to help finding new approaches to thermoelectric materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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