

Cu/synthetic and impact-diamond composite heat-conducting substrates

E N Galashov, A A Yusuf and E M Mandrik

Department of Applied Physics, Scientific Research Department Novosibirsk State University, 2 Pirogov str., Novosibirsk 630090, Russia

E-mail: chessplanet86@yandex.ru

Abstract. Composite material with high thermal conductivity was obtained by the method of thermal sintering of diamonds (synthetic and impact) and copper powder and by further hot isostatic pressing. The content of diamond (the particle size is 20 – 250 μm) in the diamond copper composite was 30 – 45 weight percent. The coefficient of thermal conductivity of copper diamond composite materials based on synthetic diamonds was measured to be 700 – 750 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The coefficient of thermal conductivity of copper diamond composite materials based on impact diamonds was measured to be 850 – 900 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The coefficient of thermal expansion (CTE) was measured to be $5.5 - 6.5 \cdot 10^{-6}/^{\circ}\text{C}$ for synthetic diamonds and $6.1 - 6.5 \cdot 10^{-6}/^{\circ}\text{C}$ for impact diamonds. The obtained copper diamond composite materials are promising to be used as crystal holders for semiconductor crystals in THz and microwave devices.

1. Introduction

The technical capabilities of modern devices (locating systems, military and space applications, etc. [1-3]) lately are increasingly demanding higher and higher frequencies. However, the generation of high frequencies is accompanied by the release of an enormous amount of heat, which can adversely affect the performance of terahertz and ultra-high-frequency electronics. These electronics can be damaged by overheating. The power and the life of chips used in the terahertz and ultra-high-frequency electronics can be increased by removing heat from the crystal by raising the thermal conductivity of the crystal holder. Creating a material that can cope with this problem is a very urgent task. It should be noted that in Russia highly conducting crystal holders with thermal conductivity higher than $250 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and having a coefficient of thermal expansion corresponding to CTE of expansion crystals (GaAs, ZnSe, GaN) are not commercially available.

The most heat-conducting solid material is diamond. The thermal conductivity of diamonds reaches $2300 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [4]. However, the main disadvantage of diamonds is low CTE $1 \cdot 10^{-6}/^{\circ}\text{C}$, whereas the base semiconductor crystals have a CTE of between 4 and $8 \cdot 10^{-6}/^{\circ}\text{C}$.

We described earlier the major problems associated with the synthesis of highly conducting metal-diamond composites in our work [5]. The thermal conductivity of the substrates based on synthetic diamonds coated with tungsten carbide by the method of vapor deposition of tungsten carbonyl was in a region of $450 - 650 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The coefficient of thermal expansion CTE was in the range of $5.5 - 7.5 \cdot 10^{-6}/^{\circ}\text{C}$.



In this paper, we propose a three-step process for the synthesis of the heat-conducting metal-diamond composites based on synthetic diamonds and the impact diamonds by the methods of thermal sintering and hot-isostatic pressing.

2. Fabrication

The synthesis of conductive crystal holders (the substrates) is carried out in 3 stages: metallization of diamonds, thermal sintering of substrates and hot isostatic pressing of substrates. To avoid the formation of pores at synthesis of metal-diamond substrates (diamonds are difficult to wet by molten metals) [6] and to avoid processes of transformation of diamond into graphite at the high-temperature synthesis it is needed to cover diamond by metals such as tungsten, molybdenum, chromium, etc. These metals have a high melting point and can prevent the process of turning diamond into graphite at the formation of diamond/heat-conducting metal substrates.

2.1. Experimental setup for coated of diamonds

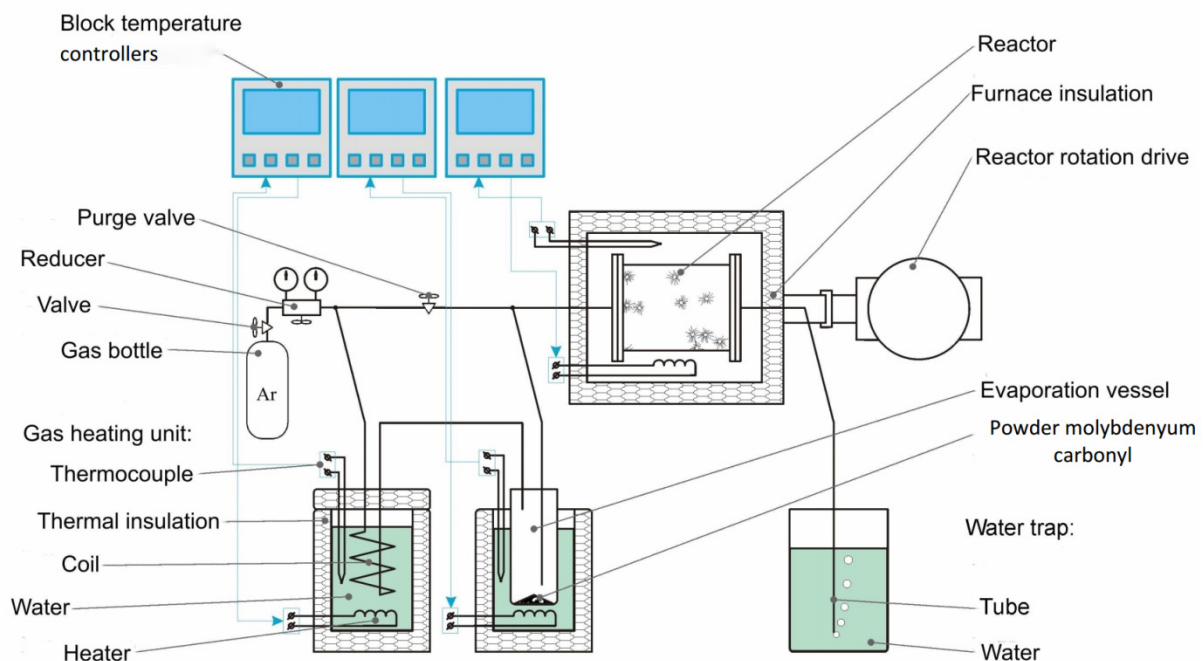


Figure 1. Diagram of the apparatus for applying coatings of molybdenum.

The diamonds sized 20 – 230 μm for synthetic ones and 50 – 100 μm for the impact ones are covered by molybdenum coating by the method of vapor deposition of molybdenum carbonyl (figure 1). The coating composition may vary within Mo-Mo₂C-MoC. The diamond coating process is described as follows: argon passes through a tube to a coil heated by a water heater. Heated argon enters an evaporation vessel, where gas and vapor of molybdenum carbonyl are mixed. Then, argon with vapor of molybdenum carbonyl moves into a reactor where diamonds are sited. The surface of diamonds is cleaned from dirt due to pre-heating. The reactor with diamonds is rotated by a reactor rotation drive, and diamonds are coated by the composition of Mo-Mo₂C-MoC. Then, unnecessary gas residues are removed into a water trap.

The use was made of initial synthetic diamonds (production of Guangdong Shuangling Diamond Industry Pty. Ltd.) and impact diamonds (Deposit Popigai impact structure, the Krasnoyarsk Territory, Yakutia).

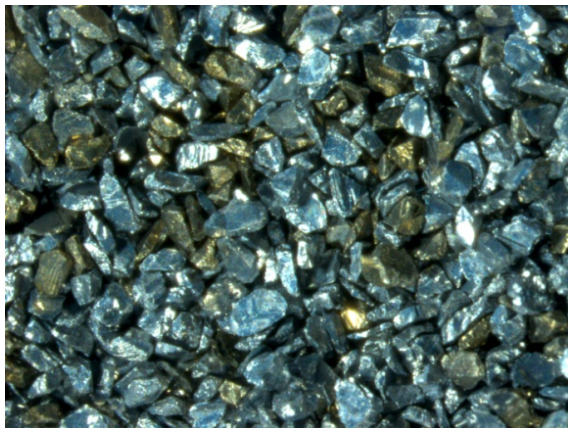


Figure 2. Covered synthetic diamonds.

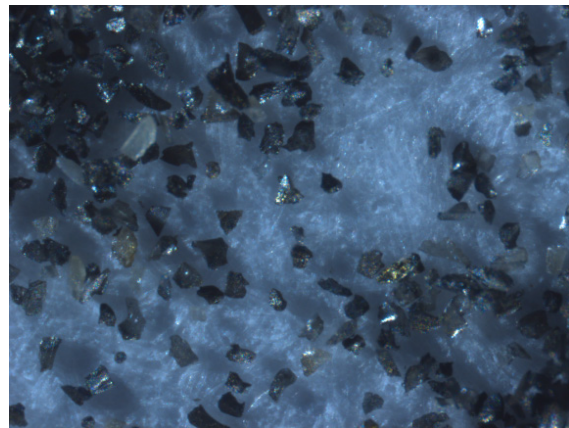


Figure 3. Covered impact diamonds.

2.2. Thermal sintering of substrates

Copper powder and diamonds are mixed in an agate mortar. The mixture of diamonds and copper is pressed under the pressure of 50 tons in a steel mold (the inner diameter is 25 mm) by a Metallkraft WPP 100 MBK hydraulic press (OPTIMUM, Germany). Then the pressed substrate is placed in a graphite mold with punches. The mold is placed in a vacuum furnace. Sintering of copper diamond substrates is occurred at 900 °C and pressure of 10^{-3} Pa for 1 hour.

The substrates based on synthetic and impact diamonds were obtained by thermal sintering of substrates (figure 4). The content of diamonds in the copper diamond composite was 30 – 45 weight percent.

2.3. Hot isostatic pressing of substrates

The sintering copper diamond composite substrate is placed in a graphite mold with punches (figure 5). This mold is placed in a hot isostatic press AIP6 – 30H. The substrates are melted at the temperature of 1050 °C and under the pressure of 200 MPa for 1 hour. The pressure was created by argon. The thickness of the melted copper diamond substrates is in the range of 0.5 – 1 mm. The surface of the substrates is smooth.

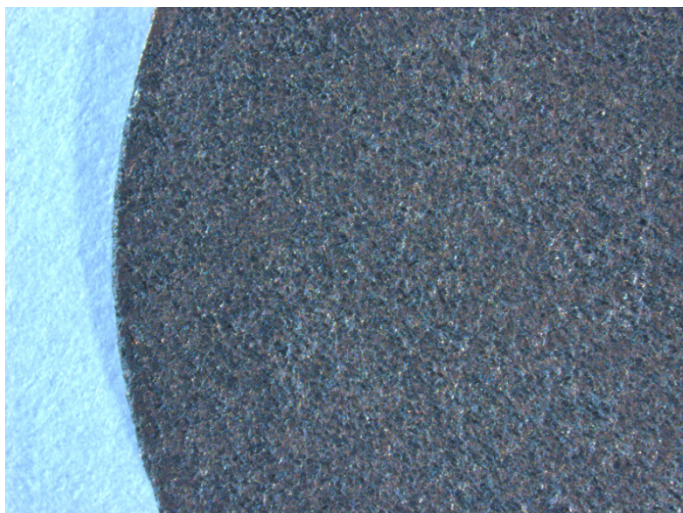


Figure 4. Thermal synthesized Cu/Diamond substrate.

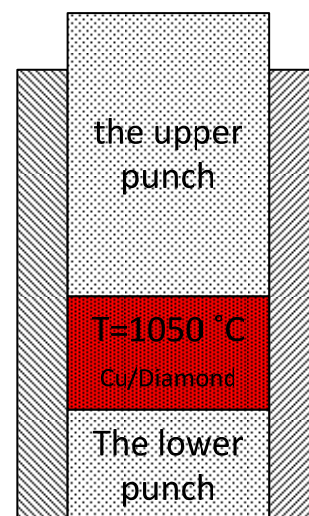


Figure 5. Press mold.

3. Results

The X-ray diffraction patterns (XRD) were recorded using a Thermo Scientific ARL X'TRA diffractometer with an angle range of $2\theta = 15 - 80^\circ$ at a step size of 0.05° and a time of 5 s.

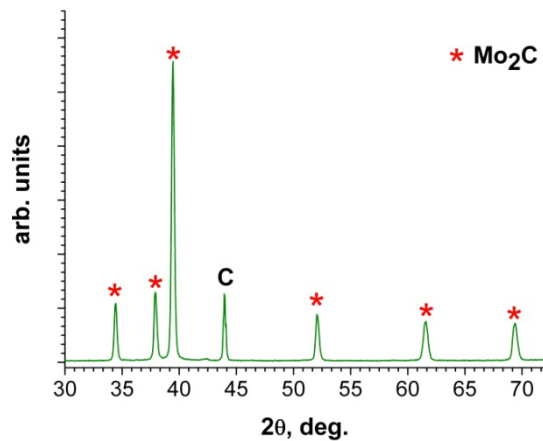


Figure 6. XRD of covered synthetic diamonds.

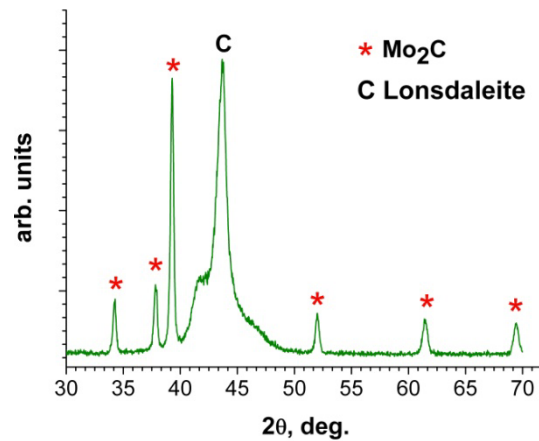


Figure 7. XRD of covered impact diamonds.

The X-ray diffraction analysis of synthetic (figure 6) and impact (figure 7) coated diamonds showed that synthetic coated diamonds have a diamond phase (cubic lattice $Fd3m$, $a = 3.559 \text{ \AA}$) and a phase of coating Mo_2C (a hexagonal lattice $P63/mmc$, $a = b = 3.006 \text{ \AA}$, $c = 4.733 \text{ \AA}$). The impact coated diamonds also have a phase of coating Mo_2C , but the phase of diamonds is a lonsdaleite phase (a hexagonal lattice $P63/mmc$).

The electron microscopy analysis by a TM-1000 electron microscope (Hitachi Science Systems Ltd.) determined that the covered synthetic diamonds (figure 8) have the developed morphology. The thickness of the coating of synthetic diamonds was estimated. It is located in the range of $0.1 - 0.3 \mu\text{m}$ (figure 8 left). The surface of impact diamonds has a porous structure, which is the reason of strong adhesion between the coating and the surface of diamonds.

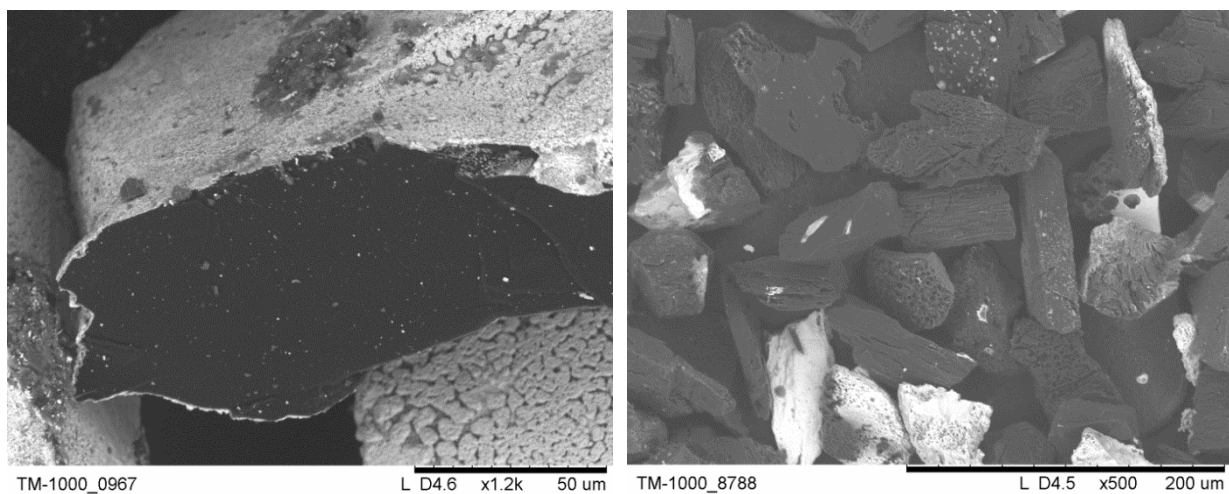


Figure 8. Electron microscopy of coated synthetic (left) and impact (right) diamonds.

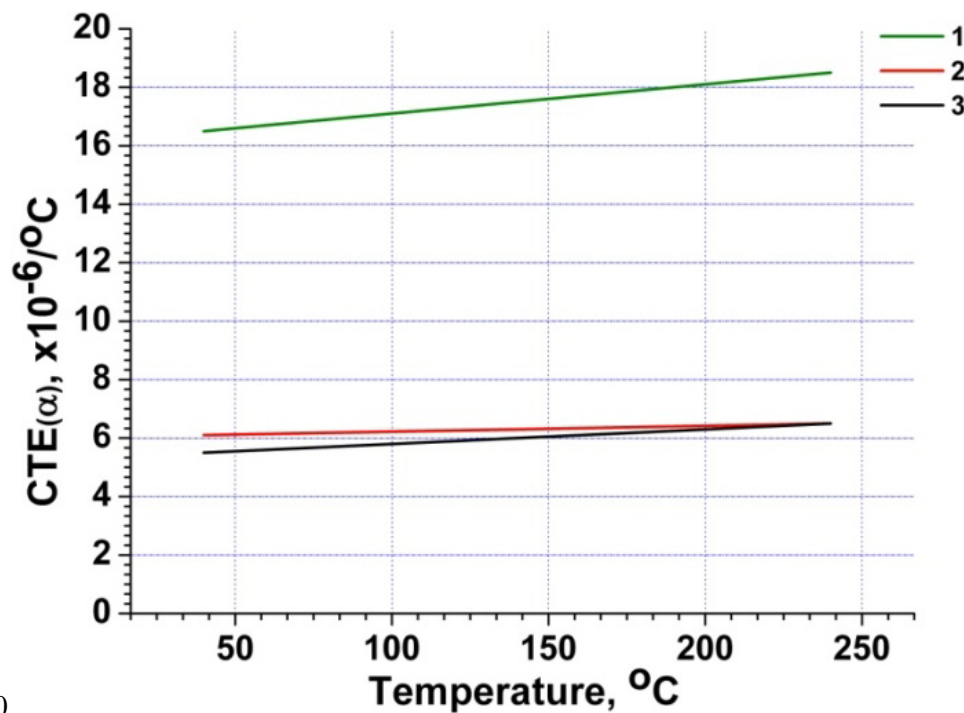


Figure 9. CTE of the samples. 1 – copper, 2 – copper with impact diamonds, 3 – copper with synthetic diamonds.

The thermal conductivity was measured by a Netzsch LFA 447 laser flash apparatus (Germany) using the laser beam pulse heating method. The thermal conductivity of copper diamond composites based on synthetic diamonds is in the range of $700 - 750 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The coefficient of thermal expansion (figure 9) was measured by a Netzsch TMA 402 F3 Hyperion thermomechanical analyzer in the temperature range of 293 – 600 K. The CTE parameter of the copper diamond composites based on synthetic diamonds is in the range of $6.4 - 6.5 \cdot 10^{-6} / ^\circ\text{C}$. The thermal conductivity of copper substrate was measured to be $400 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The coefficient of thermal expansion of copper substrate was measured to be in range of $16.5 - 18.3 \cdot 10^{-6} / ^\circ\text{C}$. The thermal conductivity of copper diamond composites based on synthetic diamonds is in the range of $850 - 900 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Perhaps, this is due to the fact that the thermal conductivity of impact diamonds is much higher than that of synthetic diamonds. Also, the structure of the impact diamond lattice and the Mo_2C coating are identical (a hexagonal lattice P63/mmc), whereas the synthetic diamond structure (a cubic lattice Fd3m) and the coating structure (a hexagonal lattice P63/mmc) are different. The CTE parameter of the copper diamond composites based on impact diamonds is in the range of $6.1 - 6.5 \cdot 10^{-6} / ^\circ\text{C}$.

4. Conclusions

The technological route for the fabrication of copper diamonds composites with a smooth surface is designed and demonstrated in the present study. The smooth surface of substrates has no significant irregularities and allows creating a compact contact between the substrate surface and the semiconductor material. The substrates can provide the efficient heat dissipation from electronic devices to prevent silicon and other semiconducting materials from overheating. The high thermal conductivity is the specific feature of copper diamond composite based on impact diamonds compared with copper diamond composite based on synthetic diamonds.

5. Acknowledgments

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