Journal of Achievements in Materials and Manufacturing Engineering

VOLUME 37
ISSUE 2
December
2009

CVD diamond: from growth to application

K. Fabisiak [a,*], E. Staryga [b]
[a] Institute of Physics, Kazimierz Wielki University,
pl. Weyssenhoffa 11, 85-072 Bydgoszcz, Poland
[b] Institute of Physics, Technical University of Łódź,
ul. Wólczańska 219, 90-924, Łódź, Poland
* Corresponding author: E-mail address: kfab@ukw.edu.pl

Received 20.09.2009; published in revised form 01.12.2009

Materials

ABSTRACT

Purpose: The main purpose of these studies was to give a short review of basic diamonds properties and indicate possibilities of different applications of this material. As an example, the application of CVD (Chemical Vapour Deposition) diamond layer in electrochemistry was shown.
Design/methodology/approach: The diamond layers were synthesized using Hot Filament CVD (HF CVD) technique from a mixture of methanol and hydrogen. The physical and electrochemical properties of the obtained layers were studied by Raman spectroscopy and Cyclic Voltammetry (CV).
Findings: It was shown that it is possible to synthesize the diamond layers of different morphology and quality. Raman microprobe measurements showed that quality of diamond films deposited by HF CVD method reflect their morphology. CV measurements showed that the fabricated electrodes had wide potential window almost twice bigger in comparison to the classical Pt electrode.
Research limitations/implications: The interaction of diamond layers with chemical and biological environment is not complete.
Practical implications: CVD diamond (synthetic diamond made by a chemical vapour deposition process) is an important family of materials used in microelectronic and optoelectronic packaging and for laser and detector windows. Its ultra-high thermal conductivity enables to increase microprocessor frequency and output power of microelectronic and optoelectronic devices. Diamond is resistant to chemical attack and chemical sensors based on the fact it can work in harsh environment.
Originality/value: The paper underlines an important role of diamond films as a promising material for production of electrodes for electrochemical applications.
Keywords: Nanomaterials; Diamond films; HF CVD method

Reference to this paper should be given in the following way:
K. Fabisiak, E. Staryga, CVD diamond: from growth to application, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 264-269.

1. Introduction

The ability to dissipate heat limits output levels of many high-power microelectronic and optoelectronic applications, such as radar and other radio-frequency (RF) devices, power semiconductors, laser diodes and light-emitting diodes (LEDs). It also controls frequency of microprocessor units (MPUs). In addition, thermal management affects device performance and reliability.

The thermal management problem places a premium on materials with high thermal conductivities. Some forms of diamond have thermal conductivities that are higher than that of any other thermal management material. In particular, polycrystalline diamond made by chemical vapour deposition (CVD) can have room temperature thermal conductivities as high as 2200 W/m·K, making it an attractive candidate for applications with high heat fluxes [1].

2. CVD diamond processes and products

Diamond, as a material, is known for its wide range of extreme properties. It offers ultra-high thermal conductivity, transparency across a variety of wavelengths, and is wear resistant, electrically insulating and chemically inert. A recent development in the field of diamond CVD led to a number of different types of methods which are capable of growing on various substrates. The common one of these methods is that the structure of diamond film strongly depends on the growth conditions (gas composition, substrate temperature and energy of particles). The presence of atomic hydrogen in the gas phase and in the layer of plasma sticking to the surface is responsible for several processes including growth formation creation of active species and abstraction of hydrogen from the surface [2].

Man-made polycrystalline CVD diamond films offer all outstanding characteristics of single crystal diamond without size and shape limitations of natural diamond. CVD diamond is a family of materials with process-dependent properties. Diamond plates can be made by a variety of CVD processes, including hot filament, microwave plasma, DC plasma, plasma jet, arc discharge, laminar oxy-acetylene flame, and turbulent oxy-acetylene combustion [3].

Polycrystalline diamond via a CVD process is grown into substrates, typically refractory metal or Si, although other substrate materials can be also used. Typical morphologies of polycrystalline diamond films prepared by HF CVD method are shown in Fig. 1. As it is seen from scanning electron micrographs shown in Fig. 1 the diamond layer can have different morphology starting from diamond layer composed of very small (below 1 μm) crystallites (Fig. 1a) to diamond layer composed of a well-faceted microcrystals (Fig. 1d) with a nominal crystallite size of ~10 μm, or even greater.

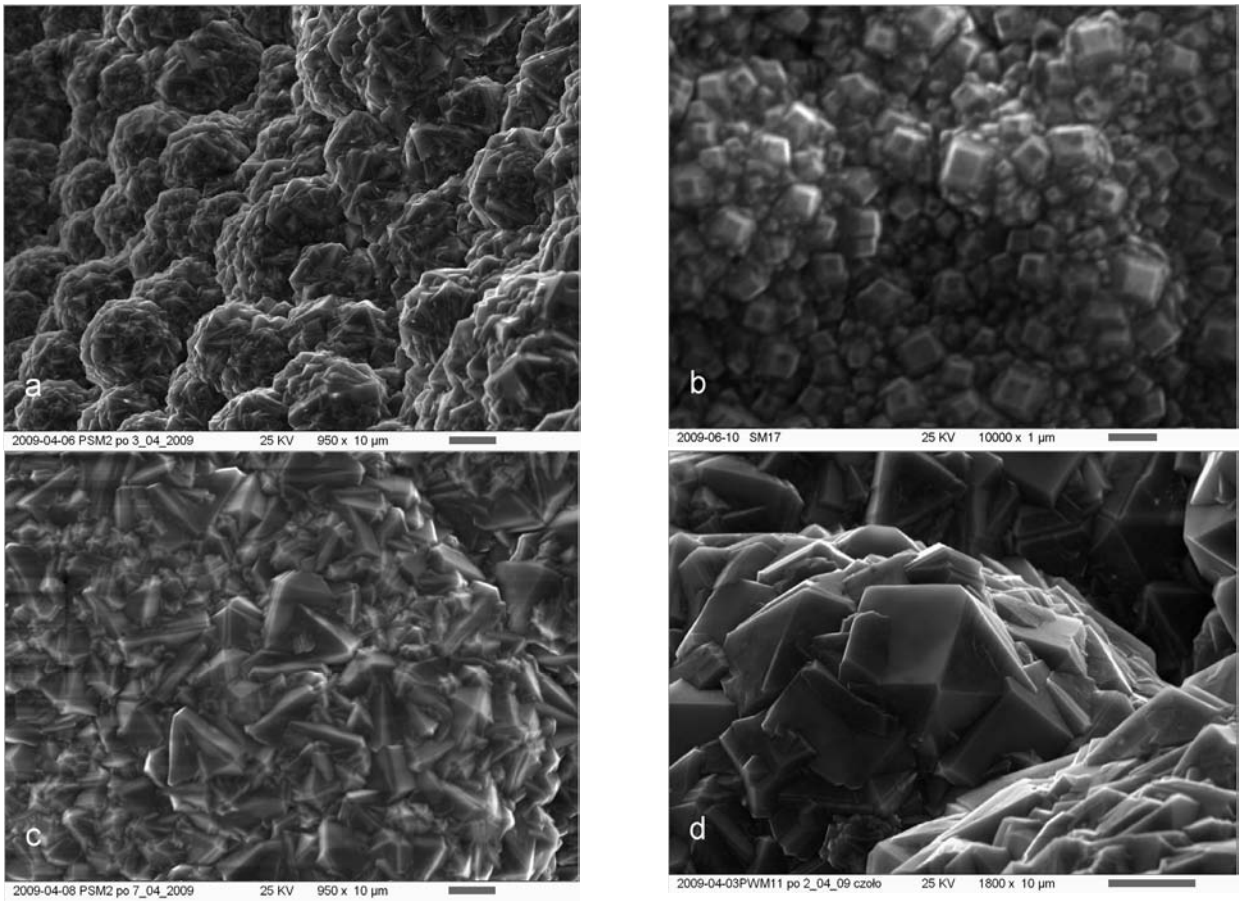

Fig. 1. SEM pictures of diamond layers deposited by HF CVD method

The example of a diamond layer cross-section (Fig. 2) reveals a columnar growth structure, which is typical for diamond films deposited by CVD methods and reflects the van der Drift growth mechanism [4]. Fig. 1b allows for estimation of diamond film thickness which is about 10 μm.

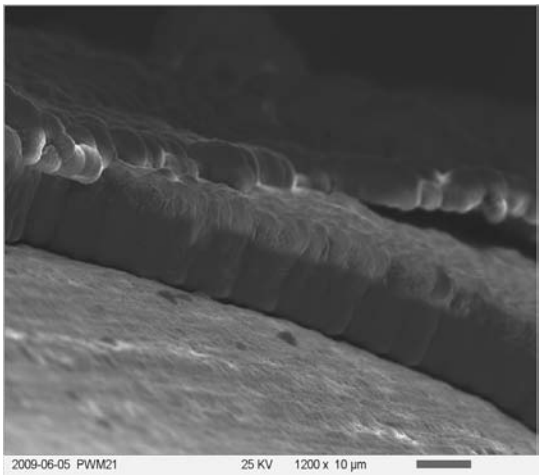

Fig. 2. Cross section of polycrystalline diamond film

Raman microprobe measurements showed that quality of diamond films deposited by HF CVD method reflect their morphology [5].This technique is widely used as a diagnostic tool for evaluation of diamond and CVD diamond films [6]. In order to estimate the CVD diamond films quality their Raman spectra are compared to that of single diamond crystal. The Raman spectrum of diamond monocrystal is characterized by sharp line at 1332.5 cm^{-1} (Full Width at Half Maximum equal 2 - 2.5 cm^{-1}) at a flat background [7].

The Raman spectra of diamond layers from Fig. 1a and Fig. 1d are presented in Fig. 3. As it is seen from presented Raman spectra the diamond layer of the morphology shown in Fig. 1d is characterized by sharp diamond Raman line on a flat background indicating on high quality diamond film. The Full Width at Half Maximum (FWHM) is equal 4.9 cm^{-1}. The Raman spectrum (Fig. 3a) of diamond layer shown in Fig.1a is characterized by much broader diamond Raman line (FWHM ≈ 9.6 cm^{-1}) and additionally, a broad band with maximum at about 1580 cm^{-1} is also clearly seen. This indicated that diamond layer, except diamond phase, contains some admixture of amorphous carbon phase [5]. This diamond layer is of a lower quality in comparison to the previous one.

Depending on quality and requirements, the diamond growth can be tailored to the specific application, which results in a range of products from tool-grade material with high fracture toughness to high clarity optical window material suitable for FTIR spectroscopy. Adjustments in growth conditions produce parts with thickness varying from about a half a micron to over a millimetre.

3. Properties of thermal management and laser window materials

In recent years, there were a number of new monolithic, composite materials and nanomaterials [8, 9] developed to meet increasing microelectronic and optoelectronic heat dissipation issues [10 - 12]. Only one, highly-oriented pyrolytic graphite (HOPG) has a thermal conductivity approaching that of CVD diamond. Although some forms of HOPG have high in-plane thermal conductivities, through-thickness values are extremely low. All forms are electrically conductive.

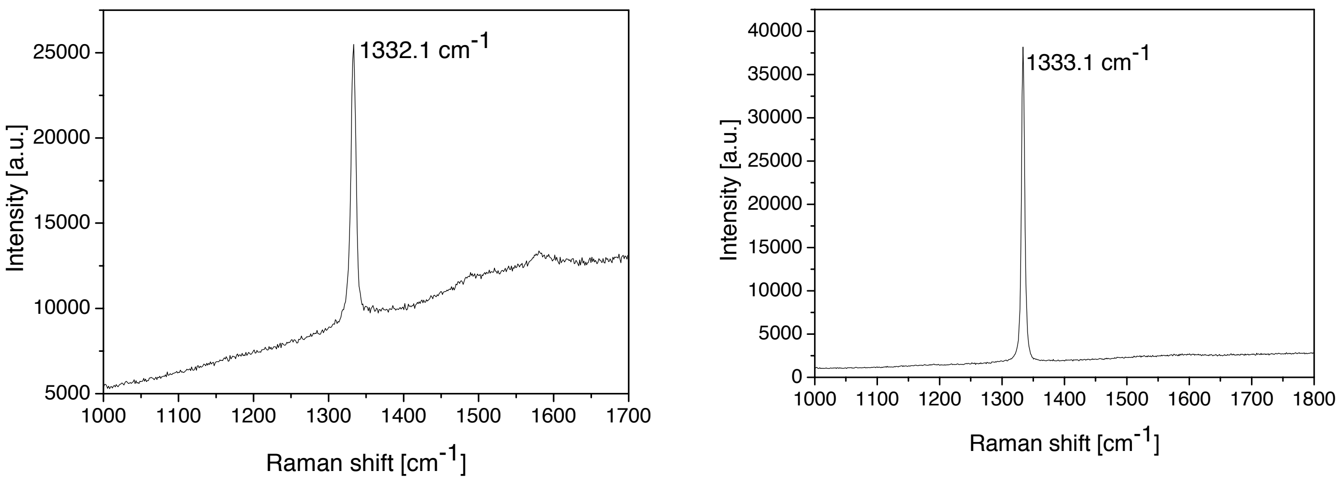

Fig. 3. Raman spectra of the diamond layers from Fig. 1a and Fig. 1d respectively

The CVD diamond films are somewhat anisotropic, with through-thickness thermal conductivities somewhat higher than in plane values. Some forms of CVD diamond are optically transparent, making it an attractive material for applications requiring both this property and high thermal conductivity. The thermal conductivity differences between that of CVD diamond and those of other packaging materials is particularly severe for electrically insulating materials. Table 1 presents properties of electrically non-conductive materials used in microelectronic and optoelectronic packaging. As discussed, CVD diamond is slightly anisotropic, and through-thickness values are presented. Table 1 clearly shows the significant advantage of CVD diamond over the other dielectric materials. This is particularly true when optical transparency is required, because materials like glasses, acrylics and zinc selenide have low thermal conductivities. Table 2 presents the properties of CVD diamond and electrically conducting materials used in microelectronic and thermoelectric packaging. Here, again, CVD diamond has a significant advantage over competing materials, except for HOPG, which is strongly anisotropic. Its through-thickness thermal conductivity is only about 25 W/m·K.

Table 1.
Properties of selected electrically insulating materials used in microelectronic and optoelectronic packaging and laser windows [13]

Material	Thermal Conductivity	CTE	Density
CVD Diamond	500-2200	1.0-2.0	3.5
Alumina (96%)	20-35	6.0-7.1	3.7-3.9
Aluminum Nitride	60-250	3.5-5.7	3.2-3.3
Beryllia	254-275	5.9-9.0	2.9
Quartz	3	0.5-1.0	2.2
Glass-Ceramics	1.7-3.5	0.4-5.8	2.5-2.6
Zinc Selenide	16-18	7.6	5.3
FR-4 PCB	0.3	12-24	1.7

Table 2.
Thermal properties of CVD diamond and selected electrically conductive materials used in microelectronic and optoelectronic packaging ([1]Though-thickness, [2]In plane) [12]

Material	Thermal Conductivity (W/m·K)	CTE (ppm/K)	Density (g/cm^3)
Copper	400	17	8.9
Aluminum	218	23	2.7
HOPG	1300-1700[2]	-1.0[2]	2.3
Natural graphite	150-500[2]	-	-
Silicon/aluminum	126-160	6.5-17	2.5-2.6
SiC particle/aluminum (Al/SiC)	170-220	6.2-16.2	2.8-3.0
Beryllia particle/beryllium	240	6.1	2.6
Natural graphite/epoxy	370[2]	-2.4[2]	1.94
Continuous carbon fibre/aluminum	330[2]	-1[2]	1.8
Discontinuous carbon fibre/copper	300[2]	6.5-9.5[2]	6.8
Continuous carbon fibre/SiC	370[2]	2.5[2]	2.2
Continuous carbon fibre/copper	400-420[2]	0.5-16[2]	5.3-8.2
Continuous carbon fibre/carbon	400[2]	-1.0[2]	1.9
Continuous carbon fibre/SiC	370[2]	2.5[2]	2.2
Diamond particle/aluminum	550-600	7.0-7.5	3.1
Diamond particle/copper	600-1200	5.8	5.9
Diamond particle/cobalt	>600	3.0	4.12
Diamond particle/SiC	600	1.8	3.3

We note that the density of CVD diamond is much lower than that of most packaging materials, which is important in weight-critical applications, such as aircraft and spacecraft electronic systems, notebook computers and other mobile devices. In addition, density is important even for stationary applications, because stresses arising from shock loads during shipping (50 g is a common requirement) depend directly on component mass.

Another unique characteristic of CVD diamond is that some forms have extremely high elastic moduli, which range up 1050 GPa, compared to 70 GPa for aluminum [14]. It is also one of the hardest known materials.

Coefficient of thermal expansion (CTE), another important packaging material property, it allows to construct devices working with high heat fluxes. This property is also important for high power laser windows applications.

4. Applications

CVD diamond is used in a large number of microelectronic, optoelectronic and specialty applications [15], including: laser diode, laser crystal cooling, microwave device and power semiconductor heat spreaders, submounts and substrates [16-18]. In one case, it was an enabling material for reduction of multi-chip power module packages size [16], and flip chip packaging has increasingly incorporated diamond into the design.

The exceptional broad band infrared, terahertz and ultraviolet transparency of diamond combined with its low scatter makes it highly applicable in optical applications. The unique combination of optical transparency and high thermal conductivity led to use CVD diamond in a variety of applications requiring these properties. For example, CVD diamond windows are used in short-wave UV, infrared, CO_2 laser exit windows and output couplers and high-power microwave devices [17]. The parts can be anti-reflection coated for further transparency increase. These windows can be supplied as free-standing parts or mounted to a flange.

The properties of diamond are increasingly utilized in high energy research for both detection and imaging applications. As a detector material, diamond's key characteristics include beam resistance, fast response and low noise. The radiation resistance of CVD diamond led to its use in particle physics detectors [17] and millimetre-wave vacuum edge-cooled windows for electron cyclotron heating in thermonuclear plasma fusion energy research [1]. also found its use as lenses, monochromators and beam s Diamond splitters.

High-power military and space applications, challenged for size and weight found diamond to be a useful material. CVD diamond also found its way into the designs of RF Power packages, amplifiers, radar devices and infrared cameras.

5. Applications in electrochemical processes

In the recent past, the electrochemical research focused a lot on anode development in order to improve the electrochemical efficiency of the process. Discoveries concerning the deposition and the electrochemical properties of synthetic thin films of diamond opened a new branch of electrochemistry. Fig. 4 shows the SEM image of working electrode head covered with diamond used in cyclic voltammetry [18]. The results of cyclic voltammetry measurements show that diamond electrode on platinum is electrochemically stable in KCl electrolyte over a wide potential range (-3000 mV to 2000 mV). Pleskov et al. [19] showed that electrodes formed from polycrystalline diamond possess physical properties similar to those of bulk diamond including: hardness and resistance to chemical attack. It was demonstrated that the wide potential window at diamond electrodes can be used in the generation of ammonia from aqueous nitrate solutions [20].

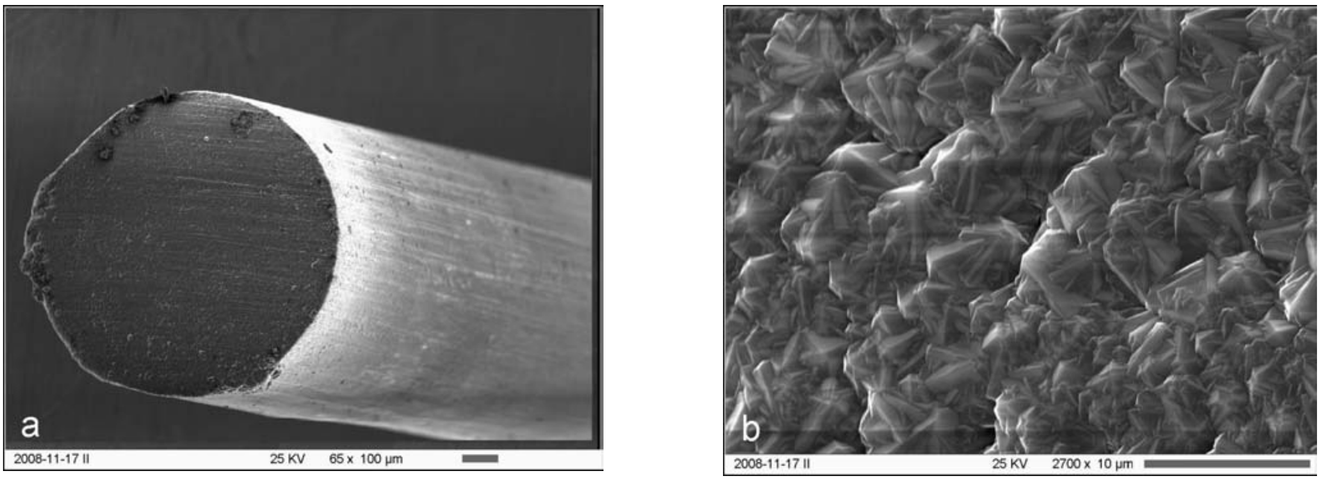

Fig. 4. SEM image of working electrode head covered with diamond films: (a) general view, (b) details of diamond film morphology

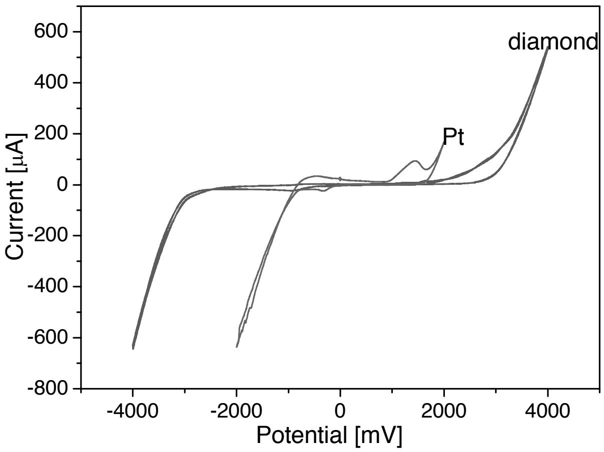

Fig. 5. Cyclic voltammograms registered by Pt and diamond electrodes in 0.025M NaCl at a scan rate of 200 mV/s

In Fig. 5 there are voltammographs presented recorded by Pt and diamond elelectrodes. The good electrode should fulfil two main conditions: a/ should have wide potential window and b/ low background current. As it is clearly seen (Fig. 5) diamond electrode fulfils both conditions: shows almost twice broader potential windows and lower background current in comparison to the same parameters obtained for classical Pt electrode.

6. Summary and conclusions

CVD diamond is a family of materials that has unique combinations of properties, including ultra-high thermal conductivity, optical transparency and very high elastic modulus and hardness. This led to increasing application in micromechanical, opto-mechanical heat spreaders, laser windows and other applications. Because material cost increases along with increasing properties and material volume, it is important to define requirements carefully, using finite element models. As production volumes increase, cost will decrease, encouraging greater use of this important class of materials.

References

[1] M. Thumm, MPACVD-diamond windows for high-power and long-pulse millimetre wave transmission, Diamond and Related Materials 10 (2001) 1692-1699.

[2] A. Badzian, T. Badzian, X.H. Wang, T. Hartnett, Growth Sectors of CVD Diamond, Proceedings of the International Conference "New Diamond Science and Technology", Washington, 1990, 549-556.

[3] D. Choudhary, J. Bellare, Manufacture of gem quality diamonds: a review, Ceramics International 26 (2000) 73-85.

[4] A. Van Der Drift, Evolutionary selection, a principle governing growth orientation in vapour- deposited layers, Philips Research Reports 22 (1967) 267-288.

[5] K. Fabisiak, W. Masierak, E. Staryga, M. Kozanecki, The Diamond Films and Single Diamond Micro-crystals Studied by Micro-Raman Spectroscopy, Optical Materials 30 (2008) 763-766.

[6] B.S. Prawer, R.J. Nemanich, Raman spectroscopy of diamond and doped diamond, The Philosophical Transactions of the Royal Society A 362 (2004) 2537-2565.

[7] S.A. Solin, A.K. Ramdas, Raman spectrum of diamond, Physical Review B 1/4 (1970) 1687-1698.

[8] S. Mitura, Nanodiamonds, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 166-171.

[9] S. Mitura, K. Mitura, P. Niedzielski, P. Louda, V. Danilenko, Nanocrystalline diamond, its synthesis, properties and applications, Journal of Achievements in Materials and Manufacturing Engineering 16 (2006) 9-16.

[10] C. Zweben, Electronic Packaging: Heat Sink Materials, in: Encyclopaedia of Materials: Science and Technology, Vol. 3, Elsevier Science, Oxford, 2001, 2676-2683.

[11] C. Zweben, Ultrahigh-Thermal-Conductivity Packaging Materials, Proceedings of the "Semiconductor Thermal Measurement and Management Symposium" SEMI-THERM 21, San Jose, 2005.

[12] C. Zweben, High-Performance Thermal Management Materials, Advanced Packaging February (2006).

[13] K.A.A. Johnstone, PhD thesis, University of London, 2000.

[14] Y. Gurbuz, Diamond semiconductor technology for RF device applications, Solid State Electronics 49 (2005) 1055-1070.

[15] J. Grabarczyk, D. Batory, P. Louda, P. Couvrat, I. Kotela, and K. Bakowicz Mitura, Carbon coatings for medical implants, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 107-110.

[16] A.P. Malshe W.D. Brown, Diamond Heat Spreaders and Thermal Management, in: Diamond Films Handbook, Marcel Dekker Inc, New York, 2002.

[17] E.J. Lerner, Industrial Diamonds Gather Strength, The Industrial Physicist August/September (2002) 8-11.

[18] E. Staryga, R. Torz-Piotrowska, A. Wrzyszczyński, K. Paprocki, J. Szmidt, Diamond Electrodes Produced by HF CVD Method for Electrochemical Applications, Proceedings of the 6th International Exhibition of Inventions, Suzhou, China, 2008, 122.

[19] Yu.V. Pleskov, M.D. Krotowa, V.I. Polyakov, A.V. Khomich, A.J. Rukovischuikov, B.L. Druz, I. Zaritsky, Electrochemical behaviour of a-C:N:H films, Journal of Electroanalytical Chemistry 519/1-2 (2002) 60-65.

[20] R. Tenne, K. Patel, H. Hashimoto, A. Fujishima, Efficient Electrochemical Reduction of Nitrate to Ammonia Using Conductive Diamond Film Electrodes, Journal of Electroanalytical Chemistry 347 (1993) 409-415.