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Chapter

Development, Properties, and Applications of CVD Diamond-Based Heat Sinks

José Vieira da Silva Neto, Mariana Amorim Fraga and Vladimir Jesus Trava-Airoldi

Abstract

Heat sink is an essential component to nanoelectronics, microelectronics, and optoelectronics applications because it allows the thermal management of devices such as integrated circuits (ICs), microelectromechanical systems (MEMSs), and graphic unit processing. There are different materials being employed for heat sink production. Among them, diamond has stood out due to its excellent chemical and physical properties. This book chapter focuses on the development, properties, and applications of CVD diamond heat sinks. It covers the basic concepts of heat conduction applied to CVD diamond as a heat sink material and its production as freestanding CVD wafers of polycrystalline CVD diamond, since the literature about this topic is extensive, giving the reader a comprehensive overview. We will comprise the use and potential widening of applications of in CVD diamond heat sink technology, providing the reader with a substantial background at the current development of solutions and new frontiers in the practical use of CVD diamond thermal management devices.

Keywords: CVD diamond, deposition, heat sinks, thermal management, freestanding diamond films

1. Introduction

Diamond is widely known as the best thermally conductive material in nature, despite having no electrical conductivity when free of dopant impurities, its unique combination of lattice configuration and strong covalent electronic bonds result in a great capacity of heat conduction through phonons. This type of heat flow also occurs in some other insulating materials, in the form of waves and wave packets [1]. Combined with its low dielectric loss, low friction coefficient, transparency for a large range of light spectrum, high hardness, and chemical inertness, diamond is certainly an exceptional material choice [2]. This set of specific properties makes diamond an ideal candidate for use in thermal management tools, especially heat management deviecs [3]. Unfortunately, there are still limiting factors for this technology, as for example, limited size substrate and impurity control besides low availability of natural diamond. In recent years, the synthesis of diamond in the laboratory has been widely studied and improved and large-scale industrial facilities were developed around two major technologies of synthetic diamond production,

known as high pressure and high temperature (HPHT) and chemical vapor deposition (CVD) [4, 5]. HPHT produces single crystalline synthetic gems similar to natural diamond. However, size availability and control of impurities, such as substitutional atoms of other elements and nondiamond carbon inclusions, are limitations of this method [6]. It is not uncommon to find HPHT diamond with a yellow to brown hue, characteristic of the absorption of C-defects or nitrogen impurities [7, 8]. On the other hand, CVD diamond synthesis takes advantage of the capability of producing polycrystalline films, which present closely the same properties of single crystal diamonds, with the possibility of deposition over nondiamond substrates and large deposition areas [9]. Additionally, this method provides better control over impurities and doping once it is based on the breakdown of hydrocarbon molecules inside a controlled atmosphere chamber [10]. Currently, the CVD diamond industry is evolving fast, with larger area of deposition and in the high growth rate for single- and polycrystalline CVD diamond, but many efforts are still being made in order to achieve larger areas, thickness, and quality uniformity [11]. The main prerequisite for CVD diamond films to be applied as heat sink components is that thicker freestanding films with good uniformity should be grown through a reasonable large area [12]. Thick films are easily laser cut and polished to nanometer level smoothness of the surface. However, an additional issue is that polycrystalline films present some fragility caused by grain boundaries, an additional issue to deal with [13, 14]. In high power or high frequency electronic applications, with the increasing switching speed of components, the heat generated consequently increases, leading to higher thermal power densities to dissipate which is also affected by the size reduction of electronic components, creating a growing demand of performance for heat management components [15]. However, good thermal conductivity is not the key by itself, to an adequate heat extraction system, a good homogenous contact between heat generating component and heat sink is crucial to rapidly conduct excess heat and suppress the formation of "hot spots" which critically decreases the performance and efficiency of electronic devices [13, 16].

Since the 1960s, studies have reported the use of diamond heat sink. In 1967, Swan mounted silicon avalanche diodes on diamond to achieve a continuous power density more than twice that found on copper [17]. That same year, Dyment and D'Asaro achieved continuous operation of GaAs junction lasers at a heat sink temperature of 2000 K using diamond heat sinks [18]. In 1968, Josenhans discussed diamond as an insulating heat sink for a series combination of IMPATT diodes [19]. In a subsequent study, Decker and Schorr demonstrated that the performance of IMPATT diodes is significantly improved using diamond heat sinks [20].

Between the 1970s and 1980s, more theoretical and experimental studies were published on diamond heat sinks. In 1972, Bernick calculated the steady-state temperature profile and thermal-spreading resistance for a uniform heat source on a semi-infinite type IIa-diamond heat sink [21]. Also in 1972, Russell and Thomson described a new technique for diamond heat sink fabrication based on diamond embedded in a copper rod [22]. In 1976, Hudson measured the thermal resistivity of diamond heat-sink bonds in the form of sputtered titanium and gold films at temperatures from 1.2 to 300 K [23]. In 1977, Burgemeister showed the practical improvements obtained in the use of diamonds as heat sinks comparing the thermal resistances of samples with various kinds of metal/diamond interface measured at about 400 K with a radiation detector [24]. In 1979, Ino et al. fabricated 80 GHz band silicon d.d.r. Impatt diodes with diamond heatsinks [25].

In the 1980s, the researches on diamond for electronics continued to be motivated by the use of diamond heat sink substrates for semiconductor device applications. In 1984, Leistner fabricated a high-power silicon pnn + impatt diodes by a simple diffusion process for operation on diamond heat sinks [26]. In 1988, Doting

and Molenaar developed a mathematical model of a copper-supported diamond heat sink using an iterative scheme to compute the temperature and flux distribution at the diamond-copper boundary [27]. In 1990, Csanky reported a thermal model of double-drift IMPATT diodes on diamond heat sinks. This thermal model approximates the temperature-dependent thermal conductivities of Si and diamond (Type II) by means of simple empirical formulae [28].

In early 1990s, Ramesham et al. reported a novel method of fabrication of microchannels in synthetic polycrystalline diamond thin films for heat sinking applications [29]. In 1993, Beck et al. discussed the maximum temperatures in diamond heat spreaders using the surface element method [30]. Subsequently, the enhanced performance in GaAs TUNNETT diode oscillators above 100 GHz through diamond heat sinking and power combining was reported by Eisele and Haddad [31]. An interesting study on a novel cooling system for high-power laser-diode arrays using microchannels in CVD diamond was developed by Goodson et al. They proposed a system which uses a microchannel heat sink made of chemical-vapor-deposited diamond in order to reduce the array-to-coolant thermal resistance using a simple model for the combined conduction and convection problem [32]. In 1999, Bewley et al. demonstrated a high-temperature continuous-wave laser with diamond-pressure-bond heat sinking [33].

From the 2000s to the present, an increase in the number of publications related to diamond-based heat sinks has been observed. In 2003, Labudovic and Burka developed a three-dimensional finite element model of heat transfer and residual stress within high-power laser diodes and their heat sinks. The model addresses both p-side down and p-side up laser diodes mounted on a variety of commercially available gold plated diamond heat sinks [34]. In 2006, Jessen et al. reported the operation of AlGaN/GaN high-electron mobility transistors (HEMTs) atomically attached to a CVD diamond substrate. The results demonstrated the feasibility of producing GaN-based devices on polycrystalline CVD diamond substrates to maximize heat extraction from devices operating at high power [35]. In 2008, Schneider et al. reported a study on CVD polycrystalline diamond films for heat sink applications. The measurements of dielectric strength confirmed the potential of CVD diamond for thermal management in power electronics [36]. Still in 2008, Ekimov et al. reported the thermal conductivity of diamond composites sintered under high pressures [37]. In 2010, Parashchuk et al. reported that the use of diamond heat sinks extends the drive current range of pulsed diode bars by a factor of 2-3 and enables them to operate at more than one order of magnitude [38]. In 2018, Rogalin et al. discussed several applications of diamonds in high-power optics and electronics. The main features of diamond optics of heat sinks for high-power electronics were highlighted [3].

This chapter focuses on the application of CVD diamond in heat sinks. It covers three main aspects of this technology: (i) heat transfer in diamond, (ii) CVD diamond heat sinks, and (iii) free-standing CVD diamond wafers. The first explains the mechanisms of heat transfer in diamond and correlates to its properties. The second introduces the principles and concepts related to diamond heat sinks. Finally, we briefly introduce the prospects of development and processing of CVD diamond wafers.

2. Heat transfer in diamond

Heat can be understood as the transfer of some quantity of movement between particles, whether inside a solid, liquid, or gas. This transfer can be mediated by different physical mechanisms, such as vibrational waves in the lattice of solids, known as phonons, free electrons, fluidic particles, and photons. Particularly for solids, the kinetics of heat transfer is in its majority caused by free electrons moving through the bulk material for conductors and by vibrational waves through the lattice for insulator compounds [1].

Diamond is a unique case when it comes to heat transfer, the nature of carbon covalent bonding of the structure results in a strong interaction between atoms. Carbon has four electrons in its valence band which in the fundamental energy state are distributed as $2s^2$, $2p_x^1$, $2p_y^1$, so it is natural to think that it would only form two bonds with other atoms. However, with the addition of sufficient energy, a special configuration can be achieved, promoting an electron from an sorbital to an empty p orbital, a phenomenon named sp³ hybridization resulting in a $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$ distribution and allowing four bonds with other atoms. This promotes the characteristic tetrahedral organization of the atoms in the diamond lattice [39].

Upon those characteristics combined with light atomic mass, phonons inside this material lattice possess extremely high frequencies and acoustic velocities; moreover, phonon-phonon umklapp scattering around room temperature is low [40], this phonon scattering being the cause of thermal resistance [41].

In dielectric crystals, thermal conductivity reaches a maximum depending on temperature, and for diamond, this maximum is reached near 100 K for pure natural type IIa single crystals, increasing at \sim T³ rate from lower temperatures until this peak and then decays as the temperature continues to rise since umklapp scattering begins to activate [42].

The general approach considers an analogy from gas conductivity as follows in Eq. (1) [43]:

$$\kappa = \frac{1}{3}CV\Lambda \tag{1}$$

where κ is thermal conductivity, C is the specific heat, V is phonon velocity, and Λ is the mean free path for phonons in the solid; the mean free path is a function of many factors, and scattering of phonons can be induced by other phonons, by the walls of the crystal, grain boundaries, chemical impurities, vacancies, dislocations, and isotopes [43].

The specific heat or heat capacity per unit mass C, and thermal diffusivity D can be related to the thermal conductivity through the material mass density ρ , described in Eq. (2):

$$\kappa = \rho \text{CD}$$
(2)

Thermal diffusivity governs the transient response to heat input. It is often more easily measured than thermal conductivity, which governs steady-state response. Nontheless, thermal conductivity is the usually required property of interest in heat management applications [44].

With a rising temperature, thermal conductivity rises, but as there are more phonons to transport heat and as this population of phonons rises, the probability of phonon-phonon interactions also rises leading to higher probabilities of phonon decaying into other frequency phonons; this process will be dominant in any kind

¹ Umklapp Scattering: first described by Rudolf Peierls, in a general manner, umklapp scattering differs from normal phonon-phonon scattering in momentum conservation, the first does not conserve phonon momentum while normal process conserves it; Maznev and Wright discuss in-depth nuances in a more recent work, where they shed some new light on this scattering mechanisms and suggest other parameters to determine differences between these two processes; once as stated by these authors, "conservation of momentum" can cause some confusion and may be inaccurate to describe the phenomenon.

of diamond at sufficiently high T. For intermediate temperatures, scattering time τ is determined by impurities or other crystalline imperfections in diamond, such as isotope disorder. For temperatures below 100 K, only low frequency phonons are thermally excited; for this case, the dimensions of the sample are significantly more important as they determine τ [45], what explains for example, the anisotropy of κ in polycrystalline diamond films. In large, high quality diamond single crystals, phonon scattering that causes thermal resistance is predominantly caused by phonon-phonon and phonon isotope scattering [43].

In their work, Morelli et al. used an approach based on the Debye model to predict and analyze thermal conductivity of CVD diamond films produced by HFCVD and MPACVD. With this model and experimental data, they reported values ranging from 1200 to 1500 W m $^{-1}$ K $^{-1}$ at room temperature, reaching a peak at 220–250 K for HFCVD films, and ~1400 W m $^{-1}$ K $^{-1}$ for MPACVD film with a peak at 170 K [46].

Debye temperature indicates the temperature for which the occupation number of optical phonons becomes significant, indicating the crystal's highest normal mode of vibration [1, 47]. In diamond, it is 2200 K [48] and this high Debye temperature is what gives diamond low thermal resistance and low expansion coefficient.

2.1 CVD diamond thermal properties

For CVD diamond, the success as a heat sink or heat spreader device is influenced by grain size and point defect scattering of the deposited film. In addition, it is also affected by the distance from the nucleation side of the films [49–52].

The thermal properties are also influenced by the C-H bonding in the deposited layer because the process of thermal conductivity in diamond is controlled by phonon scattering rate on different kinds of defects, grain boundaries and phonon-phonon interactions. Since hydrogen decorates the defects, hydrogen concentration is a convenient indicator of imperfections in CVD diamond, as well as the isotopical nature of carbon [42]. The natural occurrence of carbon stable isotopes in diamond ¹²C and ¹³C is 98.9, and 1.1%, respectively; the enrichment of the isotopic ¹²C carbon up to 99.9% has showed to enhance the thermal conductivity of diamond at room temperature by nearly 50%, and calculations made from Callaway's theoretical model shows that a 99.999% ¹²C isotope content should enable a thermal conductivity higher than 2000 W/mK [43, 53]. **Table 1** demonstrates this variance with a comparison between common heat sink materials and natural and CVD diamond, emphasizing the variety of reported thermal conductivities for different kinds of CVD diamond films, depending on its production method and chemical nature.

Within this set of data, it is interesting to notice that some CVD diamond films with impaired quality by defects or smaller grain size present a still higher thermal conductivity at room temperature when compared to conventional metallic materials.

However, diamond is a homopolar solid. It is of primary importance to notice that thermal conductivity values change depending on which direction heat flows in CVD diamond films; this is due to a singular characteristic of this material. The CVD of diamond produces significantly high quality diamond thin films but the initial ~100 nm of grown material at the nucleation side of the film, also called coalescence layer, contains a higher density of grain boundaries due to smaller grain size what usually reduces thermal properties due to higher nondiamond carbon content; in addition, the columnar structure of films causes a sensible anisotropy of thermal conductivity, being higher in growth direction when compared to bulk crystals [12, 49, 55]. This difference between in-plane ($\kappa\parallel$) and perpendicular ($\kappa\perp$)

Thermal conductivity (W/mK)	Thermal expansion (10 ⁻⁶ /K) [*]	Reference
247	23.8	[54]
398	16.8	[54]
2200	0.8–1.0	[49]
790–1800 (varying with C-H bonding)	1.0–1.5	[42]
141		[55]
551		[56]
950 (double layer, MPACVD)	기())(-	[57]
1000		[58]
700–2100		[49]
1000–1500 1200–1500 (HFCVD) and 1400 (MPACVD)	_	[59]
	_	[46]
1000–2000 (varying with film quality)	_	[60]
80–800	_	[51]
7.8–26	_	[56]
	247 398 2200 790–1800 (varying with C-H bonding) 141 551 950 (double layer, MPACVD) 1000 700–2100 1000–1500 1200–1500 (HFCVD) and 1400 (MPACVD) 1000–2000 (varying with film quality) 80–800	(10 ⁻⁶ /K)* 247 23.8 398 16.8 2200 0.8–1.0 790–1800 (varying with C-H bonding) 141 551 950 (double layer, MPACVD) 1000 700–2100 1000–1500 1200–1500 (HFCVD) and 1400 (MPACVD) 1000–2000 (varying with film quality) 80–800

Table 1.Comparison between thermal conductivity and expansion coefficients of common heat sink materials, natural diamond and CVD diamond.

to growth direction is usually in the range of 10%, but can reach up to 50% [57]. It is worth emphasizing that in diamond, for room temperature, almost all heat is conducted through phonons with ~10 μ m mean free path; as a consequence, polycrystalline diamond films with average grain size smaller than ~20 μ m have reduced thermal conductivity for room temperature and above [52].

One of the limiting factors in the use of CVD diamond as a heat transfer layer in the industry of high power electronic devices is the direct deposition over other composition devices, for example GaAs, due to its difference in thermal expansion coefficients. The thermal mismatch often causes an accommodation-related stress of the film-substrate system and in some cases can lead to complete detachment of deposited layer, a property strongly influenced by film quality and also grain size [62, 63]. This characteristic is what probably brought the practical use to the technologies applied nowadays, the deposition over a substrate chemically and structurally compatible with diamond properties and growth conditions, etching or mechanical removal of substrate material, and proper post deposition processing for matching application requirements, detailed in the subsequent section.

3. CVD diamond heat sinks

Laboratory-grown CVD diamond has been extensively studied, not only for its exceptional set of properties but also because the CVD method exceeds limiting barriers for exploration niches in science and industry [64, 65]. This technology is

based on the metastability of the crystalline phase of carbon and diamond, under certain environmental conditions. By using a mixture of hydrocarbon gas in excess of hydrogen gas under pressures below of atmospheric, with an energy source for gas dissociation and subsequent reaction, carbon condensate to solid state enabling diamond crystals growth and then multiple growth nuclei coalescence form a continuous film over a surface [66].

As a brief summary of some applications that found in CVD technique a way to apply the properties of diamond where it was either not possible or excessively expensive, we have optical windows [67, 68], cutting tools [69–71], dental application tools [72, 73], conductivity and radiation sensors [74–76], and as a special matter for this chapter, heat sinking components, such as but not limited to transistor high power devices and high power laser diodes [32, 77].

Many deposition methods have been developed since its first report in academia by Derjaguin and Fedoseev in 1975, between the most used methods to grow diamond at low pressures from hydrocarbon gas hot filament, and microwave plasma activation techniques are the ones chosen for either cost efficiency and low complexity apparatus or higher quality films and better growth rates [2, 70].

The hot filament chemical vapor deposition (HFCVD) method came along with a discovery made by Matsumoto et al. in 1982 and is based on the heating of a refractory metal filament by appling an electrical current to about 2000°C; gases dissociate by heat and filament surface reactions. Indeed, there is an interesting chemical kinetics involving hydrogen dissociation in the HFCVD; besides its activation through heat irradiated from the filaments, its dissociation also occurs at the filament surface which acts like a catalyst for the adsorption of molecular hydrogen and desorption of atomic hydrogen. When using methane as a carbon source gas, methyl radicals (CH₃) are assumed to be the major responsible specimens in the growth of CVD diamond films; the dissociation of methane into this radical is also promoted by heat and especially by atomic hydrogen chemical reactions in gas phase [66]. **Figure 1** brings a schematic design of the growth environment for the HFCVD method, where growth and filament surface regions are highlighted.

Microwave plasma-assisted chemical vapor deposition (MPACVD) was developed a year later by Kamo et al.; this technique uses a microwave radiation coupled inside a resonant cavity to activate the gas mixtures. Different geometries have been studied with the intention of reaching a closely confined plasma sphere, or

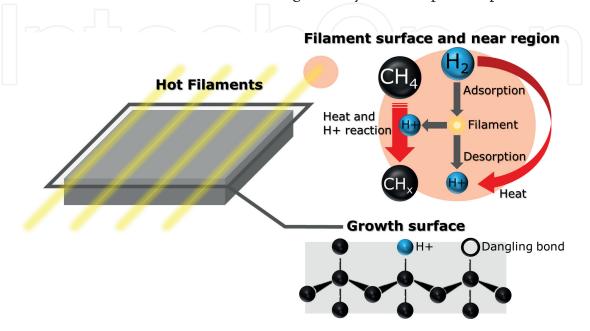


Figure 1. *HFCVD growth environment.*

in other cases, a better distributed plasma region that enables larger deposition areas [78–80]. This technology promotes the dissociation of molecular hydrogen at considerably higher rates, once the plasma region has a larger volume and free electrons accelerated by the electric field collide with hydrogen uniformly through this volume; this also occurs to methane, the heat generated by the microwave discharge keeps the generation of free electrons and also promotes gas dissociation [81]. **Figure 2** brings a schematic design of the growth environment for the MPACVD method, where growth and plasma regions are highlighted.

The growth mechanisms involved in diamond CVD are not fully understood, but they are accepted to be similar in both HFCVD and MPACVD, starting at the point which diamond, seeded particles at nondiamond substrates or single crystalline for homoepitaxial growth, suffer reactions at its surface when exposed to gas phase with atomic hydrogen, free atomic bonds appears at the surface by atomic hydrogen abstraction, this are known as dangling bonds. Methyl radicals subsequently bind to these free sites and then atomic hydrogen keeps removing hydrogen from CH₃ molecules at the surface maintaining the sp³ coordination, what keeps the deposition continuously occurring. Atomic hydrogen also etches graphite in a higher rate than diamond, allowing that only diamond continues to grow [65, 81].

A special issue to deal with is film surface roughness, what is generally achieved through a variety of polishing procedures detailed in a posterior section of this chapter; some deposition methods were specially developed to overcome this problem. Depending on specific growth conditions, diamond can preferentially develop different film textures varying with which crystalline plane orientation is favored or not by those conditions [82–84]. **Figure 3** shows idiomorphs or kinectic Wulff shapes, representations of individual crystallites more likely to grow depending on deposition conditions, that influence the growth velocities of {100} or {111} oriented faces.

This relation of growth velocity is given by the as-known α parameter that can be expressed by Eq. (3):

$$\alpha = \sqrt{3} \frac{V_{100}}{V_{111}} \tag{3}$$

where V_{100} is the velocity of $\{100\}$ oriented facet growth and V_{111} is the velocity for $\{111\}$ oriented facets [85]. Films with a $\{100\}$ dominant morphology tend to have lower surface roughness when compared to $\{110\}$ or $\{111\}$ morphologies [83].

The epitaxy of diamond over iridium/YSZ (yttria-stabilized zirconia), iridium/SrTiO₂, or iridium/MgO substrates has successfully been adopted as a method of obtaining a crystalline diamond oriented layer using bias enhanced nucleation (BEN) to grow oriented growth nuclei, and its posterior coalescence and thickening result in high quality smooth diamond layers. In this method, diamond is nucleated by the application of a negative bias for a short period of time. This potential accelerates carbon reactive species to substrate surface, forming sp³ and sp² hybridization nuclei for growth; as soon as the bias is turned off, atomic hydrogen etches nondiamond phases and only the diamond oriented particles grow until they coalesce and form a continuous oriented film [86–91].

3.1 Free-standing CVD diamond wafers

To be used as a heat transport device, diamond films have to be free of the substrate material, also known as its free standing form. There are several methods in the literature, and this section will cover the most used for fabrication of CVD diamond thermal management tools.

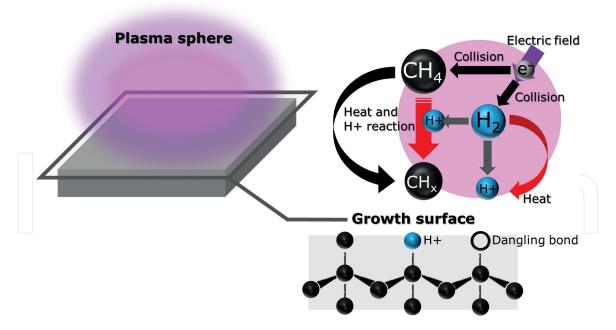


Figure 2. *MPACVD growth environment.*

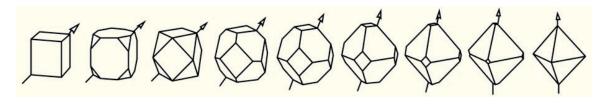


Figure 3. Idiomorphs of diamond crystallite shapes as a function of facet velocity growth ratio α , which increases from 1 to 3 in a step of 0.25. The arrow indicates the fastest growth direction. From Ref. [85].

In the fabrication of free-standing polycrystalline CVD diamond wafers, plasma-assisted methods are preferred once they promote higher growth rates, better film quality (i.e. lower metallic inclusions), and homogeneity [92–94] however, this kind of film is also produced by the hot filament method [95].

The practical approach shown in **Figure 4** for the fabrication of CVD diamond heat sinks follows the procedures of: (1) growing diamond film over a compatible substrate, (2) removal of the substrate by mechanical procedures or chemical etching, (3) cutting and polishing of the CVD diamond top surface for reducing rough morphology in addition or not to the polishing of nucleation side to remove excessively small particles as well as the nondiamond carbon included in grain boundaries, and (4) metallization through PVD or brazing of metallic alloys or pure elements to mounting requirements, or metallization of CVD diamond surface layer by the inclusion of a dopant element, such as boron, until the metal/insulator transition is achieved.

In a recent work, Dai et al. achieved the deposition of a double layered polycrystalline diamond in order to reduce the detrimental effect of nucleation layer without removing it, on the average value of κ by a two growth step process in which diamond is deposited over silicon; then the substrate material is etched chemically by a solution of HNO3 and HF, and the freestanding film is again exposed to growth environment with nucleation side up. However, presenting a slight decrease in κ for the temperature range of 250-400 K, their solution achieved a 950 ± 14 W m⁻¹ K⁻¹ thermal conductivity at room temperature [57]. This study shows the deposition method versatility and the still emerging technologies we can expect on the development and use of enhanced thermal management device fabrication.

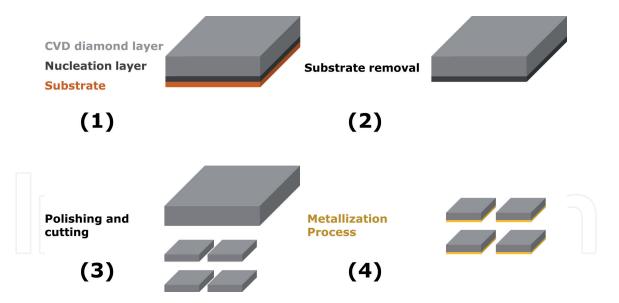


Figure 4.Simplified scheme for production of CVD diamond heat sinks.

3.2 Post deposition processing

3.2.1 Laser cutting

The exceptional properties of CVD diamond, added to its conventional small thickness, make traditional machining and cutting methods difficult, expensive, slow, and lead to high probability of contamination at the worked surface. Lasers have been studied and applied as an inexpensive technique when compared to traditional machining, at high speed without significant surface contaminants [96, 97].

Conventionally, laser cutting of diamond is based on the transfer of energy between laser beam and workpiece; this increases the temperature at the surface of the cutting region and this heating effect can rise local temperature to above 1300°C (for a 1064 nm wavelength laser) creating an opaque zone by graphitization, resulting in a very high absorption of the incident luminous radiation. This process is practically independent of laser beam wavelength [98].

The laser cutting of diamond is affected by laser characteristics in one hand and workpiece characteristics in the other hand, for lasers wavelength, pulse energy, pulse length focal position, frequency and absorptivity at the incident radiationare the main parameters involved, the material contribution comes from chracteristics such as thermal diffusivity and presence of impurities [99]. Nd: YAG lasers at 1064 nm wavelength have less efficient coupling with diamond requiring a higher energy dose to achieve material removal by thermally dominant mechanisms. For ArF lasers with a 193 nm wavelength, more efficient optical coupling is achieved minimizing thermal load and reducing photon-affected zone to regions in close proximity to the point of beam incidence [96]. Excimer lasers have been described as the most suitable for diamond and diamond-like film processing due to higher absorption coefficient in these materials for UV phonons, as compared to visible and infrared radiation [100].

In addition to be a widely used method in diamond cutting, lasers are also an alternative in the smoothening of polycrystalline diamond films. The KrF excimer lasers (248 nm) show a high etching rate of 100 nm per pulse, with resulting roughness depending on laser pulse duration and incidence angle [101]. Watanabe et al. proposed a novel method for ultraprecision diamond polishing using UV lasers of wavelengths lower than 225 nm; their work describes a mechanism of carbon atom oxidation by UV irradiation and final mechanical removal as CO2 or CO [102].

3.2.2 Polishing

Polycrystalline diamond growth via CVD processes tends to present a granular cone-shaped rough top surface morphology that may cause poor contact between heat generating device and diamond piece; this is also combined with the effect of reduced grain size and consequent increase of grain boundaries and nondiamond phases present in the nucleation region of the film severely decreasing thermal conductivity. Dielectric surface roughness can also aggravate the conductor roughness due to conformal nature of the metallization process. The thinning and polishing of the diamond piece is then of great importance to reduce the thermal conductivity of the affected region and smoothing of the film surface to promote better contact between pieces [12, 59].

Traditional abrasive polishing methods for natural diamond are not suitable for CVD diamond films because diamond exhibits nearly a factor of 600 of polishing rate difference depending on the direction it is being polished. In a polycrystalline film, the mix of present planes limits the material removal rate to the slowest direction. A method used for the efficient polishing of CVD diamond films is the thermochemical polishing, which consists in the friction of diamond workpiece with a heated iron disk; this takes advantage of the high solubility of carbon in pure iron, 170 mg cm⁻³ at eutetic temperature and also by high carbon diffusion rate [103, 104].

Another promising method called dynamic friction polishing can be applied to both single and polycrystalline diamond polishing due to its high efficiency and flexible environment (free of abrasives). Furthermore, it is performed at room temperature and open atmosphere. The use of this polishing method on CVD diamond thin films is sensitive to two factors: (i) the applied pressure during polishing, which in excess causes films to crack and (ii) lower pressures reduce material removal rate and time of polishing and long times induce higher thermal stress [14].

An alternative method for polishing is the planarization-by-filling, which is a method that offers a simple and conventional approach to the reduction of surface roughness without any kind of surface polishing. This technique consists basically in filling of the growth surface microcavities by adding a polymer, glass, diamond-filled glass, or similar material. The thin overlayer applied can also be polished to adequate thickness and expose some of the diamond surface [105].

3.2.3 Metallization

The process of adding a metallic layer to CVD diamond films, metallization, are conducted by several different systems, most employing a refractory metal adhesion layer which when deposited under appropriate conditions, forms an interfacial refractory metal-carbide phase. Some metallization systems are based on processing noble metal surface chemistry or ion beam surface chemistry to provide a "near surface" chemically and structurally modified diamond suitable for non-refractory bonding metallurgies [59].

The need of a metal layer is dependent on application, diamond heat management devices are often metal coated for grounding, signal and power connections, and if that is the case, plating is preferred over thermal evaporation or sputtering because its simple and less costly [105].

The adhesion of the metallic layer is of paramount importance. The conductive metals like gold or copper are not suitable for direct deposition over CVD diamond due to diamond chemical inertness; then these metals platings require the application of other metal seed layers. Generally, these seed layers are of refractory metals due to their strong adhesion to diamond forming carbide complexes when exposed

to annealing process at high temperatures (700–900°C). It is important to emphasize that the previously mentioned roughness of diamond can cause serious blistering of the plated metal if not made under proper conditions [105, 106].

4. Conclusion

Diamond and its laboratrial synthesis have been extensively studied and improved in the last decades. As diamond becomes more feasible as an engineering material, many industrial and technological uses begin to be economically attractive. This chapter aimed to bring an overview of current developments and remaining challenges on CVD diamond heat sink production and applications; CVD diamond polycrystalline films already reached all the properties of perfect IIa single crystal diamonds. Despite their first run in the market by the early 1990s, some technical issues still remain such as the rough surface obtained at regular growth rates, defects, and grain boundaries and intrinsic drawbacks on the CVD of diamond. Taking this into account, CVD diamond is still a better heat management material when compared to conventionally applied metals, and can be used in different levels of quality and physical properties to match specific application demands.

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Conflict of interest

The authors declare that there are no conflicts of interest.

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References

- [1] Kittel C. Introduction to Solid State Physics. 2nd ed. John Wiley & Sons; 1956
- [2] May PW. Diamond thin films: A 21st century material. Philosophical Transactions of the Royal Society A. 2000:358
- [3] Rogalin V, Krymskii M, Krymskii K. Several applications of diamonds in high-power optics and electronics. Journal of Communications Technology and Electronics. 2018;63(11):1326-1334
- [4] Bundy EP, Hall HT, Wentorf RJ Jr. Man-made diamonds. Nature. 1955;**176**(4471):51-55
- [5] Angus JC. Diamond synthesis by chemical vapor deposition: The early years. Diamond and Related Materials. 2014;49:77-86
- [6] Hei LF et al. Interface features of the HPHT Ib substrate and homoepitaxial CVD diamond layer. Diamond and Related Materials. 2016;**69**:33-39
- [7] Kazuchits NM et al. Comparison of HPHT and LPHT annealing of Ib synthetic diamond. Diamond and Related Materials. 2019;**91**:156-164
- [8] Willems B, Tallaire A, Achard J. Optical study of defects in thick undoped CVD synthetic diamond layers. Diamond and Related Materials. 2014;41:25-33
- [9] Kumar Mallik A, Bhar R, Bysakh S. An effort in planarising microwave plasma CVD grown polycrystalline diamond (PCD) coated 4in. Si wafers. Materials Science in Semiconductor Processing. 2016;**43**:1-7
- [10] Achard J et al. High quality MPACVD diamond single crystal growth: High microwave power density regime. Journal of Physics D: Applied Physics. 2007;40(20):6175

- [11] Weng J et al. Deposition of large area uniform diamond films by microwave plasma CVD. Vacuum. 2018;147:134-142
- [12] Jin S, Mavoori H. Processing and properties of CVD diamond for thermal management. Journal of Electronic Materials. 1998;27(11):1148-1153
- [13] Malshe A et al. A review of techniques for polishing and planarizing chemically vapor-deposited (CVD) diamond films and substrates.

 Diamond and Related Materials.

 1999;8(7):1198-1213
- [14] Feng HB, Chen YQ, Zhang LC. Polishing of CVD Diamond Wafers and Films in Key Engineering Materials. Trans Tech Publications; 2013
- [15] Chen Y-J, Young T-F. Thermal stress and heat transfer characteristics of a Cu/diamond/Cu heat spreading device. Diamond and Related Materials. 2009;**18**(2-3):283-286
- [16] Han Y et al. Enhancement of hotspot cooling with diamond heat spreader on Cu microchannel heat sink for GaN-on-Si device. IEEE Transactions on Components, Packaging and Manufacturing Technology. 2014;4(6):983-990
- [17] Swan CB. Improved performance of silicon avalanche oscillators mounted on diamond heat sinks. Proceedings of the IEEE. 1967;55(9):1617-1618
- [18] Dyment JC, D'Asaro LA. Continuous operation of GaAs junction lasers on diamond heat sinks at 200°K. Applied Physics Letters. 1967;11(9):292-294
- [19] Josenhans JG. Diamond as an insulating heat sink for a series combination of IMPATT diodes. Proceedings of the IEEE. 1968;56:762-763

- [20] Decker DR, Schorr AJ. High-power IMPATT diodes on diamond heat sinks. IEEE Transactions on Electron Devices. 1970;17(9):739-743
 - [21] Bernick RL. Temperature profile and thermal-spreading resistance for a semi-infinite type-IIa-diamond heat sink. Electronics Letters. 1972;8(7):180-181
 - [22] Russell EM, Thomson I. Embedded diamond heat sinks for avalanche diodes. Proceedings of the IEEE. 1972;**60**(8):1014-1015
 - [23] Hudson PRW. The thermal resistivity of diamond heat-sink bond materials. Journal of Physics D: Applied Physics. 1976;9(2):225-232
 - [24] Burgemeister EA. Thermal resistance at metal/diamond interfaces in relation to the mounting of microwave diodes. Journal of Physics D: Applied Physics. 1977;10(14):1923-1930
 - [25] Ino M et al. 80 GHz silicon diamond-heatsink impatt diodes. Electronics Letters. 1979;15(1):2-3
 - [26] Leistner D. Single drift impatt diodes on diamond heat sinks for W-band frequencies. IEE Proceedings I: Solid-State and Electron Devices. 1984;131(2):56-58
 - [27] Doting J, Molenaar J. Isotherms in diamond heat sinks, non-linear heat transfer in an excellent heat condition. In: Fourth Annual IEEE Semiconductor Thermal and Temperature Measurement Symposium. 1988
 - [28] Csanky G. Reliability critical thermal model for double-drift IMPATT diodes on diamond heat sinks. Quality and Reliability Engineering International. 1990;**6**(2):73-84
 - [29] Ramesham R et al. Fabrication of microchannels in synthetic polycrystalline diamond thin films

- for heat sinking applications. Journal of the Electrochemical Society. 1991;138(6):1706-1709
- [30] Beck JV, Osman AM, Lu G. Maximum temperatures in diamond heat spreaders using the surface element method. Journal of Heat Transfer. 1993;115(1):51-57
- [31] Eisele H, Haddad GI. Enhanced performance in GaAs TUNNETT diode oscillators above 100 GHz through diamond heat sinking and power combining. IEEE Transactions on Microwave Theory and Techniques. 1994;42(12):2498-2503
- [32] Goodson KE, Kurabayashi K, Pease RFW. Improved heat sinking for laser-diode arrays using microchannels in CVD diamond. IEEE Transactions on Components, Packaging, and Manufacturing Technology: Part B. 1997;20(1):104-109
- [33] Bewley WW et al. Hightemperature continuous-wave 3-6.1 µm "W" lasers with diamond-pressurebond heat sinking. Applied Physics Letters. 1999;74(8):1075-1077
- [34] Labudovic M, Burka M. Heat transfer and residual stress modeling of a diamond film heat sink for high power laser diodes. IEEE Transactions on Components and Packaging Technologies. 2003;26(3):575-581
- [35] Jessen G et al. AlGaN/GaN HEMT on diamond technology demonstration. in Compound Semiconductor Integrated Circuit Symposium Proceedings. 2006
- [36] Schneider H et al. Study of CVD diamond films for thermal management in power electronics. In: 2007 European Conference on IEEE Power Electronics and Applications. 2007
- [37] Ekimov E et al. Thermal conductivity of diamond composites sintered under high pressures.

- Diamond and Related Materials. 2008;17(4-5):838-843
- [38] Parashchuk VV et al. Improving the efficiency of high-power diode lasers using diamond heat sinks. Quantum Electronics. 2010;**40**(4):301
- [39] Atkins P, Atkins PW, de Paula J. Atkins' Physical Chemistry. Oxford: OUP; 2014
- [40] Ward A et al. Ab initio theory of the lattice thermal conductivity in diamond. Physical Review B. 2009;**80**(12):125203
- [41] Maznev A, Wright O. Demystifying umklapp vs normal scattering in lattice thermal conductivity. American Journal of Physics. 2014;82(11):1062-1066
- [42] Sukhadolau A et al. Thermal conductivity of CVD diamond at elevated temperatures. Diamond and Related Materials. 2005;**14**(3-7):589-593
- [43] Anthony T et al. Thermal diffusivity of isotopically enriched C12 diamond. Physical Review B. 1990;**42**(2):1104
- [44] Graebner J. Measurements of specific heat and mass density in CVD diamond. Diamond and Related Materials. 1996;5(11):1366-1370
- [45] Callaway J. Model for lattice thermal conductivity at low temperatures. Physical Review. 1959;**113**(4):1046
- [46] Morelli DT, Hartnett TM, Robinson CJ. Phonon-defect scattering in high thermal conductivity diamond films. Applied Physics Letters. 1991;59(17):2112-2114
- [47] Debye P. Zur theorie der spezifischen wärmen. Annalen der Physik. 1912;**344**(14):789-839
- [48] Varshni YP. Temperature dependence of the energy gap in semiconductors. Physica. 1967;34(1):149-154

- [49] Graebner J et al. Anisotropic thermal conductivity in chemical vapor deposition diamond. Journal of Applied Physics. 1992;**71**(11):5353-5356
- [50] Wörner E et al. Thermal conductivity of CVD diamond films: High-precision, temperature-resolved measurements. Diamond and Related Materials. 1996;5(6-8):688-692
- [51] Anaya J et al. Thermal conductivity of ultrathin nano-crystalline diamond films determined by Raman thermography assisted by silicon nanowires. Applied Physics Letters. 2015;**106**(22):223101
- [52] Simon RB et al. Effect of grain size of polycrystalline diamond on its heat spreading properties. Applied Physics Express. 2016;9(6):061302
- [53] Wei L et al. Thermal conductivity of isotopically modified single crystal diamond. Physical Review Letters. 1993;**70**(24):3764
- [54] Callister WD, Rethwisch DG. Materials Science and Engineering: An Introduction. 8th ed. Wiley; 2009
- [55] Nazari M et al. Optical characterization and thermal properties of CVD diamond films for integration with power electronics. Solid-State Electronics. 2017;**136**:12-17
- [56] Shamsa M et al. Thermal conductivity of nitrogenated ultrananocrystalline diamond films on silicon. Journal of Applied Physics. 2008;**103**(8):083538
- [57] Dai B et al. Thermal conductivity of free-standing CVD diamond films by growing on both nuclear and growth sides. Diamond and Related Materials. 2017;**76**:9-13
- [58] Ono A et al. Thermal conductivity of diamond films synthesized by

- microwave plasma CVD. Japanese Journal of Applied Physics. 1986;25(10A):L808
- [59] Fabis PM. The processing technology and electronic packaging of CVD diamond: A case study for GaAs/CVD diamond plastic packages. Microelectronics Reliability. 2002;42(2):233-252
- [60] Coe S, Sussmann R. Optical, thermal and mechanical properties of CVD diamond. Diamond and Related Materials. 2000;**9**(9-10):1726-1729
- [61] Railkar TA et al. A critical review of chemical vapor-deposited (CVD) diamond for electronic applications. Critical Reviews in Solid State and Materials Sciences. 2000;25(3):163-277
- [62] Berry B et al. Internal stress and elasticity of synthetic diamond films. Applied Physics Letters. 1990;57(3):302-303
- [63] Abreu C et al. Grain size effect on self-mated CVD diamond dry tribosystems. Wear. 2005;**259**(1-6):771-778
- [64] May PW. Diamond thin films: A 21st-century material. Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences. 2000;358(1766):473
- [65] May PW, Mankelevich YA. From ultrananocrystalline diamond to single crystal diamond growth in hot filament and microwave plasma-enhanced CVD reactors: A unified model for growth rates and grain sizes. Journal of Physical Chemistry C. 2008;2008, 112:12432-12441
- [66] Gracio J, Fan Q, Madaleno J. Diamond growth by chemical vapour deposition. Journal of Physics D: Applied Physics. 2010;43(37):374017

- [67] Campos R et al. Development of nanocrystalline diamond windows for application in synchrotron beamlines. Vacuum. 2013;**89**:21-25
- [68] Dodson J et al. Single crystal and polycrystalline CVD diamond for demanding optical applications. In: Window and Dome Technologies and Materials XII. International Society for Optics and Photonics; 2011
- [69] Cabral G et al. A study of diamond film deposition on WC–Co inserts for graphite machining: Effectiveness of SiC interlayers prepared by HFCVD. Diamond and Related Materials. 2008;17(6):1008-1014
- [70] Schäfer L, Höfer M, Kröger R. The versatility of hot-filament activated chemical vapor deposition. Thin Solid Films. 2006;515(3):1017-1024
- [71] Arumugam PU, Malshe AP, Batzer SA. Dry machining of aluminum—silicon alloy using polished CVD diamond-coated cutting tools inserts. Surface and Coatings Technology. 2006;**200**(11):3399-3403
- [72] Trava-Airoldi VJC, Evaldo J, Bosco ED, Leite NF, Valera MC, Pena AFV, Baranauskas V. CVD Diamond Burrs for Odontological and Related Uses. 1998
- [73] Sein H et al. Comparative investigation of smooth polycrystalline diamond films on dental burs by chemical vapor deposition. Journal of Materials Engineering and Performance. 2006;15(2):195-200
- [74] Adam W et al. Performance of irradiated CVD diamond micro-strip sensors. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment. 2002;476(3):706-712
- [75] Schmid G et al. A neutron sensor based on single crystal CVD

- diamond. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment. 2004;527(3):554-561
- [76] Mazzeo G et al. Deep UV pulsed laser monitoring by CVD diamond sensors. Sensors and Actuators A: Physical. 2004;**113**(3):277-281
- [77] Seelmann-Eggebert M et al. Heatspreading diamond films for GaNbased high-power transistor devices. Diamond and Related Materials. 2001;**10**(3-7):744-749
- [78] Gu Y et al. Microwave plasma reactor design for high pressure and high power density diamond synthesis. Diamond and Related Materials. 2012;**24**:210-214
- [79] Hemawan K et al. Improved microwave plasma cavity reactor for diamond synthesis at high-pressure and high power density. Diamond and Related Materials. 2010;**19**(12):1446-1452
- [80] Vikharev AL et al. Multimode cavity type MPACVD reactor for large area diamond film deposition. Diamond and Related Materials. 2018;83:8-14
- [81] Kasu M. Diamond epitaxy: Basics and applications. Progress in Crystal Growth and Characterization of Materials. 2016;**62**(2):317-328
- [82] Choi IH et al. Growth of highly oriented diamond films by the MPCVD technique using CO $-H_2$, CH $_4$ $-H_2$ and CH $_4$ $-N_2$ $-H_2$ gas mixtures. Diamond and Related Materials. 2004;**13**(4-8):574-580
- [83] Silva F et al. Control of an MPACVD reactor for polycrystalline textured diamond films synthesis: Role of microwave power density. Diamond and Related Materials. 1996;5(3):338-344
- [84] Gicquel A et al. CVD diamond films: From growth to applications.

- Current Applied Physics. 2001;**1**(6):479-496
- [85] Smereka P et al. Simulation of faceted film growth in three dimensions: Microstructure, morphology and texture. Acta Materialia. 2005;53(4):1191-1204
- [86] Lee KH et al. Epitaxy of iridium on SrTiO₃/Si(001): A promising scalable substrate for diamond heteroepitaxy. Diamond and Related Materials. 2016;**66**:67-76
- [87] Ohtsuka K et al. Epitaxial growth of diamond on iridium. Japanese Journal of Applied Physics. 1996;35(8B):L1072
- [88] Saito T et al. Epitaxial nucleation of diamond on an iridium substrate by bias treatment, for microwave plasma-assisted chemical vapor deposition. Diamond and Related Materials. 1998;7(9):1381-1384
- [89] Schreck M et al. Domain formation in diamond nucleation on iridium. Diamond and Related Materials. 2003;**12**(3-7):262-267
- [90] Gsell S et al. A route to diamond wafers by epitaxial deposition on silicon via iridium/yttria-stabilized zirconia buffer layers. Applied Physics Letters. 2004;84(22):4541-4543
- [91] Bauer T et al. Growth of epitaxial diamond on silicon via iridium/SrTiO₃ buffer layers. Diamond and Related Materials. 2005;**14**(3-7):314-317
- [92] Lee J-K et al. Free-standing diamond wafers deposited by multicathode, direct-current, plasma-assisted chemical vapor deposition. Diamond and Related Materials. 2000;9(3-6):364-367
- [93] Aleksov A et al. Diamond-based electronics for RF applications. Diamond and Related Materials. 2004;**13**(2):233-240

[94] Zuo S et al. Investigation of diamond deposition uniformity and quality for freestanding film and substrate applications. Diamond and Related Materials. 2008;17(3):300-305

[95] Ohmagari S et al. Characterization of free-standing single-crystal diamond prepared by hot-filament chemical vapor deposition. Diamond and Related Materials. 2014;48:19-23

[96] Fabis PM. Laser machining of CVD diamond: Chemical and structural alteration effects. Surface and Coatings Technology. 1996;82(3):320-325

[97] Riva R et al. Cutting and drilling of CVD diamond using a copper vapor laser. In: High-Power Lasers: Applications and Emerging Applications. International Society for Optics and Photonics; 1996

[98] Migulin VV, Ralchenko VG, Baik Y-J. Oxygen-assisted laser cutting and drilling of CVD diamond. In: Lasers in Synthesis, Characterization, and Processing of Diamond. Vol. 3484. SPIE; 1998. p. 5

[99] Boutinguiza M et al. Cutting of CVD diamond by optical fibre guided Nd:YAG laser. International Congress on Applications of Lasers & Electro-Optics. 2003;**2003**(1):525

[100] Kononenko TV et al. Excimer laser etching of diamond-like carbon films: Spalling effect. Applied Surface Science. 1995;86(1):234-238

[101] Pimenov SM et al. UV laser processing of diamond films: Effects of irradiation conditions on the properties of laser-treated diamond film surfaces. Diamond and Related Materials. 1993;2(2):291-297

[102] Watanabe J, Touge M, Sakamoto T. Ultraviolet-irradiated precision polishing of diamond and its related

materials. Diamond and Related Materials. 2013;**39**:14-19

[103] Hickey CF et al. Polishing of filament-assisted CVD diamond films. San Diego, '91. Vol. 1534. SPIE 10; 1991

[104] Zaitsev AM et al. Thermochemical polishing of CVD diamond films. Diamond and Related Materials. 1998;7(8):1108-1117

[105] Brown WD et al. State-of-theart synthesis and post-deposition processing of large area CVD diamond substrates for thermal management. Surface and Coatings Technology. 1996;86-87:698-707

[106] Katz A et al. Au-Sn/W and Au-Sn/Cr metallized chemical vapor deposited diamond heat sinks for InP laser device applications. Journal of Applied Physics. 1994;75(1):563-567