

Chemical Vapour Deposited Diamond for Thermal and Optical Applications

P. Koidl, C. Wild, E. Woerner, W. Müller-Sebert, M. Fünér and M. Jehle

Fraunhofer-Institut für Angewandte Festkörperphysik (IAF) D-79108 Freiburg, Germany

(Received November 5, 1996)

Considerable progress in the development of CVD techniques for the deposition of diamond films has been achieved recently. Despite the polycrystalline structure of this material, its physical properties are now approaching those of natural type IIa diamond crystals. This paper will give some insight into the current status of CVD diamond technology with emphasis on optical and thermal applications. The role of process gas impurities like nitrogen will be discussed.

Key words : Chemical vapour deposition, Diamond

I. Introduction

Diamond has always been an outstanding and desirable material.¹⁾ With the invention of synthetic growth techniques at high pressures and temperatures in the fifties, it became a technical material, especially for mechanical applications. However, it was the advent of low pressure deposition techniques that made accessible the excellent mechanical, thermal, optical and electronic properties.²⁾ With these chemical vapour deposition (CVD) techniques diamond became available in the form of extended thin films and free-standing plates or windows, opening up a wealth of new applications.

We will report on the CVD of diamond films and free-standing windows. Possible optical applications of CVD diamond as a radiation window will be discussed. The excellent thermal conductivity leads to applications as heat spreaders and submounts for high power electronic and optoelectronic devices.

II. Deposition from the Gas phase

There is a variety of diamond CVD techniques that differ mainly in the way of gas phase activation and dissociation.³⁾ The distinguishing features from an applicational point of view are the deposition rate, the deposition area and the quality of the deposited diamond. The maximum growth rate reported so far amounts to almost 1 mm/h.⁴⁾ However, those high growth rates are usually limited to very small deposition areas ($\approx 1 \text{ cm}^2$). In general there is an inverse relationship between film quality and growth rate.

Optically transparent films with high thermal conductivities are usually deposited at rates not exceeding 10 $\mu\text{m/h}$, regardless of the deposition technique.

We have concentrated on hot filament CVD for the de-

position of thin films with thicknesses of typically 1 μm and microwave-plasma CVD for the growth of much thicker samples. Methane diluted in hydrogen has been used as process gas. Typical deposition conditions in a 6 kW, 2.45 GHz microwave CVD system were 1.5-3% methane, 700-900°C substrate temperature and pressures around 200 mbar.

The development of deposition reactors and its optimization is an important topic in current research. At present, the most advanced depositions systems use a high power (60-75 kW) plasma sustained by 915 MHz microwave radiation. At the Fraunhofer-Institut IAF in Freiburg a 60 kW system with a novel reactor design has been developed recently.

III. Optical Applications

Diamond combines a number of excellent properties for optical applications. It is transparent from the UV (230 nm) to the far infrared. Only minor absorption bands resulting from two phonon absorption exist between 2.5 and 6 μm . Due to the large band gap there is no thermal generation of charge carriers at elevated temperatures, hence no "thermal run away" as in the case of Germanium under intense laser irradiation. Furthermore, diamond does not become nonlinear at high radiation intensities. Because of the excellent thermal conductivity absorbed energy is quickly dissipated to the edges of a diamond window where it can be removed by appropriate heat sinks and cooling techniques.

Based on these properties, diamond windows are of considerable current interest for multispectral and infrared applications as well as high power radiation. In Table 1 several properties of infrared optical materials are summarized.

CVD diamond may be used either as a coating for con-

Table 1. Properties of infrared optical materials, semiconductors and packaging materials

Material	Diamond	ZnSe	ZnS	Ge	Si	GaAs	Cu	AlN
refractive index @ 10.6 μm	2.38	2.40	2.19	4.00	3.42	3.28	-	2.2
transmission* @ 10.6 μm	71%	71%	76%	47%	54%	56%	-	-
absorption coeff. @ 10.6 μm (cm^{-1})	0.1~0.3	0.0005	0.2	0.02	0.35	0.01	-	-
band gap (eV)	5.48	2.7	3.9	0.664	1.11	1.42	-	6.0
dn/dT ($10^{-5}/\text{K}$)	1.0	6.4	4.1	40	13	15	-	-
melting point (K)	4100	1799	2103	1210	1685	1513	1356	3070
micro hardness (kg/mm^2)	8900	137	230	780	1150	721	50~100	1200
thermal conductivity (W/cmK)	20-22	0.19	0.27	0.59	1.63	0.55	4	0.7~2.0
thermal expansion coefficient (ppm/K)	1.3	7.6	7.9	5.9	2.56	5.9	16.8	2.9~3.3

*without antireflection coating.



Fig. 1. Free-standing CVD diamond window.

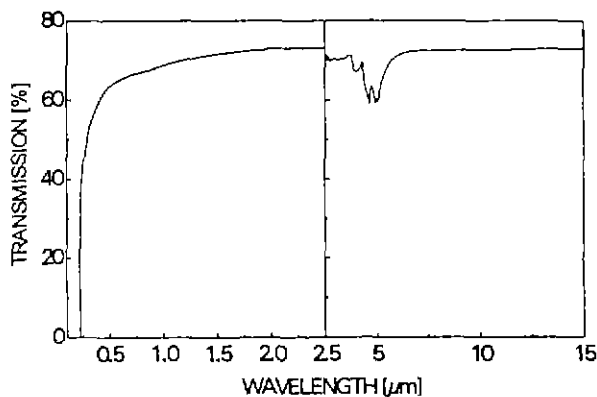


Fig. 2. Optical transmission of a free-standing CVD diamond window, not corrected for reflection.

ventional windows or as stand-alone window. While diamond coatings are still a challenging task (bad adhesion, large differences in thermal expansion) the preparation of free-standing diamond windows has been realized with greater success. Fig. 1 shows a photograph of a 45 mm diam. diamond window prepared by microwave plasma CVD (2.45 GHz, 6 kW). The diamond window was deposited on a silicon substrate. After deposition the sub-

strate was removed by etching in hydrofluoric acid, a disc was cut using a Nd:YAG laser and both surfaces of the window were ground and polished in order to obtain a constant thickness and a smooth surface finish.

IV. Thermal Applications

The increasing packaging density of integrated circuits and the development of high power laser diodes have led to extreme cooling demands. The dissipation of heat at a rate exceeding $1 \text{ kW}/\text{cm}^2$ has become necessary. In this context, CVD diamond heat-spreaders offer a very promising solution to many heat dissipation problems.

At room temperature type IIa diamond crystals exhibit thermal conductivities in the range 20-22 W/cmK . For comparison, the thermal conductivity of copper amounts to only 4 W/cmK . Under optimized growth conditions it became possible to grow diamond films with thermal conductivities approaching those of natural diamond. Fig. 3 shows the temperature dependence of the thermal conductivity for a phase-pure polycrystalline diamond sample prepared by microwave plasma CVD.⁵ At room temperature the thermal conductivity amounts to 20.2 W/cmK . At low temperatures, the thermal conductivity is even higher. The maximum value of 54 W/cmK at -155°C is -to our knowledge-the highest value reported so far for CVD diamond. For comparison, a sample grown with 10 ppm N_2 added to the process gas has been measured (see below).

In Table I the thermal properties of relevant semiconductors and thermal packaging materials are summarized. Apart from the high thermal conductivity diamond exhibits a rather low thermal expansion coefficient. It is significantly lower than that of common semiconductors such as Si or GaAs, however, the match is still better than that of copper. Some heat-spreading applications require an electrical insulation of the electronic components. For those applications, diamond electronic components. For those applications, diamond is an

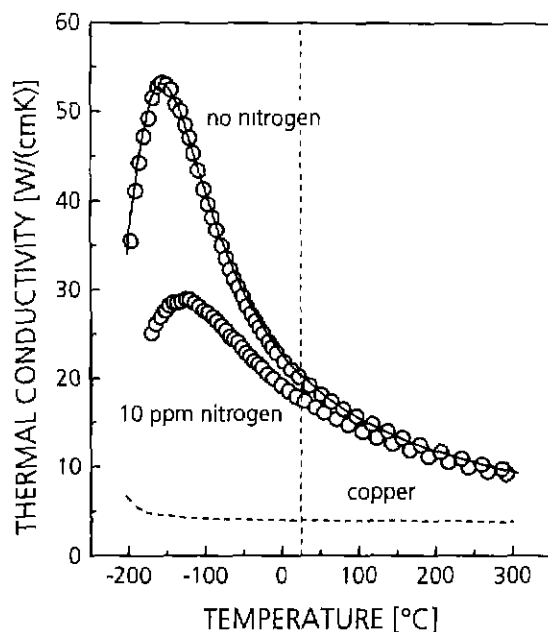


Fig. 3. Thermal conductivity of CVD diamond films deposited with and without 10 ppm nitrogen in the process gas (open circles). Solid line: fitted theoretical curve, Dashed line: thermal conductivity of copper

even better material, since it exhibits a high electrical resistivity ($> 10^{15} \Omega\text{cm}$) and a high dielectric strength ($\approx 10^7\text{V/cm}$). High frequency applications also benefit from the low dielectric constant ($\epsilon=5.7$) and low dielectric losses.

The advantages of diamond heat spreaders are illustrated by theoretical simulations. Fig. 4 depicts the results of two-dimensional computer simulations. The configurations considered are a laser diode array mounted directly on a silicon microchannel cooler (Fig. 4a) and the same configuration, but with a diamond heat spreader positioned between laser diode array and microchannel plate (Fig. 4b). For the calculation a heat flux of 1 kW/cm^2 was assumed. In Fig. 4 the temperature distribution is shown with isothermal increments of 1°C . Without diamond heat-spreader the maximum temperature rise in the laser diode array (relative to the cooling water) amounts to $\Delta T=45^\circ\text{C}$. By adding a diamond heatspreader the heat flux is distributed over many more microchannels resulting in a significantly reduced temperature rise of $\Delta T=18^\circ\text{C}$.

Even more important, the diamond heat-spreader strongly influences the temperature gradient across the active zone in the laser diode. It is reduced from 17°C to below 3°C . Taking into account, that elevated operation temperatures strongly affect the lifetime and efficiency of semiconductor lasers and that there is a wavelength shift of several angstroms per $^\circ\text{C}$, the importance of diamond heat-spreaders becomes obvious.

1. Optimization of diamond CVD

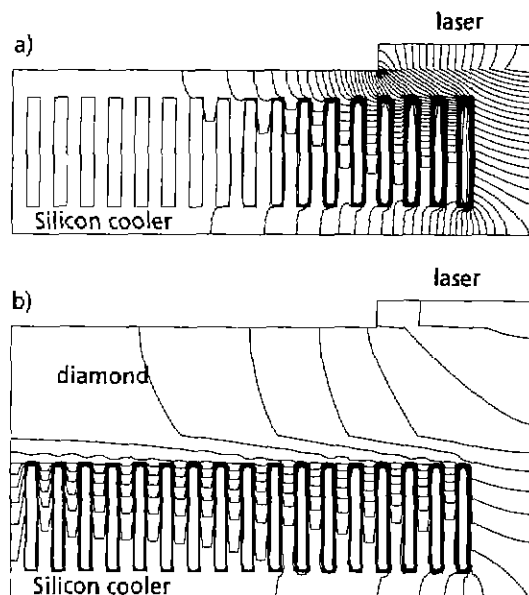


Fig. 4. Thermal simulation of a laser diode array mounted on a silicon microchannel cooler, a) without b) with diamond heat-spreader; isothermal contours with 1°C increment are shown.

Optical and thermal applications of CVD diamond generally require very phase-pure material. Defects and impurities are detrimental to good optical transparency and high thermal conductivity.

In order to get the best optical and thermal properties CVD was performed under very clean conditions. High purity methane and purified hydrogen have been used as process gases. On the other hand cost is an important issue and it would therefore be desirable to work with less expensive technical gases.

The most common impurity in the process gas is nitrogen which may enter the CVD system either via leaks or as a contamination of the process gases. We have therefore studied the effect of nitrogen on the CVD process. Starting with purified gases, nitrogen was added to the process gas with concentrations between 0 and 50 ppm. As an unexpected result, the deposition rate was found to increase significantly due to the addition of nitrogen. In a 4.2 kW microwave CVD system working with 3% CH_4 diluted in hydrogen, the addition of up to 25 ppm N_2 gave an increase in growth rate from 3 to $12 \mu\text{m/h}$.⁶

The effect of nitrogen addition on the optical and thermal properties has also been reported by Müller-Seibert *et al.*⁶ The thermal conductivity is reduced by the addition of 10 ppm of N_2 . While the reduction of the low temperature maximum of the thermal conductivity (see Fig. 3) is significant, at room temperature the reduction is less severe. A concentration of 10 ppm N_2 in the process gas gave a reduction in the thermal conductivity at room temperature of only 10% from 20 to 10 W/cmK , which might be tolerable in view of the beneficial increase in growth rate.

The optical transmission was reduced mainly in the short wavelength region leading to a brownish colour of the diamond samples grown with nitrogen addition. The infrared transparency, however, was not degraded. Especially in the 10 μm region there was an indication of any defect-induced one-phonon absorption suggesting that nitrogen is incorporated into CVD diamond with a low distribution coefficient.

In fact, it has been shown that the incorporation rate of nitrogen from $\text{H}_2/\text{CH}_4/\text{N}_2$ plasmas is between 10^{-4} and 10^{-3} , depending on the growth sector.⁷⁾

V. Conclusions

Recent progress in the CVD of high purity polycrystalline diamond has opened up applications as windows especially for infrared and high-power radiation and as a material for thermal management in micro- and opto-electronics. It has been shown that the controlled addition of small amounts of nitrogen may increase the CVD growth rates without seriously degrading the optical and thermal properties. Work to-

wards the up-scaling of the deposition technique is under way and will lead to a further reduction of the cost of CVD diamond.

References

1. "The Properties of Natural and Synthetic Diamond," ed. by J.E. Field, Academic Press, London, 1992.
2. "Properties and Growth of Diamond," ed. by Gordon Davies, Emis Datareviews Series No. 9, Inspec, London, 1994.
3. P. K. Bachmann, in Ref. 2, P. 349ff.
4. N. Ohtake, H. Tokura, Y. Kuriyama, Y. Mahimo and M. Yoshikawa, Proc. 1st Int. Symp. on Diamond and Diamond-Like Films, The Electrochemical Society, Pennington, NJ, Proceedings Vol. 89-12, 93 (1989).
5. E. Wörner, C. Wild, W. Müller-Sebert, R. Locher and P. Koidl, *Diamond and Related Mat.* **5**, 688 (1996).
6. W. Müller-Sebert, E. Wörner, F. Fuchs, C. Wild and P. Koidl, *Appl. Phys. Lett.* **68**, 759 (1996).
7. R. Samlenski, C. Haug, R. Brenn, C. Wild, R. Locher and P. Koidl, *Appl. Phys. Lett.* **67**, 2798 (1995).