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Synthesis of Submicron Diamond Powders by CO_2-Laser Pyrolysis of C_2H_4

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Abstract. Diamond powders with grain diameters up to 0.3 μm were obtained by CO_2-laser induced decomposition of C_2H_4 and mixtures of $C_2H_4/H_2/SiH_4$ at low pressures and temperatures in a gas-flow reactor. Solid products were produced in a yellow-to-orange coloured flame (500–550°) and collected in filters. The product contained polyaromatic species, high molecular polymers, graphite, amorphous carbon, and spherical diamond particles. Several diamond particle populations, with mean diameters of 6.2–122 nm, were observed by transmission electron microscopy. Both diamond modifications, cubic and hexagonal, were identified by electron diffraction.

Introduction

The synthesis of diamond in the region of thermodynamic stability gave rise to the development of a new industry in the fifties [1–5]. The first synthesis routes to produce diamond thin films by Chemical Vapour Deposition (CVD) in the region of thermodynamic metastability were developed in the fifties and were greatly improved during the seventies and eighties. They have now reached industrial application. Several excellent and extensive reviews covering the recent history of CVD-diamond films have been published [6–8].

CVD-diamond films are grown by heterogeneous nucleation on a variety of substrates [6]. However, the homogeneous nucleation of diamond at low pressures in the gas phase in the absence of any surface was believed to be impossible up to 1987, when the discovery of nm-sized diamonds in meteorites [9][10] and theoretical considerations [11–13] indicated that low-pressure homogeneous nucleation of diamond grains cannot be absolutely ruled out. In 1989 and 1990, *Frenklach et al.* reported for the first time the homogeneous nucleation of diamond particles at low-pressures in CH_2Cl_2/O_2 and $ClCH{=}CCl_2/O_2$ [14] and $HC{\equiv}CH/O_2$ mixtures [15] exposed to 2.45-GHz microwave radiation. Recently, we have reported the successful synthesis of submicron diamond powders by CO_2-laser induced decomposition of gaseous C_2H_4 [16][17]. It is important to stress that *heterogeneous* nucleation of CVD-diamond films and *homogeneous* nucleation of diamond particles in the gas-phase are two totally different diamond synthesis routes.

Experimental

Mixtures of C_2H_4, H_2, and in some cases SiH_4 were pyrolyzed by the beam of a continuous wave CO_2-laser (wavelength 10.532 μm) in a gas-flow reactor flushed with Ar or N_2. The laser intensity was between 6000 and 8000 W/cm². In a yellow-to-orange reaction flame, a variety of products was obtained. The flame temp. were between 500 and 550°. The total pressure was fixed at 1000 mbar (1 mbar = 100 Pa). The majority of the reaction products (~ 99%) were gaseous hydrocarbons not analyzed in this study. The solid reaction products were trapped in filters. Apart from a mixture of polyaromatic species, polymers, amorphous carbon, and graphite, they consisted of a minor fraction of submicron diamond grains. In those cases, where SiH_4 was added, amorphous silicon carbide powder was the main product.

The products were directly prepared for transmission electron microscopy (TEM), without concentrating the diamond phase and without any oxidation steps to remove non-diamond C phases. The solid products were identified by their electron diffraction patterns. Selected areas containing enough diamond particles to obtain meaningful electron diffraction images were used to characterize the diamond phases.

Results and Discussion

Five out of seven synthesis runs produced diamond powder, as shown in *Table 1*.

The diamond grain sizes were quite variable, showing uni- or bimodal size distributions with mean particle diameters ranging from 6 up to 120 nm. Each subpopulation showed a normal size distribution. The largest particles detected had diameters of 280 nm.

Two diamond modifications, cubic and hexagonal, were obtained: the cubic phase (3C-diamond) occurred in all diamond containing samples, the hexagonal phase (6H-diamond) was found additionally in two samples (*Runs 3, 4*). We did not detect the lonsdaleite modification (2H-diamond), due to the absence of the most intense (100) reflex for a lattice spacing of 2.19 Å and mismatches or lacking of several other reflexes (*hkl* = 102, 103, 201). Particles below 17 nm were perfectly spherical, larger particles showed small deviations from sphericity. However, the runs containing hexagonal diamond showed large (diameter 50 nm) faceted grains, often with hexagonal shape. We assume that these particles represent the hexagonal phase, but we are not able to decide whether sphericity is restricted to the cubic phase or not. The terminal size of the largest particles was approximately proportional to the residence time in the reaction flame, which was varied from 2 to 160 ms. Diamond was formed at flame residence times up to 60 ms, but not at longer residence times (160 ms).

Table 1. *Summary of Synthesis Parameters, Detection of Diamond Phases, and Size Distributions*

Run	Reactant gas ratio [%]			Residence time in reaction [$\cdot 10^{-3}$ s]	Diamond modifications flame	Size distributions [nm]
	C_2H_4	H_2	SiH_4			
1	100	0	0	2–10	cub	16.60 ± 6.84
2	100	0	0	16	cub	16.91 ± 7.08
3	76–89	11–24	0	6–9	cub + hex	17.02 ± 12.40
4	89.3	10.7	0	17	cub + hex	6.30 ± 2.38 46 ± 24
5	70.8	27.6	1.6	160	no diamond	
6	49.3	43.3	7.4	160	no diamond	
7	51.5	41.2	7.2	62.5	cub	10.06 ± 7.39 122 ± 43

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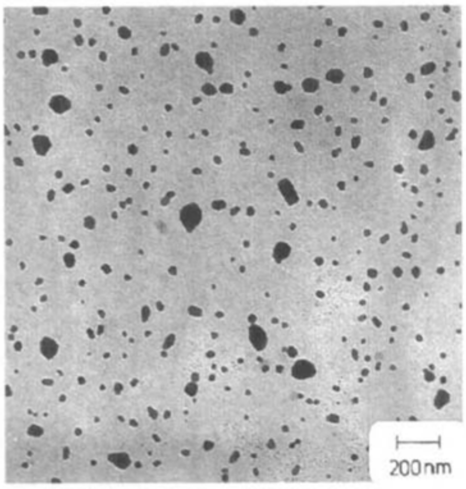

Fig. 1. *Bright field TEM image of diamond synthesized in* Run 4 (diameters 6.3 ± 2.4 nm and 46 ± 24 nm)

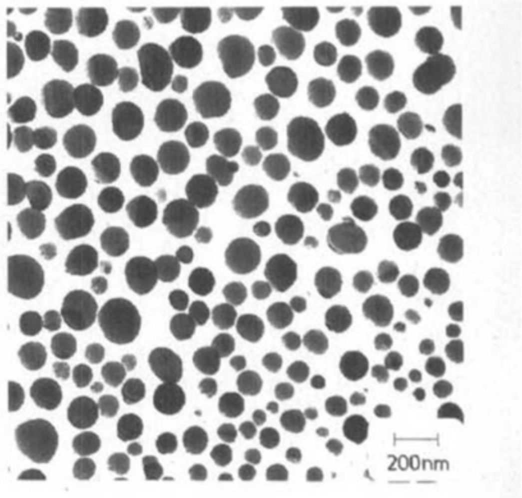

Fig. 2. *Bright field TEM image of diamond synthesized in* Run 7 (coarse particle population, diameter 122 ± 43 nm)

In *Figs. 1* and *2*, bright field TEM images of two representative diamond powder samples are shown. *Fig. 1* shows diamond (cubic (3C) and hexagonal (6H) modification) of *Run 4* with spherical and faceted grains. The size distribution is bimodal with diameters of 6.3 ± 2.4 nm and 46 ± 24 nm. *Fig. 2* shows the large diamond particle population obtained in *Run 7*, having a size distribution of 122 ± 43 nm. The diamond modification obtained in this run is cubic (3C). The particles have a spheroidal shape.

The purity of the diamond phase was variable. In *Runs 1, 3*, and *4*, additional electron diffraction rings were detected (*Table 2*). They could partially be attributed to the d_{002}-spacings of poorly graphitized C species (PCG) reported by *Rietmeijer* and *Mackinnon* [10] (d = 3.4–4.1 Å). We could not determine so far whether the non-diamond phases were attached to the diamonds, or whether they represent a separate phase.

From the residence time in the flame and the terminal size, the average radial growth rates can be calculated: for small (10 nm), large (120 nm), and very large (280 nm) particles these were 0.2, 2.4, and 5.7 µm/s, respectively. These (radial) growth rates are several orders of magnitude larger than surface growth rates of diamond coatings produced by CVD [6].

The reaction conditions in laser pyrolysis of C_2H_4 are far from thermodynamic equilibrium. Fast heating rates (~ 10^5°/s), high quench rates (10^4°/s), high supersaturations of small, C-containing molecules (C_xH_y, x = 1–2, y = 0–4), fast radial growth rates (up to 5.7 µm/s), and high radiation intensities (6000–8000 W/cm^2), all favour kinetically controlled reactions over thermodynamic equilibrium reactions. Especially, the occurrence of spherical or poorly faceted diamond particles indicates that surface reactions leading to facetation were suppressed before thermodynamic equilibrium was established. Fast surface growth rates may also explain the occurrence of the unusual hexagonal modifications.

Tab. 2. *Lattice Constants of Diamond Phases* (Synthesis *Runs 1–7*) *Determined by Electron Diffraction, Comparison with Reference Data* (ASTM powder diffraction file) *of Cubic (3C) and Hexagonal (6H) Diamond*

Lattice constants [Å] *Run*							3C Diamond ASTM 6-0675		6H Diamond ASTM 26-1082	
1	*2*	*3*	*4*	*5*	*6*	*7*	*d* [Å]	*hkl*	*d* [Å]	*hkl*
3.96										
		3.38								
3.26										
		3.06								
			3.11							
		2.83		n	n					
2.76				o	o					
2.26										
				d	d				2.151	101
2.06	2.06	2.06	2.06	i	i	2.06	2.06	111	2.059	102
		1.96	1.92	a	a				1.930	103
1.77	1.77	1.76	1.78	m	m	1.78	1.77	200f		
		1.61	1.62	o	o				1.637	105
				n	n				1.373	107
1.25	1.26	1.24	1.27	d	d	1.25	1.26	220	1.2610	110
			1.22							
									1.1620	109
		1.13								
									1.0880	201
1.06	1.06		1.07			1.06	1.0754	311	1.0750	202
									1.0560	203
	1.02									
									0.9287	207
							0.8916	400	0.8917	208
									0.8547	209
									0.8237	211
							0.8182	331	0.8183	1014
									0.8095	213
									0.7830	215

Conclusions

A new method to produce ultrafine diamond powders was developed. If the diamond yields could be enhanced and the reaction conditions, which control the particle growth rates, formation of cubic and hexagonal modification, and purity, will be better understood, laser pyrolysis of C_2H_4 or other hydrocarbons could be a promising new method to synthesize ultrafine, spherical diamond powders with narrow size distributions.

If such diamond powders could be produced in larger quantities, the following applications could be imagined: *i)* use as abrasives and polishing means to produce improved surfaces for optical and electronic purposes; *ii)* material scientists are waiting for the availability of large quantities of ultrafine diamond powders [6]. If diamond could be sintered, one could imagine that engine parts or tools consisting of pure diamond could be produced. Maybe sinterable diamond powders can be obtained by the method just described. The powders produced have all the properties found essential for sintering: spherical shape, sometimes monosized size distribution, particle size below 1 mm, and high purity. *iii)* Using $^{12}C_2H_4$, it is possible to synthesize isotopically pure ^{12}C-diamond powder with our method. The recently reported process to synthesize isotopically enriched ^{12}C-diamond of up to 1 carat [18] could be simplified and maybe improved. The present procedure to make ^{12}C-diamond consists of three steps: *a)* synthesis of ^{12}C-diamond films by CVD, *b)* crushing and milling of the diamond films to powder, *c*) recrystallization of the diamond powder at 52000 atm and 1200°. The first two steps could easily be replaced by our method. Additionally, the purity of ^{12}C-diamonds could be enhanced further by the process described, since the laser-induced pyrolysis of C_2H_4 takes place in the gas phase in the absence of walls. Therefore, the purity of the diamond powder obtained depends exclusively on the purity of the educt gases.

Finally, the homogeneous gas-phase synthesis of diamond grains may shed light on the origin of interstellar diamond grains found in high concentrations in meteorites [9][18].

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Chirale stationäre Phasen mit (+)-(*R*)-*N*-(1-Phenylethyl)-*N*'-[3-(diethoxymethylsilyl)propyl]harnstoff für die direkte Enantiomerentrennung mit Kapillargaschromatographie und überkritischer Fluidchromatographie

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Abstract. Five different polymer stationary phases with (+)-(*R*)-*N*-(1-phenylethyl)-*N*'-[3-(diethoxymethylsilyl)propyl]urea as the chiral selector have been synthesized and tested for direct enantiomer separation in capillary gas and supercritical fluid chromatography.

Einleitung

Die komplexe Chemie der Lebensvorgänge basiert weitgehend auf Wechselwirkungen zwischen chiralen Molekülen. Enantiomerenreine Wirkstoffe können durch asymmetrische Synthesen, Verwendung enantiomerenreiner Synthesebausteine oder durch Enantiomerentrennung erhalten werden. In jedem Fall ist eine Überprüfung der Enantiomerenreinheit notwendig. Da sich die Enantiomere nur in ihren Wechselwirkungen mit anderen chiralen Substanzen unterscheiden, ist für die Trennung eine chirale Umgebung nötig. Eine meist aufwendige Möglichkeit für die Trennung der Enantiomere ist die klassische Methode der fraktionierten Kristallisation diastereoisomerer Salze. Wesentlich einfacher sind chromatographische Trennverfahren, bei welchen auch weitere Begleitstoffe abgetrennt werden können: neben der Herstellung diastereoisomerer Derivate mit anschliessender Trennung in achiralem Milieu und der Trennung mit chiralen Zusätzen in der mobilen Phase ist vor allem die Trennung auf einer chiralen stationären Phase (CSP) eine wichtige Trennmethode.

In der Kapillargaschromatographie (GC) ist die Trennleistung sehr hoch, aber es können nur leichtflüchtige Verbindungen enantioselektiv getrennt werden. Weiter ist eine hohe Temperatur für die Trennung notwendig, wobei die Enantioselektivität mit zunehmender Temperatur abnimmt. Idealer wäre die Chromatographie in Kapillarsäulen mit einem überkritischen Fluid als mobiler Phase (SFC = supercritical fluid chromatography), wo Trennungen mit hoher Trennleistung bei tieferen Temperaturen möglich sind. In der SFC muss die stationäre Phase in der Kapillare immobilisiert, das heisst kovalent an die Kapillarwand gebunden und/oder räumlich vernetzt sein, da sie sonst durch die mobile Phase herausgewaschen wird. Als stationäre Phasen für die Kapillar-SFC wurden bereits immobilisierte Polysiloxane mit chiralen Gruppen verwendet [2–4].

In dieser Arbeit wird die Immobilisierung eines Harnstoff-Derivates für die Enantiomerentrennung mit GC und Kapillar-SFC untersucht. Ähnliche Phasen sind für die Hochleistungs-Flüssigchromatographie (HPLC) bereits kommerziell erhältlich [5]. Es wurden fünf Phasen mit (+)-(*R*)-*N*-(1-Phenylethyl)-*N*'-[3-(diethoxymethylsilyl)-propyl]harnstoff als chiralem Selektor auf verschiedene Art polymerisiert (*Schema*). Als Vergleich wurde eine Phase mit (+)-(*R*)-*N*-(1-Naphthylethyl)-*N*'-[3-(diethoxymethylsilyl)propyl]harnstoff hergestellt. Die Phasen konnten zum Teil immobilisiert werden. Eine Phase mit hohem Immobilisierungsgrad wurde in der SFC verwendet.

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