DIAMOND CHEMICAL VAPOUR DEPOSITION

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Abstract - Preparation, characterisation and selected applications of vapour deposited diamond coatings and free-standing membranes are reviewed. General trends and implications of a C/H/O-phase diagram, which provides a common basis for all diamond CVD methods are discussed.

1.-Properties and Applications of CVD Diamonds

The possibility of depositing diamond coatings onto non-diamond substrates at low pressures and moderate temperatures by means of chemical vapour deposition methods [1-13] puts the industrial use of many of diamond's extreme properties within reach. Possible applications range from wear-resistant coatings to active semiconducting devices and from x-ray windows to new types of displays. Table 1 summarizes the most important properties of bulk

Fig.1: Projected Japanese sales of "New Diamond" products. The data are based on a market survey by the Japanese "New Diamond Forum".

diamond along with competing materials in possible application fields. A market forecast by the Japanese "New Diamond Forum" with its more than 100 industrial member companies [14] illustrates the high potential of vapour grown diamond. A multi-billion dollar market is predicted for the year 2000.

Table 1: The extreme properties of diamond compared to some currently used competing materials and the (possible) fields of applications.

properties of diamond		comparison with competitors	possible applications
Vickers' hardness [kg/mm^2]	12 000-15 000	hardest material known	drill bits, polishing material, cutting tools, sintered or brazed diamond compacts
coefficient of friction	0.1 (in air)	very low in air; (higher if kept clean under vacuum!)	wear resistant coatings on windows and bearings
Young's modulus [N/m^2]	1.2×10^{12}	twice the value of alumina; highest mechanical strength	stiff membranes for lithography masks, lightweight coatings for audio devices
sound propagation velocity [km/s]	18.2	1.6 x the value of alumina	
chemical inertness	inert	at room temp. resistant to all acids, bases and solvents	coatings for reactor vessels
range of high transmittance [μm]	0.22 - 2.5 and >6	in the IR orders of magnitude lower than other material	UV-Vis-IR windows and coatings microwave windows optical filters optical wave guides
refractive index	2.41	1.6 x the value of silica	
band gap [eV]	5.45	1.1 for Si; 1.43 for GaAs 3.0 for β -SiC	high power electronics high frequency semiconducting devices hot thermistors, hottransistors lasers, detectors
electron/hole mobility [$\text{cm}^2/\text{V s}$]	1900/1600	1500/600 for Si 8500/400 for GaAs	
dielectric constant	5.5	11 for Si 12.5 for GaAs	
thermal conductivity [W/cm K]	20	value for type Ila natural diamond at room temp. 4 x the value of Cu or Ag	insulating heat sinks for electronic devices
thermal expansion coeff. [$1/\text{K}$]	0.8×10^{-6}	value at room temp. close to silica value of 0.57×10^{-6}	thermally stable substrates, e.g. for x-ray lithography masks
luminescence [μm]	430	blue luminescence scarce (β -SiC works)	blue LEDs ; displays

Some applications such as "new diamond" based cutting tools, sliding parts or loudspeaker diaphragms are already on the market or close to market introduction. Other fields, e.g., the use of diamond coatings in optics and opto-electronics are likely to be next to reach customers, followed by passive electronic devices, such as thermistors or radiation detectors. The use of CVD diamonds for active electronic devices is less advanced. Although prototype Schottky diodes and field effect transistors exist and operate at elevated temperature of up to 600 °C, these applications are still in need of certain technological breakthroughs such as heteroepitaxy on simple substrates and low resistivity phosphorous doping. However, there is little doubt that many of the applications shown and listed in Table 1 and in Fig. 1 will, sooner or later, reach the market

The current worldwide status with respect to individual applications will be illustrated and discussed during the conference.

2.- Diamond Deposition Methods and the C/H/O-Phase Diagram

Currently all major techniques to produce the desired diamond films rely on the pyrolysis of a carbon carrier gas and, simultaneously, the activation of the CVD gas phase by a hot filament, a chemical flame or a gas discharge to produce a selective etchant, e.g., atomic hydrogen, in order to remove non-diamond carbon phases from the growing diamond film.

Fig. 2 depicts the experimental set-ups for the hot filament method [2], microwave plasma CVD [3,11], thermal DC jet diamond deposition [4,12] and oxy-acetylene torch diamond synthesis [5] and Table 2 summarizes the current status of all CVD based methods with respect to achieved rates, coated areas, commonly used substrates, quality of the deposited material and some of the advantages and drawbacks of each method.

Recently, we developed a C/H/O-phase diagram that, for the first time, provides a common basis for diamond CVD [15,16]. This diagram (Fig.3, see [16] for detailed explanations) allows to determine the concentration coordinates of any ternary carbon/hydrogen/oxygen-containing CVD gas phase from given flow rates or flow ratios. Evaluation of published data as well as the results of specifically designed test experiments revealed that, independent from the method and the starting materials used, diamond synthesis is only feasible within a surprisingly well defined area, a diamond domain, within the C/H/O-phase diagram. Additional details about this new approach, the general trends that can be derived from the existence of a diamond domain, experimental data verifying the concept and its implications on the future directions of the field will be discussed.

Figure 2:
Experimental set-ups of four major diamond CVD methods:

- (A) Hot Filament CVD, (B) Microwave Plasma CVD,
(C) DC Plasma Jet Deposition (D) Flame synthesis from an oxy-acetylene torch.

All four methods are capable of producing high quality polycrystalline diamond on a variety of substrates.

Table 2. Diamond Deposition Processes: Summary of Methods and Results

Results Method	rate [$\mu\text{m}/\text{hour}$]	area [cm^2]	quality [Raman]	sub- strates	advantages	drawbacks
flame	30-100	<1	+++	Si, Mo, TiN	simple	area, stability
heated filament	0.3-2	100	+++	Si, Mo, silica etc	simple large area	contaminations stability, no O_2
DC discharge (low pressure)	< 0.1	70	+	Si, Mo, silica etc	simple large area	quality, rate
DC discharge (medium P)	20-250	<2	+++	Si, Mo, alumina	rate, quality	area
DC plasma jet	930	<2	+++	Mo, Si	highest rate, quality	area, stability, homogeneity
RF (low pressure)	< 0.1	?	-/+	Si, Mo, silica BN, Ni	scale-up	quality, rate, (contaminat.)
RF (thermal, 1 atm)	180	3	+++	Mo	rate	area, stability, homogeneity
Microwave (0.9-2.45 GHz)	1 (at low P) 30 (high P)	40	+++	Si, Mo, silica WC, etc. etc.	quality, stability, (reasonable rate & area)	rate, area
Microwave (ECR 2.45 GHz)	0.1	<40	-/+	Si	area (?), low P	quality, rate, (contaminat.)

Fig. 3: The C/H/O/-phase diagram of diamond CVD. The diagram comprises more than 80 experiments from over 25 different sources and provides a common basis for all diamond CVD methods. Successful diamond synthesis is, independent from the method and the starting materials used, only feasible within a well-defined diamond domain in the diagram (see [16] for detailed explanations).

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