OPTI 521 Synopsis of a technical report

Paul W. May, *Diamond thin films: a 21st-century material*

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Abstract

I discuss the synthesis of diamond film by chemical vapor deposition. The unique features of diamond, and its consequent applications to high power laser window and missile domes are pointed out

1. Introduction

Yes, diamond optics are expensive. Now, let's see what is nice about them. This report is a review of the paper [May 2000]. The applications are in papers [Douglas-Hamilton 1974] and [Klein 1991].

2. Synthesis of diamond

2.1. High-pressure high-temperature

Diamond was first synthesized at General Electric in 1954 [Strong 1991, 1971]. This was a high-pressure (48-60 kbar), high-temperature (1200-1500 C) process, and was successful in producing diamond crystals of 1 carat (200 mg) size over a period of 4-7 days. Imitating geological processes, this approach depends on subjecting the carbon to conditions where the diamond form is the thermodynamically stable phase. Crystal size is limited to several millimeters by the dimensions of the growth chamber and the fixed inventory of reactants.

2.2 Chemical vapor deposition

A major advance was the development of the chemical vapor deposition (CVD) process [May 2000]. Carbon-containing gases (usually methane) are broken down by microwave or plasma discharge, and carbon atoms, one at a time are deposited on a heated (approximately 700 C) substrate. The enabling breakthrough was the discovery that a high concentration of hydrogen was critical to the success of CVD.

- Hydrogen is needed to terminate dangling bonds at the surface, and prevent a rearrangement into graphitic carbon.
- Atomic hydrogen preferentially etches away graphitic carbon compared to diamond carbon, thus preventing the growth of the undesired but more thermodynamically stable form.
- Atomic hydrogen breaks up long-chain hydrocarbons in the gas phase, preventing the deposition of polymers onto the surface, which could inhibit further diamond growth.
- Atomic hydrogen reacts with CH_4 to produce reactive CH_3 radicals that can attach to surface sites.
- Atomic hydrogen can abstract a surface H atom, making the bond available for CH_3 adsorption.

3. CVD diamond films

Adherent diamond films require the formation of a thin carbide interfacial layer that acts as a glue. Ferrous metals cannot be diamond coated by simple CVD methods due to the their solubility of carbon; diamond growth begins only after the substrate is saturated with carbon. On the other hand, carbides themselves, such as SiC, TiC, and WC are particularly amenable to diamond deposition.

Substrates that do not react with carbon do not form adherent diamond films. This is one way to make free-standing diamond films, since they readily delaminate. This category includes Cu, Sn, Pb, Ag, Au, Ge, and Al_2O_3. Silicon is also a preferred substrate, and a free film is obtained by etching away the Si.

Microwave excited CVD can produce growth rates of 10 μm per hour. Plasma jet coating has achieved growth rates in excess of 100 μm per hour, but only over the area of the jet, about 1 cm^2.

For substrates other than diamond, nucleation is promoted either by scratching the surface with diamond grit, or, for better fine scale control biasing the substrate to negative 100-200 V for the first few minutes to implant carbon ions. The upper layers are generally superior to the initial nucleating layer, and it is usual to polish off the lower 50-100 μm.

CVD diamond films are being produced with diameters up to 20 cm and thickness exceeding 1 mm.

4. Optical properties of diamond

Pure diamond is transparent from its bandgap of 225 nm in the ultraviolet to at least 100 μm in the far infrared, except for a band from 2.5-6.5 μm. Since diamond contains only a single kind of atom, there is no electric dipole coupling between photons and phonons, and only multiphonon processes can lead to absorption. However, impurity atoms will allow these electric dipoles to form, and the presence of nitrogen in particular should be avoided. Nitrogen impurities absorb below 450 nm, and impart a yellow color. See the absorption spectra at the end of the report.

The coefficient dn/dt is a rather large 10 ppm/K.

With a refractive index of about 2.4, both in the visible and at 10.6 μm, diamond can be AR coated with conventional glass. Furthermore, soft IR optics with high indices can be coated with diamond, serving both as an AR and a protective coating.

5. Mechanical properties of diamond

CVD Diamond has an elastic modulus of 1.2 TPa [May 2000], and a tensile strength of 200-400 MPa [Feldman 1995]. Its thermal expansion is 1 ppm/K [May 2000]. Pure samples can have a heat conductivity of 2000 W m^{-1} K^{-1}[May 2000]. No other known material can match these.

Thermal conductivity is very sensitive to impurities. One intrinsic impurity in diamond is the natural isotopic abundance, being 98.1% C^{12} and 1.1% C^{13}. Diamond grown from carbon depleted to 0.1% of C^{13} was found to have a 50% higher thermal conductivity, 3300 W/m/K [Strong 1991].

6. Applications

Diamond optics are well suited for use with high power CO_2 lasers at 10.6 μm [Douglas-Hamilton 1974]. Conventional IR window materials, such as alkali halides or ZnSe are either hygroscopic or have low thermal conductivity, and require face cooling at high power. It appears that the maximum power they can handle is about 10 kW. In contrast, with an absorption of 0.05 cm^{-1}, a diamond window should be able to handle 1 MW of power with edge cooling with a resulting temperature difference of about 200 K. This is safely below the onset of diamond oxidation of 550 C and the graphitic transition

of 800 C.

The authors [Douglas-Hamilton 1974] report an experiment in which a natural diamond window survived a 1 s exposure to a focused 1 kW laser beam with a peak irradiance of 1MW cm^{-2}. Even though the metal holder exploded, from reflected light, and surface dust contaminants were vaporized, the diamond window was unscathed. The authors speculate the ultimate capacity could be 1 GW cm^{-2}.

Another application is to missile domes [Klein 1991]. The authors calculate that a 5 cm diameter dome 1 mm thick can withstand the required load.

References

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Figures.

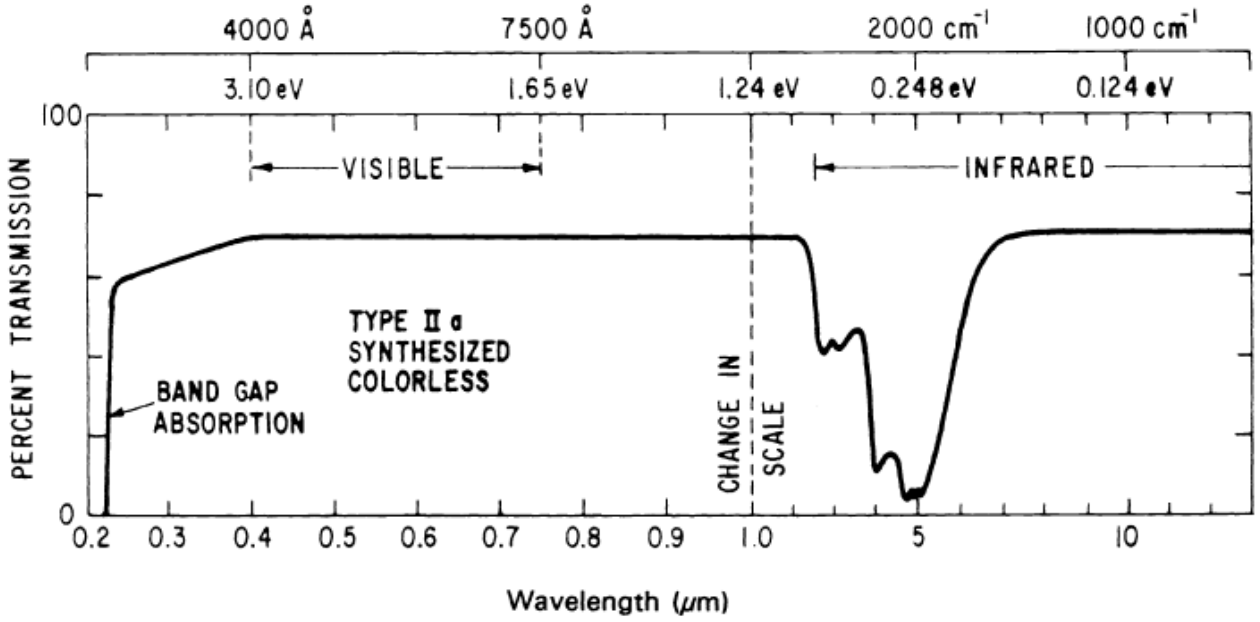

Figure 1. Transmission spectrum of type IIa single crystal diamond[4].

[Feldman 1995]

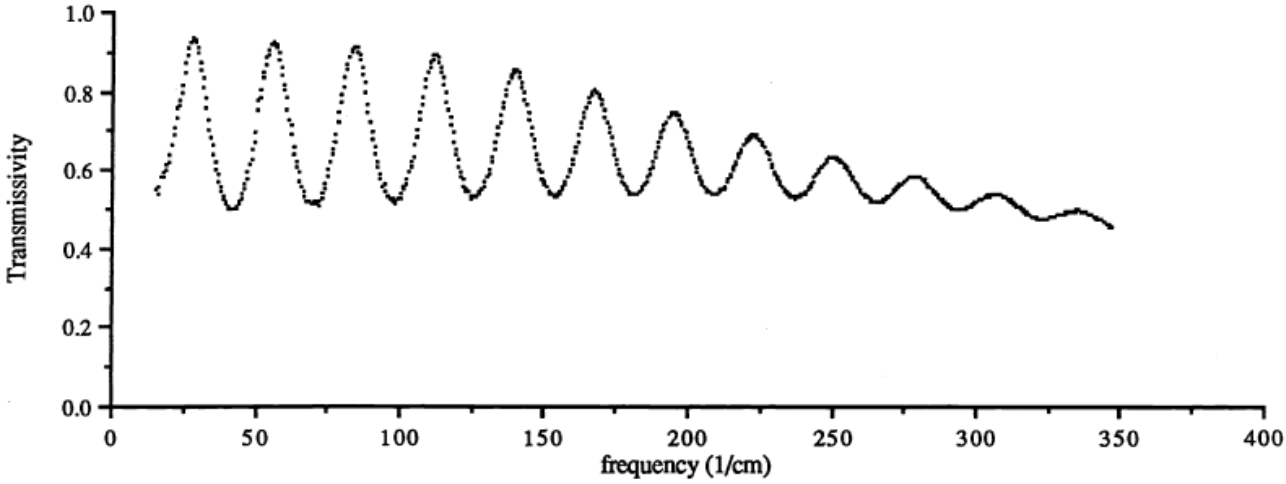

Figure 3 FTIR transmissivity data of sample "a" as a function of frequency

[Gatesman 1990]

Note that the oscillations above are etalon effects.