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What do a human, a plant, the photoresist used in the microfabrication, and a polymer have in common? Why has carbon become a crucial part of all known living systems? The answer to these questions may be embedded in carbon’s hybrid bonding structure (sp, sp², and sp³ C–C bonds). Carbon has 4 electrons in its outermost shell (the valence shell), which is the second shell. At first sight, one would expect that these 4 electrons are distributed among its one 2s and three 2p orbitals. However, it is well known that, in the diamond lattice, each carbon atom bonds with its four neighbors. Are the electrons in 2s and 2p orbitals responsible for the four bonds? One possible answer is that the 2s, 2pₓ, 2pᵧ, and 2pz orbitals of the carbon atom form bonds with its neighbors. There are two problems with this answer. First, these bonds will have different strengths (s and p orbitals), which is in contradiction with the experimental fact indicating an equal strength for all the four C–C bonds in the diamond. Second, the computed strength of such bonds will be lower than that found experimentally. What is then the nature of C–C bonds found in organic compounds?

The answer to this difficult question was provided in 1931 by Linus Pauling (1901–1994), the winner of two Nobel prizes. With the help of quantum mechanical calculations, Pauling showed how one s orbital and three p orbitals can mix, or hybridize, to form four equivalent atomic orbitals with tetrahedral orientation. The resulting hybrid orbitals are called sp³ orbitals as shown in Figure 1. The sp² or sp³ orbital results if two or one p orbital combine with the s orbital, respectively, to form the hybrid. While sp³ C–C bonds lead to a diamond lattice, the sp² C–C bonds lead to graphite, and a material which contains both sp² and sp³ C–C bonds is called diamond-like carbon (DLC). The optical properties, such as the bandgap, of DLC depend on the sp³/sp² ratio. If a sheet consisting of a monolayer of graphite, which consists of sp² bonds, is wrapped into a pipe, the resulting structure is called a single-wall nanotube (SWNT), as shown in Figure 2a. A multiwall nanotube (MWNT) has many such layers (Figure 2b–c). Other elements such as oxygen (in H₂O) and nitrogen (in NH₃) also form sp³ orbitals but carbon seems to be only one which is capable of forming sp, sp², or sp³ bonds, depending upon the bonding environment (Figure 3). This may explain why nature has selected carbon (perhaps due to its bonding flexibility, to form long C–C chains and rings) as the material of choice for building living systems.

The sp³ bonding in a diamond lattice makes it a very unique material with a combination of properties not matched by any other known materials (Table 1). In fact, the C–C sp³ bond in diamond is responsible for its remarkable properties leading to current and potential applications as shown in Figure 4. Although diamond (for centuries) and its bonding structure (for over 70 years) has been known for a long time, the growth of diamond films using chemical vapor deposition (CVD) took a long time to mature. Again, this delay relates to the difficulty with which the diamond lattice with sp³ C–C bonds is fabricated.

Diamond Growth by CVD

First evidence of diamond growth by CVD, by Eversole in 1952–1953, led to the use of H₂ and CH₄ in the hot filament CVD (HFCVD) to grow diamond on diamond substrates (homoepitaxial growth) by Angus in 1971. The inexpensive CVD polycrystalline diamond (poly-C) was grown on non-diamond substrates by Deryagin in 1976, Spitsyn...
in 1981, and by Matsumoto et al. in 1983. Currently, it is believed that, during the CVD of diamond, the CH₃ is responsible for deposition of C as diamond and non-diamond phases. The atomic hydrogen, present in the growth environment, removes the non-diamond phases leaving behind the diamond phase. Near the end of the 1990s, basic science of CVD diamond was well understood, and today diverse plasma and thermal techniques have been developed to produce poly-C films several mm thick and over 12 inches in diameter. Optically smooth 300-micrometer thick undoped poly-C wafers are available on the market. Although there are some reports of n-type poly-C and crystalline diamond growth, the well-established techniques exist only for in situ doping of p-type diamond.

A number of diamond growth techniques are currently available for the growth of diamond and carbon nanotubes. Microwave plasma CVD (MPCVD) can be used for the growth of both diamond and carbon nanotubes. As shown in Table 2, the deposition rate of diamond shows a large variation (0.1–3600 micrometers/hour) depending on the growth technique. For applications...
of diamond in optical coatings, optoelectronic devices and optical systems, the study of transmission, reflection and absorption of light for diamond is very important. These properties of diamond are responsible for its beauty and glamor. For applications in optoelectronic materials, devices and systems, the micro-fabrication and -machining technologies are crucial, particularly in the case of inexpensive poly-C films.

### Table 1 Comparison of semiconductor properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Diamond</th>
<th>Si</th>
<th>GaA</th>
<th>Poly-C</th>
<th>Crystalline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. of merit</td>
<td>73,856</td>
<td>9</td>
<td>62.5</td>
<td>10,240</td>
<td></td>
</tr>
<tr>
<td>Keyes, $10^5$ W cm$^{-1}$ s$^{-2}$ C</td>
<td>444</td>
<td>13.8</td>
<td>6.3</td>
<td>90.3</td>
<td></td>
</tr>
<tr>
<td>Sat. electron vel., $10^7$ cm s$^{-1}$</td>
<td>2.7</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Carrier mobilities, (cm$^3$ V$^{-1}$ s$^{-1}$)</td>
<td>1–165</td>
<td>1600</td>
<td>600</td>
<td>400</td>
<td>50</td>
</tr>
<tr>
<td>Resistivity, $\Omega$ cm</td>
<td>$10^{-2}$–$10^8$</td>
<td>$10^{-3}$–$10^{13}$</td>
<td>$10^{-4}$–$10^8$</td>
<td>6–10^8</td>
<td>150</td>
</tr>
<tr>
<td>Breakdown field, MV cm$^{-1}$</td>
<td>10</td>
<td>0.3</td>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Band gap, eV</td>
<td>5.45</td>
<td>1.12</td>
<td>1.42</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>6.7</td>
<td>5.5</td>
<td>11.7</td>
<td>12.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Thermal exp. coeff., $10^{-6}$ C$^{-1}$</td>
<td>2.6</td>
<td>1.1</td>
<td>2.6</td>
<td>5.9</td>
<td>4.7</td>
</tr>
<tr>
<td>Thermal cond., W cm$^{-1}$ K$^{-1}$</td>
<td>20</td>
<td>4–22</td>
<td>1.5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>Lattice constant, Å</td>
<td>3.57</td>
<td>5.43</td>
<td>5.65</td>
<td>4.36</td>
<td></td>
</tr>
<tr>
<td>Density, g/cm$^3$</td>
<td>3.52</td>
<td>2.32</td>
<td>5.31</td>
<td>3.215</td>
<td></td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>4000</td>
<td>1412</td>
<td>1240</td>
<td>2540</td>
<td></td>
</tr>
<tr>
<td>Hardness, kg mm$^{-2}$</td>
<td>10,000</td>
<td>1000</td>
<td>600</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.11</td>
<td>0.15</td>
<td>0.23</td>
<td>0.315</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus, $10^{12}$ Pa</td>
<td>0.8–1.2</td>
<td>1.1–1.2</td>
<td>0.155</td>
<td>0.085</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Diamond may convert to graphite well below 4000 °C depending upon the ambient and it oxidizes at 6500 °C to form CO$_2$/CO in O$_2$.

### Absorption, Reflection, andTransmission in Diamond

The optical properties, which have been studied for hundreds of years, of naturally occurring single crystal diamond have led to the gem commerce. The fundamental concept involved in the tremendous historical fame of diamond is its high refractive index, $n_d$ (in the range of 2.38–2.64 depending upon the wavelength of light). The refractive index of a material is a measure of decrease of velocity of light (which is also true for all electromagnetic waves) when the wave enters the material. Mathematically, $n_d$ is defined by

$$n_d = \frac{V_{\text{vac}}}{V_d}$$  \[1\]

where $V_{\text{vac}}$ and $V_d$ are velocities of light in vacuum and diamond, respectively.

When a beam of light of intensity $I_0$ in air is incident normally on the surface of diamond, the reflected part of the beam, characterized by the reflection coefficient $R$, depends on $n_d$, and $R$ is given by

$$R = \left(\frac{n_a - n_d}{n_a + n_d}\right)^2$$  \[2\]
where \( n_a \) is refractive index of air and \( n_d \) is given by Sellmeier dispersion equation:

\[
\frac{1}{n_d^2} - 1 = \frac{4.3\lambda^2}{\lambda^2 - 0.0121} + \frac{0.33\lambda^2}{\lambda^2 - 0.031}
\]  \[3\]

where \( \lambda \) is the wavelength of light expressed in micrometers. When the beam enters diamond, part of it is absorbed in diamond. The absorption, characterized by the absorption coefficient \( \alpha \), is caused by: (i) impurities (such as nitrogen, boron, hydrogen, etc.); and/or (ii) intrinsic defects (such as dangling bonds, sp\(^2\) bonds, and sp bonds). However, if the energy of light is close to or above the bandgap of diamond (5.5 eV), the absorption can be caused by electronic transitions from valence to conduction bands. The intensity \( I(x) \) at a distance \( x \) below the diamond surface is given by

\[
I(x) = I_0 (1 - R) \exp(-\alpha x)
\]  \[4\]

The fundamental expressions for \( \alpha \) are different for indirect and direct type semiconductors. However, the modeling of \( \alpha \), for energies close to the bandgap of diamond, can be accomplished empirically using Urbach’s rule according to the following equation:

\[
\alpha = \alpha_0 \exp \left( \frac{\sigma (T)(E - E_0)}{kT} \right)
\]  \[5\]

Where \( \alpha_0 \) and \( \sigma \) are Ubach tail parameters, and \( E_0 \) (6.5 eV) is direct gap energy of diamond. \( K \) is Boltzmann constant and \( T \) is the temperature. As \( T = 300 \text{ K} \), \( \alpha_0 = 4.23 \times 10^{11} \text{ cm}^{-1} \) and \( \sigma = 0.585 \), eqn [5] can be simplified:

\[
\alpha = 4.23 \times 10^{11} e^{22.6 (E - 6.5)}
\]  \[6\]

where the units for \( \alpha \) and \( E \) are in cm\(^{-1}\) and eV, respectively. Using the expression \( E = 1.24/\lambda \), where \( E \) is in eV and \( \lambda \) is in micrometers, eqn [6] can be written as

\[
\alpha = 4.23 \times 10^{11} e^{27.9(1/\lambda - 5.24)}
\]  \[7\]

where \( \lambda \) is in micrometers. The variations of \( \alpha \) and \( n_d \) with wavelength and energy of light are shown in Figure 5, which are plotted using eqns [3] and [7]. Impurities and intrinsic defects in diamond strongly affect \( \alpha \), \( n_d \), and its other properties.

**Impurities in Diamond**

A pure diamond with perfect lattice structure is transparent to ultraviolet (UV), visible, infrared (IR), millimeter and microwave regions of the electromagnetic spectrum. However, even an impurity-free diamond has some absorption in the infrared due to phonon excitations and an ultraviolet cutoff due to band-to-band absorption. The defects, impurity-related and intrinsic, in single crystal diamond have been extensively studied because they strongly affect its properties. In fact, diamonds are classified according to the type of defects that are dominant.

Impurities in diamond give rise to additional energy levels in its bandgap. If the density of these impurities is sufficiently high, they can cause absorption of electromagnetic radiation (including light) on one hand and break the lattice symmetry on the other.

**Figure 5** Wavelength and energy dependence of absorption coefficient and refractive index of diamond.
The breaking of the lattice symmetry can lead to one-phonon IR absorption, which is forbidden in pure diamond. The fact that impurities affect the optical properties of diamond led to its classification into types Ia, Ib, IIa, and IIb which correspond to pale yellow, golden yellow, no color, and blue, respectively. The transmission properties of these various types of diamond are depicted in Figure 6. The dominant impurities are nitrogen (5–2500 ppm atomic) in type I and boron (10 ppm atomic) in type II. It may be pointed out that boron-doped diamond is a semiconductor with p-type conductivity measured at room temperature. Nitrogen-doped diamond does not show n-type conductivity at room temperature as the donor levels are too deep to be ionized.

**Polycrystalline CVD Diamond**

Due to the lack of a reliable hetero-epitaxial diamond growth technique, the crystalline diamond films are very expensive (require single crystal diamond substrates for their growth) and, consequently, their widespread commercial use is severely limited. Polycrystalline diamond (poly-C) grown by CVD, which can be as inexpensive as any other material if mass produced, is very attractive for optical and other applications (Figure 2). The properties of high-quality (with high density of sp3 C–C bonds) poly-C films are comparable to those of crystalline films.

As shown in Figure 6, the transmission properties of poly-C are comparable to or better than those of type I and II diamonds for part of the energy range. Free-standing commercial poly-C films are typically polished and have thicknesses in the range of 50–300 micrometers (the least expensive are 300 μm thick). White poly-C films transparent to visible light are also available. Such films, with optically smooth surface, can be considered free of scattering effects. These films can be considered as a transparent plate in air and, for normal incidence of light with energy less than the bandgap, the transmission coefficient is given by

\[
T = \frac{(1 - r_1^2)(1 - r_2^2)}{1 + r_1 r_2 + 2 r_1 r_2 \cos(2\delta)} \tag{8}
\]

where the Fresnel coefficients are given by

\[
r_1 = \frac{n_a - n_d}{n_a + n_d}, \quad r_2 = \frac{n_d - n_a}{n_d + n_a} \tag{9}
\]

where \(n_a\) and \(n_d\) are refractive indexes of air and poly-C, respectively, and \(\delta\) is phase change for a poly-C film with a thickness of \(t\):

\[
\delta = \frac{2\pi}{\lambda} n_d t \tag{10}
\]

Using \(n_a = 1.0003\), \(n_d = 2.4\) and \(t = 100\ \mu\text{m}\), eqn [8] can be written as

\[
T = \frac{1}{1.49 - 0.493 \cos\left(\frac{3015}{\lambda}\right)} \tag{11}
\]

or

\[
T = \frac{1}{1.49 - 0.493 \cos(0.048k)} \tag{12}
\]

where \(\lambda\) is in μm and \(k\), the wavenumber, is in cm⁻¹. Variation of \(T\) as a function of \(\lambda\) and \(k\), is shown in Figure 7. A similar behavior is observed for nonpolished poly-C films if the wavelength is larger than the surface roughness of the films. For a sample with a very rough surface, scattering effects need to be included in eqn [8].

![Figure 6](image1.png)  
**Figure 6** Transmission spectra of natural diamond and CVD polycrystalline diamond (poly-C).

![Figure 7](image2.png)  
**Figure 7** Transmission coefficient of a polished poly-C film with a thickness of 100 μm as a function of (a) wavelength and (b) wavenumber.
Electroluminescence in Poly-C

In a luminescence process, the electron must first be excited to higher energy, which can be accomplished by light (photoluminescence), electron beam (cathodoluminescence) or electrical energy (electroluminescence). A subsequent electron transition to lower energies leads to emission of light. A common example of electroluminescence is a forward biased p–n junction made out of direct bandgap type semiconductor such as GaAlAs. The light emitting diodes (LED) and LASERS are based on electroluminescence. Red, green, and blue LEDs are made from GaAlAs, GaP, and SiC/GaN, respectively. Indirect bandgap type semiconductors, such as diamond, typically do not exhibit electroluminescence. The fact that electroluminescence has experimentally been observed in crystalline diamond and poly-C seems to be, at first sight, a contradiction of its indirect bandgap. In fact, defects in diamond are believed to be responsible for their luminescence properties. All types of diamond are found to have a number of defects related to vacancies and impurities. Due to a unique combination of properties of diamond (Table 1), its electroluminescence properties offer a very unique application potential in optical microelectromechanical systems (MEMS), displays and communication devices in IR, visible and UV regions.

Electro-luminescence (EL) in optoelectronic devices is produced by excitation of electrons by electronic current. Yellow-green EL has been observed in Schottky diodes made of boron-doped poly-C. Blue-green and blue-violet EL has been observed in free-standing poly-C films, with thicknesses in the range of 15–400 micrometers, when the samples were subjected to applied fields in the range of 2 V/µm. The EL peaks are observed at energies in the range of 3–3.85 eV, with the main peak occurring at 3 eV.

Recently, a very interesting type of EL has been observed in poly-C and carbon nanotubes, which seems to have an application potential in displays and optical MEMS. Under applied electric fields in the range of 20–40 V/µm, electrons are known to tunnel out of a poly-C film into vacuum and the process is called field emission. EL has been observed during the field emission process, and this new effect is called field emission EL (FEEL). A typical FEEL spectra is shown in Figure 8. It is believed that FEEL results from direct type defects in poly-C, which are populated during the field emission process. The electrons in these defects, instead of being field emitted, make transitions to lower energy levels leading to light emission. The main FEEL peak is observed at 2.6 eV which is in the visible range.

Poly-C Applications

The current applications of diamond, which include optical windows, temperature sensors, heat sinks, cutting tools, surgical instruments, and optical coatings, are based on natural, synthetic, and CVD diamond. The cost of producing diamond has always been prohibitive in widespread diamond applications. Fortunately, over the past 20 years, the development of CVD diamond technologies has eradicated the fears of diamond being too expensive for its widespread applications. As the CVD poly-C can be as inexpensive as any other electronic material, widespread applications of diamond are expected for
poly-C. In the area of micro- and nanostructures, the poly-C can provide a unique opportunity for both polycrystalline and crystalline microdevices. Using the present fabrication techniques, the grain size in poly-C can be varied in the range from a few tens of nanometers (nanocrystalline diamond) to hundreds of micrometers (commercial free-standing poly-C films). This leads to a whole range of device structures ranging from inter- to intra-grain devices. An intra-grain device made in poly-C will be an inexpensive single crystal device with properties better that those found in natural/synthetic diamonds, because an intra-grain poly-C device will have a higher degree of purity (because it is grown by CVD).

The applications of poly-C in microsystems (current, in-progress, and future) include optical MEMS, biological/protective/hard coatings, sensors, field emission displays, and WIMS (wireless integrated microsystems). Intra-grain microlenses, RFMEMS, heat pipes, sensors, microabrasives, and spectrometers may lead the way for unique poly-C applications.

Optical MEMS

A basic MEMS structure, with electrostatic actuation mechanism, is shown in Figure 9. Currently, most of the Optical MEMS and RFMEMS (radio frequency MEMS) devices are made from poly-Si (polycrystalline Si) using surface or bulk micro-machining fabrication techniques. The ability to integrate micro-optical elements with movable structures and micro-actuators has opened up many new opportunities for optical and optoelectronics systems, as MEMS allow a more effective manipulation of optical structures than the conventional methods. Optical MEMS have applications in displays, sensing, data storage, and communication systems. Some of the examples are optical switches, optical cross-connects, wavelength division add/drop mixers, tunable filters/lasers/detectors, dispersion components, polarization dispersion components, and spectrometers.

Figure 9 A simple MEMS structure with electrostatic moving of the cantilever beam.

Figure 10 A poly-C MEMS combdrive for high-quality factor resonators, inertial sensors, optical MEMS, etc. Poly-C is superior to poly-Si as its Young’s modulus is 4 times higher than that of poly-Si.

Figure 11 Poly-C microabrasive structures two different densities of pyramids. (Courtesy of Dr. H. Bjorkman of Upsala University)
Material related limitations put some constraints on the current optical MEMS technologies and applications. Diamond is an excellent material for optical MEMS and can extend the application range and reliability. The use of poly-C in optical MEMS can also remove the traditional cost constraints associated with the use of single crystal diamond. Although the poly-C optical MEMS are in their infancy, recent developments are very exciting. Figure 10 shows a poly-C resonator structure fabricated using a poly-C fabrication technology compatible with Si processing techniques. Such structures, if used as filters and switches, can lead to a superior performance as compared to any other currently used material. Poly-C on-chip spectrometers are also expected to operate in a large wavelength range.

Microabrasives

Poly-C is also a very promising material for microabrasives. Micromachined poly-C MEMS structures have recently been fabricated for possible use for microabrasives. Figure 11 shows micromachined MEMS structures which are expected to enhance the life of a tool. Such abrasives by design are inherently cost-effective because they are batch fabricated.

See also

Light emitting diodes (01258).

Further Reading


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