An Overview of Synthetic Diamond and Diamond-like Carbon

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Abstract

Due to its incredible physical properties, diamond remains the subject of intense interest throughout science and industry. Within the last decade, researchers have made great strides towards efficiently synthesizing bulk diamond and diamond films from graphite and various carbon compounds. This paper will discuss the traits of several types of synthetic diamond, including diamond-like carbon, explain some of the diagnostic techniques used to determine the quality and composition of diamond and diamond-like films, and present the direction of current research and applications of this fascinating material.

1. Introduction

Crystalline diamond possesses some of the most impressive physical properties of any substance on the planet. First, it has a hardness of approximately four times that of the second hardest naturally occurring mineral, corundum. Diamond also has a thermal conductivity of about five times higher than that of the second best elemental solid, silver, and melts at the incredibly high temperature of 3820 degrees Kelvin. Additionally, it is transparent over a larger range of wavelengths than is any other material, but it maintains a relatively large refractive index of 2.418 [1]. Finally, a massive energy gap exists between its valence and conduction bands, making it a near perfect electric insulator at room temperature.

All of these qualities make diamond maximally useful for industrial and scientific applications of many kinds. Of course, bulk diamond is extremely rare and expensive, making it rather impractical for industrial use. Thus, ongoing attempts to efficiently synthesize diamond from more common forms of carbon provide the only reasonable promise for taking significant advantage of its many extraordinary characteristics.

2. Crystal Structure

The carbon atoms in a diamond crystal form a face-centered cubic lattice with the two-point basis, $\mathbf{0}$ and $(a/4)(\mathbf{x} + \mathbf{y} + \mathbf{z})$, where a is the length of the side of the cube and $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ are unit vectors in the x, y, and z directions, as shown in Figure 1 [1].

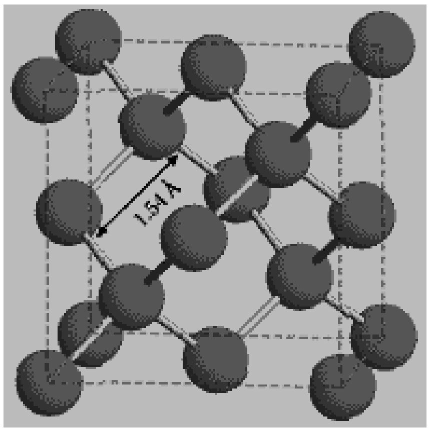

Figure 1: the diamond crystal structure

In this way, every atom has four nearest neighbors, each at a distance of 1.54 Å. The formation of covalent bonds between sp^3 hybrid electron orbitals makes this structure possible. The ground-state electron configuration of a carbon atom is of the form, $1s^2 2s^2 2p^2$. Hybridization occurs when one electron from carbons *2s* shell is excited into an empty *2p* orbital. Maximum overlap of the orbital wavefunctions occurs when the remaining *2s* electron and now three *2p* electrons reorient to produce four new wavefunctions, which are linear combinations of all four. The resulting sp^3 orbitals fill three-dimensional space (Figure 2) and create the rigid and tightly packed diamond lattice [2]. The short range and strength of the bonds result directly in the immense hardness and thermal conductivity of the crystal.

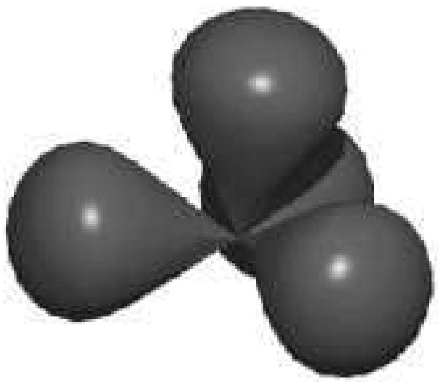

Figure 2: 3-dimensional representation of sp^3 orbitals

3. Synthetic Diamond

The production of synthetic diamond relies entirely on the ability to produce the sp^3 hybrid carbon bonds described in the previous section. In nature, carbon atoms assemble themselves in this fashion only when subjected to conditions of intense pressure and heat. The exact magnitudes of these parameters were not known until February of 1955, when the General Electric team of Francis Bundy, Tracy Hall, Herbert Strong and Robert Wentorf reported the first successful reproducible transformation of graphitic carbon to diamond. They simulated the natural process by pressurizing and heating graphite at over 55,000 atmospheres and 1400 degrees Celsius, using molten iron to facilitate the metamorphosis [3]. GE and others continued to use this method for decades to produce thousands of tons of synthetic diamonds, but this technique requires massive amounts of energy, and results in small crystals not useful for many of the applications discussed in a later section.

In the mid 1980s, several attempts to grow diamond using various chemical techniques began to show promising results. Chemical vapor deposition (CVD) is the process of chemically reacting certain gases with a volatile compound of some material, which is then deposited on a substrate [4]. For the deposition of diamond, many systems react a small percentage of methane gas (CH_4) with an excess of molecular hydrogen (H_2) and deposit on a treated substrate [5]. Several laboratories have fabricated thin diamond films in this fashion at reasonable temperatures and near atmospheric pressures.

Methods of substrate treatment vary, but the simplest idea is to aid the crystal nucleation process by seeding the substrate with a diamond powder. The deposited carbon atoms tend to reproduce the crystal structure of the powder, resulting in a thin diamond film. To deposit on a material of different atomic content and structure without a powder treatment, the substrate is often strategically biased or heated to encourage diamond nucleation [5–8].

4. Diamond-like Carbon

Diamond films are usually classified as either microcrystalline (MCD) or nanocrystalline (NCD) diamond, depending on the length scale of crystalline order [5–14]. The more general term of diamond-like carbon (DLC) commonly describes both MCD and NCD, especially if the relevant film contains a significant amount of graphitic carbon. DLC retains most of the desirable traits of diamond, and it is much easier and more cost effective to produce. Various laser-assisted deposition methods now use pulsed lasers to deposit DLC films at rates compatible with industrial implementation. By tuning the laser intensity and pulse duration, and by adjusting various parameters within the deposition environment, one can even control with some precision the relative concentrations of graphitic, sp^2 bonded carbon, and sp^3 bonded diamond [12–14].

5. Characterization

Researchers use a variety of schemes to distinguish diamond from graphite, and to measure the sp^2 to sp^3 bonding ratios of DLC samples. For example, high resolution scanning electron microscope (SEM) images show the crystalline nature of MCD and NCD, as shown in Figures 3 and 4 [12]. More indirect methods must be used, however, to gauge the exact bonding ratios.

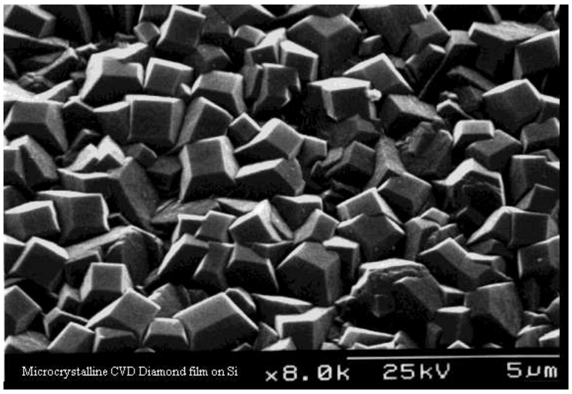

Figure 3: SEM image of MCD surface

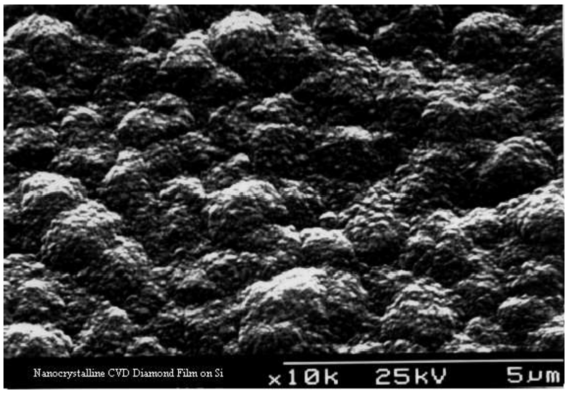

Figure 4: SEM image of NCD surface

Perfect diamond crystals exhibit several experimental signatures, which distinguish them from graphitic carbon samples. Perhaps the most striking of these is the Raman spectrum of diamond, which has a distinct peak at 1332.5 cm^{-1}. Figure 5 compares the

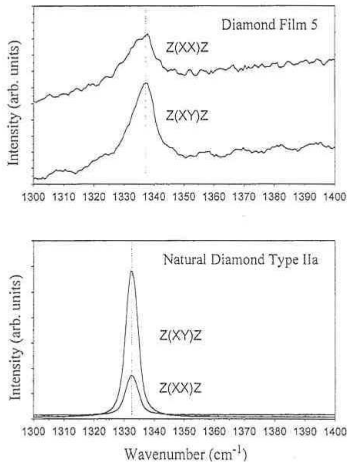

Figure 5: Raman spectra of natural diamond and CVD diamond

Raman spectra of natural diamond with that of a CVD diamond film [9]. The film displays a peak very close in wavenumber to the diamond peak, Raman shifted slightly to the right.

In general, the width of this peak and the magnitude of its Raman shift indicate the purity of the diamond in the film. Crystalline graphite has a Raman peak at about 1580 cm^{-1}. The intensities of these two peaks give a good estimate of the relative bond concentrations. In highly graphitic samples, the interference of the graphite and diamond peaks requires the use of additional characterization methods to extract meaningful data on the bonding ratio [11].

Other techniques include x-ray photoelectron spectroscopy (XPS) and the direct measurement of optical constants, namely refractive index and transmission bandwidth. XPS spectra show smoothing effects similar to those of Raman spectra when significant amounts of graphitic carbon are present.

6. Applications

Industries use natural and synthetic diamonds primarily as a durable abrasive or cutting tool, and occasionally for optical windows in precision instruments. The properties of DLC films, though, provide a wealth of new applications previously untapped by those of bulk diamond. The ability to coat large surfaces with an optically smooth and transparent, maximally hard, highly heat conductive, and electrically insulating material makes DLC ideal for numerous industrial, scientific, and commercial uses.

Hard DLC coatings already appear on commercially produced razor blades and watch faces, and should soon turn up on camera lenses and sunglasses. In the microelectronics industry, DLC is the perfect insulating finish for delicate integrated circuits. A large dialectric constant and high voltage breakdown strength also make DLC an excellent capacitor component. Finally, high-power electronics such as those used in the military benefit from the thermal conductivity of DLC heat spreaders and high melting point DLC temperature sensors [15].

7. Conclusions

Science and industry have tried for decades to put the many advantageous properties of diamond to practical use. The advent of reliable and affordable methods of production of diamond-like carbon and crystalline diamond films finally makes this aspiration a reality. In fact, the tunability of DLC traits and the relative ease of its fabrication allow it to satisfy the specific requirements of hundreds of diverse applications better than any other material.

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