CVD diamond—Research, applications, and challenges

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Diamond is a unique material that often exhibits extreme properties compared to other materials. Discovered about 30 years ago, the use of hydrogen in plasma-enhanced chemical vapor deposition (CVD) has enabled the growth and coating of diamond in film form on various substrate materials. CVD diamond research has been actively continued subsequently to develop new understanding and approaches for the growth and processing of this fascinating material. Currently, the study and development of diamond films has enabled a wide range of applications based on the combination of unique and extreme properties of diamond and the variety of film properties obtainable through tuning the microstructure, morphology, impurities, and surfaces. This issue of *MRS Bulletin* introduces the latest research, recent applications, and the challenges ahead for CVD diamond films.

Introduction

Diamond is a natural as well as a synthetic material that has captured everyone's attention. The rarity of natural diamond and the brilliance of cut and polished gems have made it one of the most esteemed components of jewelry. On any list of materials delineating specific material properties, diamond is often at the extreme. Moreover, diamond displays a number of unusual properties. We now stand at a point in time where some of the unusual or extreme properties are being used for applications that could not have been considered prior to the development of chemical vapor deposition (CVD) of diamond (**Figure 1**).

Carbon crystallized in the diamond crystal structure is a metastable phase, whereas the graphite crystal structure has a lower total energy. The diamond crystal structure can be described as two interpenetrating face-centered-cubic (FCC) sublattices, where each atom is bonded in a tetrahedral configuration to four nearest neighbor atoms of the opposite FCC sublattice. Crystalline diamond has the highest atomic density of any bulk crystal, along with the shortest average bond length, the highest bulk modulus, and the highest thermal conductivity. Diamond is transparent from the far-infrared to the ultraviolet, but natural diamond crystals are noted for their defects and impurities, many of which have been carefully categorized for their effect on the optical properties of gems. Diamond has the highest Debye frequency of any three-dimensional material, and the vibrational modes are nonpolar; consequently, it exhibits one of the lowest electron-phonon coupling constants.

In historical times, the synthesis of diamond was the goal of alchemists, and only since the 20th century were diamond crystals synthesized in high-pressure, high-temperature cells. Later, diamond films were prepared using CVD. The earliest reports of CVD growth of diamond were from Russia, the United States, and Japan.[1–6] Stimulated by both the unique characteristics of the material and potential applications, by the late 1980s, researchers from around the world were preparing diamond films largely using custom plasma-enhanced or hot filament CVD systems. Commercial microwave plasma CVD systems for diamond film growth became available around this time, and later other approaches to CVD diamond were developed, including plasma torch CVD. It was found that diamond-containing films could even be grown in a simple oxy-acetylene flame.[7]
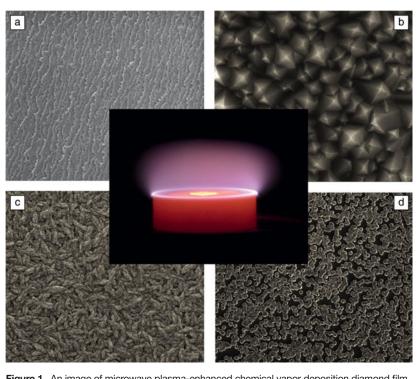
CVD diamond films are currently prepared with high purity, and these materials resist electrical breakdown in high electric fields and exhibit electron and hole mobilities that are the highest among wide bandgap semiconductors. Dopants

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Figure 1. An image of microwave plasma-enhanced chemical vapor deposition diamond film growth (center)[36] and scanning electron micrographs of (a) homoepitaxial diamond surface (~150 × 150 μm²),[37] (b) polycrystalline diamond surface (~40 × 40 μm²),[38] (c) ultrananocrystalline diamond surface (~2.5 × 2.5 μm²),[39] and (d) B-doped diamond microparticles (~70 × 70 μm²).[40]

crystalline diamond surface, thereby sustaining the film growth.

Recognizing the limitation of growing diamond films on small expensive diamond substrates, growth of CVD diamond has been concentrated on non-diamond substrates. Silicon is probably the most used substrate for diamond films, at least partially because of the similar thermal expansion characteristics of the two materials that limit strain effects. One of the most significant challenges is nucleation of the diamond layer, and a number of approaches have been developed. Most common is abrading the substrate surface with diamond grit; alternately, the surface is covered with a thin layer of diamond nanocrystals, and others have employed *in situ*-biased plasma steps. Nucleation densities of the most successful approaches are typically ~1×10^{11} cm^{-2}. In general, polycrystalline grains develop on the surface, which then grow larger as the film grows thicker. It is often possible to tune the reactor conditions such that one face (e.g., {100} or {111} facets) appears preferentially at the surface.[14] In these cases, the diamond grains at the interface with the substrate have nanometer-scale dimensions, and those at the surface can have a size of tens of micrometers.

Nanocrystalline and ultrananocrystalline CVD diamond films have advantages of smooth surfaces, lower strain, and improved fracture resistance. The films are characterized by diamond domains that are 10 nm or less in size with thin sp^2-bonded boundaries. The growth scheme is often to deposit in a reduced hydrogen gas phase that enhances re-nucleation and reduces etching of the small grains. The continuous re-nucleation leads to a grain size that is maintained throughout the film and also contributes to reduced surface roughness compared to polycrystalline films.

and impurities can be incorporated into diamond films during CVD growth, leading to tunable changes in the optical and electronic properties. Diamond film surfaces are chemically inert in most chemical environments. Hydrogen-terminated diamond surfaces exhibit a negative electron affinity (NEA), which is manifested by the conduction band minimum being at ~1.1 eV above the vacuum level.[8–10] Diamond surfaces can also exhibit hole surface conductivity that has been ascribed to electrochemical charge transfer from molecular adsorbates.[11,12]

CVD diamond deposition or alchemy?

Early researchers tried to understand the key attributes to growing diamond films. The growth of diamond is complicated by the multiple bonding configurations for carbon with fourfold sp^3 bonding (diamond) and threefold sp^2 bonding (graphite). Highly crystalline films are grown on crystalline diamond substrates by employing a carbon source (typically methane) in a predominantly hydrogen plasma.[13] Atomic hydrogen generated in the plasma is considered crucial for growth for a number of reasons. It preferentially etches graphitic sp^2-bonded carbon over sp^3-bonded carbon in the diamond lattice. The atomic hydrogen terminates the film surface during growth, thus maintaining the sp^3 bonding and resisting the formation of sp^2-bonded surface reconstructions. In addition, gas phase atomic hydrogen abstracts hydrogen bonded to the surface to produce sites where methyl components can adsorb onto the

Finding the diamond in CVD films

Early CVD diamond growth studies were typically guided by two characterization techniques: scanning electron microscopy (SEM) and Raman spectroscopy.[15,16] SEM was employed to observe and determine the grain size and morphology, and Raman spectroscopy could give insights into the relative sp^2/sp^3 bonding configurations, the residual strain, and the crystalline quality. Raman spectroscopy is particularly sensitive to sp^2 bonding configurations and also to diamond domain sizes. Consequently, growth studies often adjusted deposition parameters to minimize the intensity of sp^2-related spectral features while maximizing the intensity of the diamond phonon peak.[17] The width and position of the diamond peak were related to the strain and crystalline domain sizes. These approaches continue to be used to characterize nanocrystalline diamond (NCD) films.

For homoepitaxial CVD layers, often the problem is distinguishing the surface layer from the substrate. X-ray diffraction is typically employed to characterize the average properties of the films. Defects can be observed in TEM and by surface microscopy, where wet chemical or plasma etching techniques enhance the morphology for certain defects. Photoluminescence and cathodoluminescence spectroscopy are important to characterize defects, impurities, and carrier dynamics.[18] Observation of free exciton emission is often considered a signature of high-quality epitaxial layers. Nitrogen leads to different luminescence signatures depending on the configuration and charge state. Other common photoluminescence signatures for CVD diamond include spectral features related to Si impurities and a broad background attributed to sp^2-bonded sites.

Specific properties and applications

This issue of *MRS Bulletin* presents a series of reviews that address the most recent advances and the materials research that enables an ever more diverse set of applications of CVD diamond films. The topics covered in the issue are organized to describe homoepitaxial growth, single crystal diamond substrates, nanocrystalline materials, surface functionalization and biological applications, diamond for electrochemical applications, electron emission into vacuum, and surface conductivity due to a subsurface hole accumulation layer.

Homoepitaxy and doping

The high breakdown field, thermal conductivity, and carrier mobilities suggest diamond-based electronic devices could surpass the performance of other semiconductors. In addition, the unique properties of negative electron affinity surfaces, stable excitons, long impurity spin relaxation, and surface hole accumulation layer enable a range of electronic and optoelectronic devices not possible with other semiconductors. At the core of many of these devices is the deposition of high-quality epitaxial films with controlled doping profiles. Substantial progress has been made using boron for *p*-type doping and phosphorus for *n*-type doping. There is still much to be learned about defects and transport in diamond, and there is the additional challenge of forming a diamond heterojunction or low defect dielectric-diamond interfaces. In this issue, Yamasaki et al. describe the results of diamond homoepitaxy, doping, and heterointerfaces.

Single-crystal diamond substrates

Large-area single-crystal substrates will be necessary to enable electronic and optoelectronic applications. The recent advances in high growth rate plasma CVD for homoepitaxial layers and the use of metallic support layers for heteroepitaxial growth have enabled the development of single-crystal substrates that are expected to compete in size and defect density with other wide bandgap semiconductors. Careful studies of the growth process, defect formation, and the development of high power deposition systems have enabled high growth rate approaches. Large-area substrates have been demonstrated

using tiled overgrowth and a process that employs implantation, epitaxial regrowth, and lift off. The heteroepitaxial scalable approach employs a non-carbide-forming metal interlayer on crystalline oxide substrates. The process involves bias-enhanced nucleation and then growth to reduce the defect density. In their article, Schreck et al. describe the most recent results of scalable diamond substrates.

Nanocrystalline diamond materials

NCD films and ultrananocrystalline diamond (UNCD) films can be deposited on large-area substrates; the films exhibit mechanical properties that approach those of single-crystal diamond. Compared to polycrystalline diamond films, NCD and UNCD films are relatively flat, and the mechanical properties are uniform on scales larger than 100 nm. It was recognized that the NCD and UNCD films would have strong potential in microelectromechanical systems (MEMS), and important advances have been achieved in improving mechanical properties and reducing film stress. A materials challenge for many applications is the integration of diamond materials with other materials. Important demonstrations have included the fabrication of CVD diamond high-Q resonators and the integration of UNCD films with RF-MEMS and complementary metal oxide semiconductor technologies. In their article, Sumant et al. describe the most recent results on the growth of NCD and UNCD materials and their integration into micromechanical devices.

Surface functionalization and biological applications

Diamond has been known as a material able to withstand harsh chemical environments, but its surface was considered to be inert and unavailable for functionalization strategies that were successfully applied for other semiconductor materials. However, photo- and electrochemistry strategies opened a whole new playground of surface functionalization approaches. The advantages of diamond over other semiconductor materials include the fact that it is pure carbon, it has a very stable carbon–carbon bond, and it is biocompatible. The first step to obtain coupling of advanced (bio)molecules is usually the attachment of a linker molecule, and the specific surface termination of the diamond is important for the different approaches. The main role of the linker molecule is to introduce more complex functional groups that act as a starting point to attach targeted (biological) entities such as DNA, proteins, or aptamers based on specific surface chemistry. In their article, Szunerits et al. describe a number of surface chemistries that have been developed for surface functionalization for fields such as biosensing and drug delivery.

Diamond electrodes

The wide bandgap and doping capabilities of CVD diamond along with its stability are crucial aspects for application as electrochemical electrodes. Early reports of electrically conducting diamond identified the negative effects of the sp^2-bonded

regions of boron-doped CVD diamond electrodes. Recent studies have employed films with microcrystalline, nanocrystalline, and ultrananocrystalline microstructures as well as different dopants to achieve stable, conducting electrodes for different applications. Conducting CVD diamond films with B-doping levels > 10^{20} cm^{-3} have demonstrated the stability and required conductivity for use in electroanalytical chemistry and *in vitro* biosensing applications. In this issue, Einaga et al. describe the properties of CVD diamond films that enable a diversity of applications.

Electron emission

With the recognition that CVD diamond could exhibit a negative electron affinity, it was thought that diamond materials could be developed for field emission electron sources. Early results showed that CVD diamond films could display significant emission intensity at fields less than 50 V/µm. However, research established that the emission was dependent on defects and the sp^2 content in the films.[19] In fact, recent studies have argued that the film microstructure is more important for optimizing field emission than the NEA surface termination. In contrast, secondary electron emission, *p–n* junction emission, and thermionic emission are all cases where the electrons are supplied to the conduction band of the diamond, and NEA termination is necessary in each case. In addition, band bending and doping are particularly relevant. In their article, Lin et al. present recent advancements that establish tremendous progress in the last decade and also significant opportunities for materials research that will both bring understanding and potentially advanced applications of electron emission using diamond films.

Surface conductivity

In 1989, Landstrass and Ravi described the low electrical resistivity for the surface of hydrogen-terminated CVD diamond films,[11] and it was later established that the conductivity was governed by holes near the surface.[20] This led to much application-driven work, mostly focused on planar structures, like Schottky contacts and metal-semiconductor field-effect transistors.[21,22] A more general surface transfer model was introduced[23] that noted the subsurface hole accumulation layer was governed by electrochemical charge transfer between diamond and adsorbates.[24] The surface conductivity was dependent on the interactions between diamond and the adjoining molecular or solid materials and was governed by properties such as work function, band bending, electron affinity, and surface Fermi level.[25,26] An understanding of what governs the creation of the ~10^{12}–10^{13} cm^{-2} holes has also given rise to new device work bringing the H-terminated surface in contact with electrolytes,[27] gases,[28] and oxides.[29,30] Progress in the field continues with a study reporting evidence of Coulomb blockade effects as a direct result of the two-dimensional character of the conductive channel formed at hydrogen-terminated diamond surfaces, opening up new routes of fundamental and applied research.[31] In their article, Pakes et al. describe the formation of the surface-conducting layer in diamond and recent related applications.

Challenges and opportunities

In the last decade, there have been many advances in the materials science and applications of CVD diamond films. The development of previously introduced semiconducting materials has followed a well-established research and technology development progression. With the extreme and unique properties of diamond, past CVD diamond research has opened more doors rather than following an established development path. There are now many opportunities and challenges that will impact the broad range of technologies presented in this issue.

For homoepitaxial structures, it is necessary to improve doping efficiencies and reduce the effects of impurities and defects. Conversely, specific defect and impurity structures may enable their use for quantum devices. Identifying shallow dopants[32] and new quantum defects and effects[33,34] continues to be a challenge. In fact, research on charge transport and carrier dynamics has hardly been explored. For instance, the minority carrier lifetime, which is crucial in bipolar devices, has only been studied indirectly.[35] High-quality heterostructures and metal interfaces have mostly been studied to enable specific devices, while in-depth understanding is still missing.

Large-area single-crystal substrates will be necessary to enable electronics research. The availability of these substrates will enable device development that takes advantage of processes and equipment used in microfabrication facilities. Developing substrates with controlled doping and reducing defect densities will almost certainly be a challenge in the years ahead.

There have been striking demonstrations of the potential for nanocrystalline materials to impact MEMS and related technologies. The understanding of the relationships among growth conditions, the materials nanostructure, and film properties are at an early stage. The opportunities are so broad that potential applications may serve to focus the research.

Diamond appears to be biocompatible for many biomedical applications, and surface functionalization is necessary to enable the specific interactions and functions. Recent experiments have opened a number of approaches for modifying the functionality of diamond films. Our knowledge of electrochemistry at diamond surfaces has advanced greatly in the last decade. The field is now poised to move into new areas such as neurosignaling and stimulation.

The focus on electron emission materials has moved from field emission displays to a range of applications, including large-area vacuum electronics, power switches, electron amplifiers, and thermionic energy conversion. Advances in both NCD and homoepitaxial-doped diamond films will drive the field.

The surface hole-conducting channel continues to be a focus of basic research as the fundamental properties of the layer are still not well characterized. These structures will enable a range of "unconventional" electronics that will bring together surface chemistry and electronics in a unique way.

Research in CVD diamond is advancing to new applications based on the unique, extreme, and tunable properties of the material.

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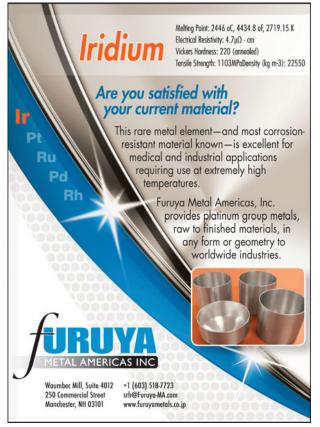
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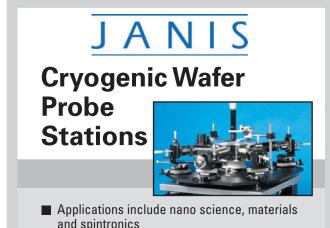36. G. Bogdan, K. De Corte, W. Deferme, K. Haenen, M. Nesládek, *Phys. Status Solidi A* **203**, 3063 (2006).
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