Chemical Vapor Deposited Diamond

Maturity and Diversity

James E. Butler

Chemical vapor deposited (CVD) diamond materials, grown from low pressure gases activated by plasmas, hot filaments, and combustion flames, were a novelty and scientific curiosity several decades ago. Now, CVD diamond is a maturing material with a wide variety of technological impacts, and with even more exciting applications to come in the future.

The driving forces for this rapid expansion in the development and application of CVD diamond materials include the exceptional material properties of diamond; growth methods that can be used to engineer desired materials properties via control of doping, crystallinity (size and texture), and morphology; the relative intellectual and computational simplicity of a single element material (carbon) with a low number of electrons; and the extensive knowledge available of organic and combustion chemistries.

The defining characteristic of CVD diamond materials, as compared to other carbon materials, is the domination of the crystalline cubic phase of carbon in domains of variable size. CVD diamond materials span a continuum of properties. Purity ranges from the intrinsic material with impurity concentrations less than ppm, to materials (un)intentionally doped with boron, nitrogen, phosphorous, sulfur, silicon, hydrogen, etc. The crystallinity of these materials varies from ultrananocrystalline, through nanocrystalline, and polycrystalline to single crystal materials. In CVD diamond materials, the crystalline domain size and extended defect structures (dislocations, twins, incoherent grain boundaries) all exist in a manner that can be engineered to varying degrees. This variability enables the design and fabrication of structures that exploit many of the desirable properties of diamond in a controllable manner.

Single Crystal CVD Diamond

Beginning on one end of the crystalline scale is single crystal diamond, most typically encountered with the natural diamond used in jewelry, or synthetic diamond grown by high pressure at high temperatures (HPHT), where diamond is the stable crystalline form of carbon. Single crystal CVD diamonds have been produced recently by numerous groups. Figure 1a presents a photo of a polished (faceted) CVD single crystal diamond. This diamond contains the nitrogen–vacancy (N-V) and substitutional nitrogen, N_s, defects (which contribute to the color observed). For a number of reasons, diamond is a candidate host material for quantum computing. Optically detected magnetic resonance of the N-V defect has been used recently to demonstrate single-qubit operations, an element of quantum computing, exploits the very long spin-spin coherence lifetimes (ca. 50 microseconds at room temperature) observed in this diamond.[1] In related work, the N-V defect has also been exploited recently for single photon quantum cryptography.[2]

Recent measurements on extremely pure CVD single crystal diamonds indicate a quality much better than that of the best diamonds found in nature or grown by HPHT processes. For extremely pure device grade CVD single crystals, with dimensions of the order of 3-5 mm, electron and hole mobilities (4400 and 3800 cm^2/sec, respectively) exceeding twice the previously measured best values were reported recently.[3]

In Fig. 1b, a ca. 4 x 4 mm single crystal CVD plate (white/clear) is shown in relation to the HPHT seed diamond on which it was grown. This homoepitaxial crystal was separated from the seed crystal using a patented liftoff technique

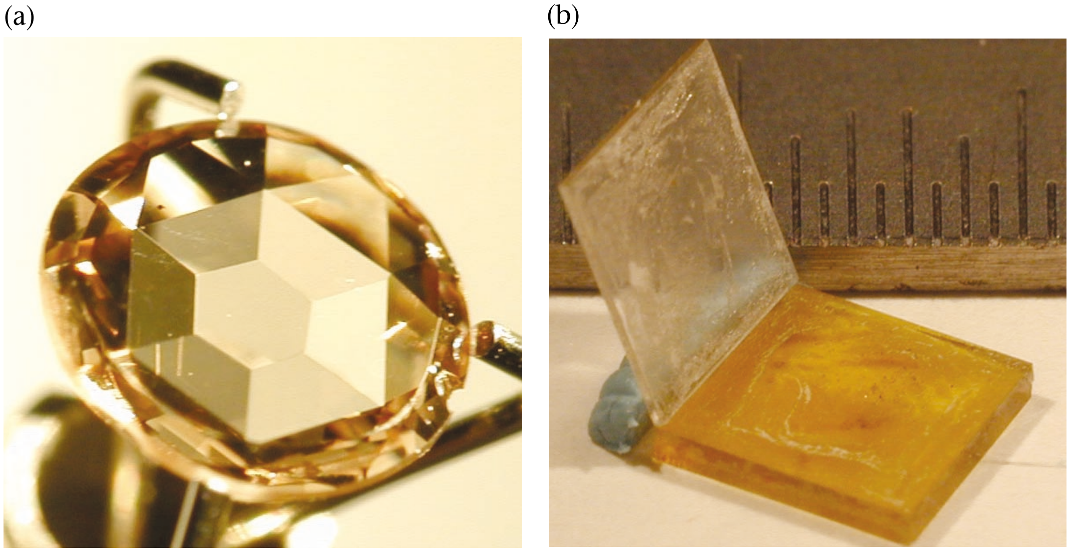

FIG. 1. Photographs of single crystal diamond grown by chemical vapor deposition (CVD) (Courtesy of Apollo Diamond): (a) a faceted stone ca. 3 mm diameter, in which single qubit operations for quantum computing have been demonstrated at room temperature using the N-V defect; and (b) a homoepitaxial layer ca. 4 x 4 x 1 mm (white/clear) after separation from the adjacent to the original HPHT seed crystal (yellow).

based on ion implantation, followed by growth, and then an electrochemical etch,[4] showing how high quality seed crystal can be reused multiple times. Various groups have also demonstrated that CVD on dense 'tiling' of similar oriented seed crystals can be used to grow larger area quasi-single crystal plates.

Polycrystalline CVD Diamond

Polycrystalline diamond films and plates are grown on non-diamond materials, usually refractory metals or ceramics, *e.g.* W, Ta, Mo, WC, Si, SiO_2, and others, by seeding the surface with particles of diamond, or by specific treatments that evolve into small diamond particles, *e.g.* biased enhanced nucleation[5,6] followed by homoepitaxial growth on the surface of these particles until they coalesce into a continuous coating. As a result of this growth process, the grain size is smallest on the nucleation surface (substrate side) and coarsens into larger grains as the film thickens due to the overgrowth of slower growing surfaces (grains) by more rapidly growing surfaces (grains). Additionally, impurity incorporation and intentional doping (with B, N, P, Si, etc.) depend on the specific growth mechanisms on each local facet (typically a (111) or (100) surface), resulting in different incorporation rates on each surface (or growth sector under each surface).[7] Examples are shown in Fig. 2 for a high quality, boron doped, polycrystalline diamond film of thickness, ca. 450 µm and diameter of 50 mm, grown by microwave plasma enhanced CVD. Figure 2a displays a scanning electron micrograph (SEM) of the growth surface of the film with characteristic microfacets of predominately (111) and (100) crystal orientation. Most of the crystallites have a <110> axis nearly parallel to the growth direction. Figure 2b is a SEM of the cross-section through a film (laser cut and mechanically polished) showing the grain coarsening as the film grows. Figure 2c is an optical picture of the white light transmission through a mechanically polished diamond plate such that the lower part of the picture was the material near the substrate (nucleation side) with small grain size and the top was near the growth side with larger grain size. The degree of blue color of a grain relates to the amount of boron incorporated in the growth sector and can vary by as much as a factor of ten.

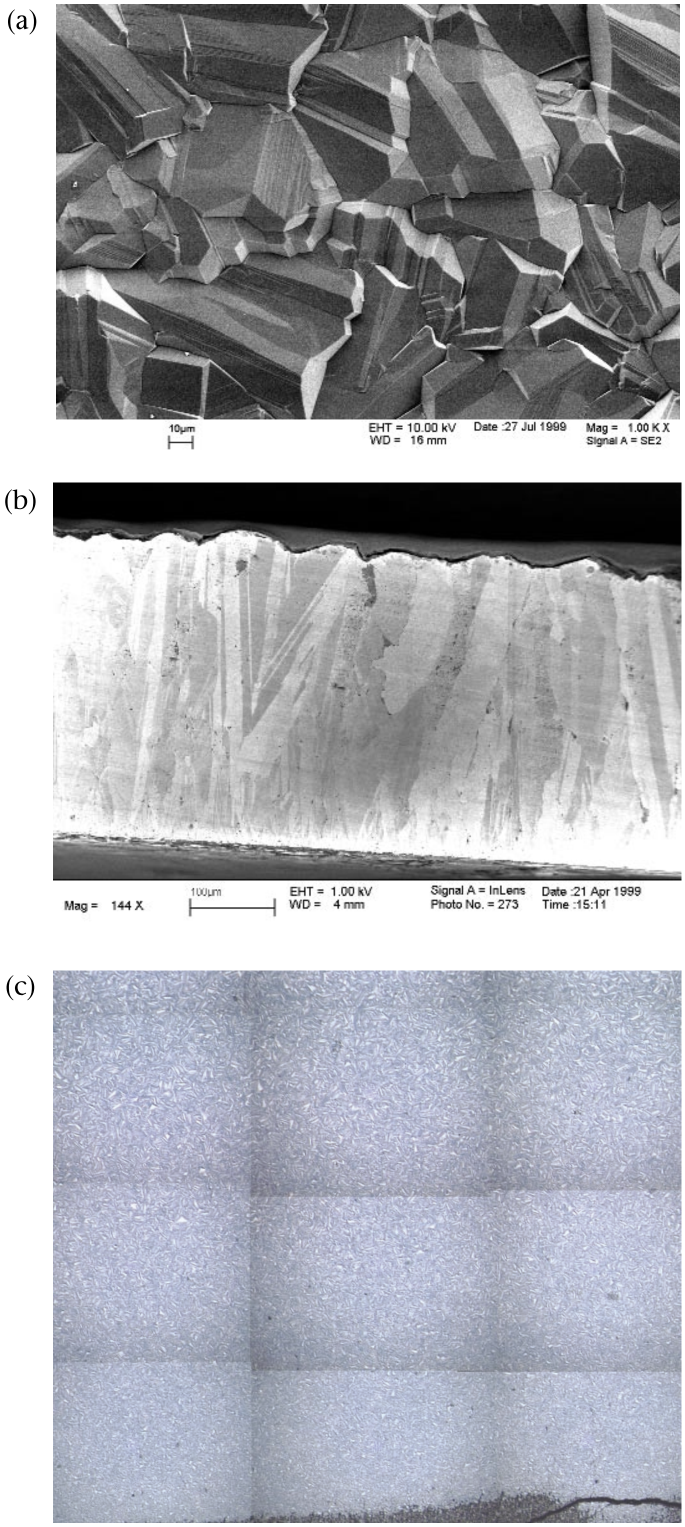

Fig. 2. Polycrystalline CVD diamond (boron doped): (a) SEM image of the faceted growth surface; (b) SEM image of the edge of the film after mechanically polishing; and (c) a transmitted light microscope image through section of the film thinned by polishing both sides such that the top portion of the image is close to the growth surface and the bottom is closer to the nucleation surface.

In polycrystalline CVD diamond, many of the apparently random grains (see Fig. 2a, for example) are really crystallographically related, generally through twinning (sharing a common (111) plane, or <110> axis), and form grain clusters which probably originate from a single nuclei.[8] Internal boundaries within the grain cluster are crystallographically related, while incoherent grain boundaries are formed between clusters evolving from different (randomly) oriented nuclei.[9] Figure 3 displays examples of this, again for a mechanically polished, boron doped polycrystalline diamond film grown by microwave plasma CVD. The contrast shown in Figs. 3a-d results from properties most sensitive to individual growth sectors or grains, *e.g.* wear resistance in polishing, surface work function, and impurity concentrations. On the other hand, the contrast in Fig. 3e results from electron backscatter intensities (a measure of electron channeling), which are more sensitive to the crystallographic orientation (alignment) of the growth sectors (grains). As seen in the figure, growth sectors (grains) that share a common <110> axis have similar backscatter intensities and thus form crystallographically related grain clusters.

Freestanding plates of polycrystalline diamond have been made industrially with dimensions up to 30 cm diameter and several mm thickness.[10] The color of such materials can vary from transparent for optical applications, to blue for electrically conductive applications, to gray/black found generally in cutting tool or thermal management applications.

Nanocrystalline CVD Diamond

Nanocrystalline CVD diamond is a form of polycrystalline diamond in which the initial seeds are of nanometer dimensions resulting in extremely high nucleation densities, typically between 10^{10} nuclei/cm^2 to over 10^{12} nuclei/cm^2. As with polycrystalline CVD diamond, the grain size coarsens with growth, reaching 100s of nm with films of several microns thickness. The purity of individual growth sectors in nanocrystalline diamond can approach that of the single crystal CVD diamond resulting in optically transparent, or colored doped films. But the existence of incoherent cluster boundaries and higher order twin boundaries often causes localized stress and sp^2 bonded carbon regions, which in turn, results in higher dislocation densities.

A related and unique material, ultrananocrystalline diamond, can be grown under conditions where the renucleation, or formation of new diamond nuclei, predominates over the homoepitaxial growth on diamond seeds (nuclei) and results in a composite material comprised of multi-nanometer sized crystalline diamond domains bounded by sp^2 bonded surface or intergranular material. This novel material is the focus of a separate article in this issue *(Ed note: See the article by Carlisle and Auciello, p. 28)*.

Nanocrystalline CVD diamond differs from polycrystalline CVD diamond in that the critical dimension of the growth sector or grain cluster (nanometers to hundreds of nanometers) is less than typical characteristic dimensions for various transport properties, *e.g.* phonon scattering, electrical carrier scattering, crack propagation length. Hence, there are important differences in some of the properties of these two classes of materials. Among the improved properties of nanocrystalline CVD diamond films are higher toughness and lower light scattering, while other properties such as carrier mobility and thermal diffusivity are decreased. Surprisingly, in fully dense nanocrystalline CVD diamond films, the Young's Modulus is nearly that of single crystal diamond.[11] In addition, many of the other properties of diamond are retained, such as corrosion resistance, surface termination and chemistry, density, optical transparency, and others.

Recently, nanocrystalline CVD diamond materials have been exploited for applications in micro-electro-mechanical systems (MEMS) and the nano variant, NEMS, where the mechanical, electrical, and corrosion properties of these fully dense films extend the range and application of these novel devices.[12-14] For example, the high stiffness (Young's Modulus) of diamond can push resonant structures of a given dimension to much higher frequencies than achievable in more traditional MEMS materials (Si, SiO_2, Si_3N_4, etc.), or relax the lithographic constraints required to achieve a particular frequency. Diamond MEMS/NEMS may also prove to be more durable, capable of surviving harsh chemical, radiation, or mechanical shock environments. The optical transparency will permit novel coupling of waveguides using MEMS structures and novel sensing configurations. Examples of the structural diversity that can be fabricated using nanocrystalline CVD diamond and relatively standard Si micro/nano lithographic/processing techniques are shown in Fig. 4. Figure 4a is a SEM image of a nano-tennis-racquet resonator fabricated from a ca. 80 nm thick diamond film deposited onto a sacrificial silicon oxide layer on a silicon wafer. The ghostliness of the structure is due to the partial electron transparency of the very thin diamond. In Fig. 4b, a SEM image of a lateral resonant filter fabricated from electrically conductive boron doped diamond is shown where the outer combs are fixed

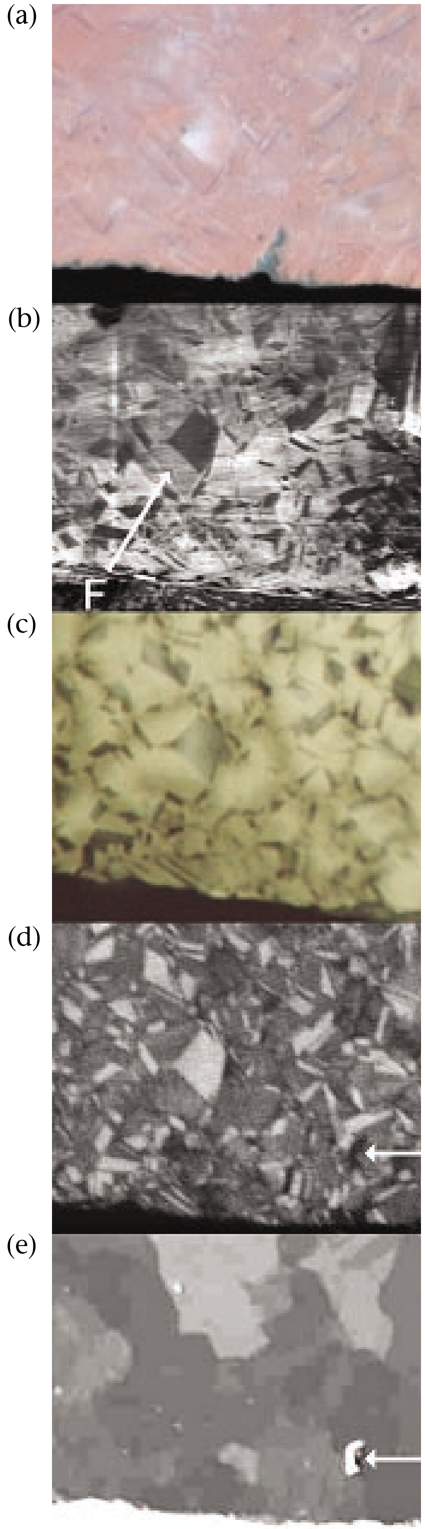

FIG. 3. Comparison of microscopy techniques for studying a bulk polished sample of boron doped CVD diamond. The images are of the same area of a <110> growth: (a) Nomarski DIC optical micrograph; (b) low voltage (1 keV) secondary electron image; (c) room temperature cathodoluminescence topograph; (d) low temperature cathodoluminescence image, passing the free and boron-bound excitons; (e) high voltage (15 keV) SEM image, the contrast produced is due to differences in the electron backscatter intensities.[9]

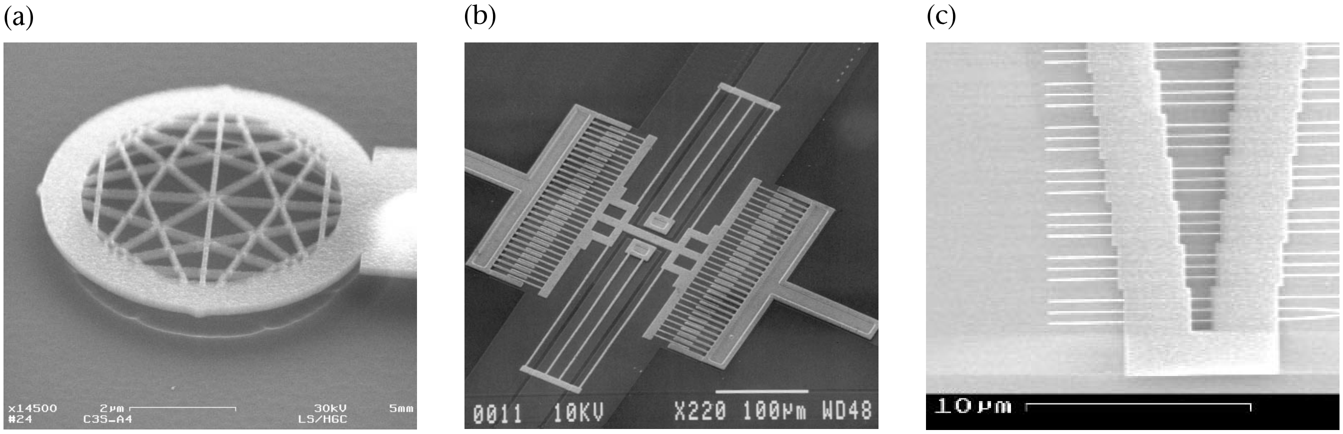

FIG. 4. SEM images of MEMS and NEMS structures formed from nanocrystalline CVD diamond films: (a) a nano-tennis-racquet resonator structure;[14] *(b) a boron doped comb resonator electronic filter with very high Q:*[13] *and (c) a nano-xylophone with mechanical resonances as high as 640 MHz.*[12]

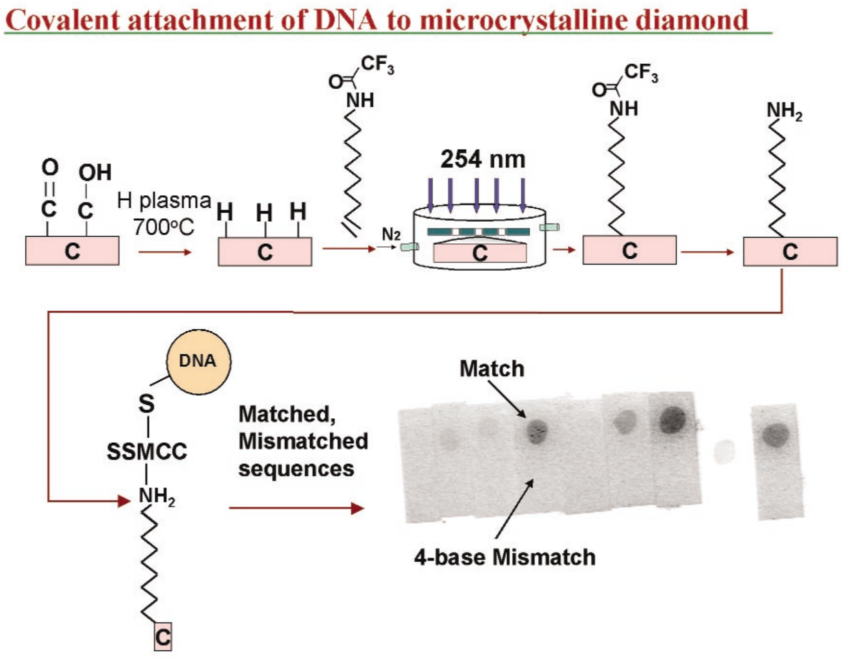

FIG. 5. A method for the covalent attachment of DNA to nanocrystalline diamond and the detection fluorescently tagged complementary DNA with excellent selectivity.[15]

to the substrate and the inner comb shuttle is clamped at two pads and nanocrystalline diamond bars form the spring. The filter operated at 27.4 KHz with a Q of 36,460. Figure 4c shows a SEM image of a nano-xylophone where mechanical resonances have been detected from less than 10 MHz to over 640 MHz.

The diversity of applications for diamond materials continues to expand. In particular, one can exploit the surface chemistry specific to diamond to sense or detect specific molecules or classes of molecules. A recent step in this direction is the exploitation of the biological compatibility of diamond surfaces. The surface chemistry of nanocrystalline and ultrananocrystalline CVD diamond films has been used for covalent attachment of specific DNA oligonucleotides in patterned areas in a prototype sensor for complementary DNA oligonucleotides. Complementary DNA (tagged with a fluorescent chromophore) is bound with very high specificity (sensitive to one acid/base pair mismatch) and the detector surface may be reused many times with no measurable degradation after many cycles of denaturing and rehybridizing.[15] Figure 5 shows a schematic of the surface modification process using uv lithography and uv fluorescence detection of the fluorescently labeled oligonucleotides. ■

Summary

This brief article attempts to highlight some of the great progress that has been made in the quality and diversity of CVD diamond materials. Great flexibility for engineering the diamond materials to match the desired properties of an application has been demonstrated. These recent results indicate a renaissance in the interest and application of CVD diamond growth and materials.

Acknowledgments

The author gratefully acknowledges support from the Office of Naval Research/Naval Research Laboratory, DARPA, and the assistance of many colleagues including B. Feygelson, T. Feygelson, D. S. Y. Hsu, J. N. Russell, Jr., R. J. Colton, T. A. Kennedy, R. C. Linares, P. J. Doering, J. W. Steeds, S. Charles, A. Mora, R. Hamers, P. Hess, J. Phillip, S. Chattopadhyay, K. H. Chen, L. C. Chen,

J. Wang, C. T.-C. Nguyen, L. Sekaric, H. G. Craighead, S. Rotter, M. W. Geis, and G. M. Swain.

References

1. T. A. Kennedy, F. T. Charnock, J. S. Colton, J. E. Butler, R. C. Linares, and P. J. Doering, *Phys. Stat. Sol. (b)*, **223**, 416 (2002).
2. A. Beveratos, R. Brouri, A. Villing, J.-P. Poizat, and P. Grangier, *Phys. Rev. Lett.,* **89**, 187901 (2002).
3. J. Isberg, J. Hammersberg, E. Johansson, T. Wikstrom, D. J. Twitchen, A. J. Whitehead, S. E. Coe, and G. A. Scarsbrook, *Science*, **297**, 1670 (2002).
4. P. E. Pehrsson, M. Marchywka, U.S. Patent #5702586 (1997).
5. S.Yugo, T. Kanai, T. Kimura, and T. Muto, *Appl. Phys. Lett.,* **58**, 1036 (1991).
6. S. D. Wolter, B. R. Stoner, J. T. Glass, P. J. Ellis, D. S. Buhaenko, C. E. Jenkins, and P. Southworth. *Appl. Phys. Lett.,* **62**, 1215 (1993).
7. M. Mermoux, B. Marcas, G. M. Swain, and J. E. Butler, *J. Phys. Chem.,* **106**, 10816 (2002).
8. A. E. Mora, J. W. Steeds, and J. E. Butler, *Diam. and Rel. Mat'ls,* **11**, 697 (2002).
9. S. J. Charles, J. W. Steeds, D. J. F. Evans, and J. E. Butler, *Materials Letters*, Submitted.
10. J. E. Butler and H. Windischmann, *MRS Bulletin,* **23**, 22 (1998).
11. J. Phillip, P. Hess, T. Feygelson, J. E. Butler, S. Chattopadhay, K. H. Chen, and L. C. Chen, *J. Appl. Phys.,* In press.
12. J. Wang, J. E. Butler, D. S. Y. Hsu, C. T.-C Nguyen, in *The Fifteenth IEEE International Conference on Micro Electro Mechanical Systems 2002*, 657, (2002).
13. J. Wang, J. E. Butler, D. S. Y. Hsu, and C. T.-C. Nguyen in *Solid-State Sensor, Actuator, and Microsystems Workshop Proceedings*, Hilton Head Island, South Carolina, 61, (2002).
14. L. Sekaric, J. M. Parpia, H. G. Craighead, T. Feygelson, B. H. Houston, and J. E. Butler, *Appl. Phys. Lett.,* **81**, 4455 (2002).
15. J. E. Butler, W. Cai, J. A. Carlisle, J. Gerbi, D. M. Gruen, T. Knickerbocker, T. L. Lasseter, J. N. Russell, Jr., L. M. Smith, and R. J. Hamers, *Nature Materials,* 1,253-257 (2002).

About the Author

***James E. Butler** has actively researched many facets of diamond chemical vapor deposition including growth mechanisms,* in situ *diagnostics, surface chemistry, defect characterization, materials properties, and device fabrication; and heads the Gas/Surface Dynamics Section, Chemistry Division, Naval Research Laboratory. He may be reached by e-mail at butler@ccf.nrl.navy.mil.*