THE STATUS OF DIAMOND ELECTRONICS

Andrzej Badzian
Penn State University, University Park, PA,, USA

THE RISE OF DIAMOND ELECTRONICS

Typical semiconductor materials are associated with group IV elements of the periodic table and AIII-BV and AII-BVI compounds and their solid solutions. The crystal structures of all these phases relate to the diamond atomic structure, so diamond crystal is the model phase for all these, tetrahedral bonded atomic structures. They appear as cubic or hexagonal phases.

The first hint for exploration of diamond as a semiconductor material was noted in 1952, when natural diamond crystals with blue color have been found to show a semiconductor type of conductivity. Boron atoms, substitutionally located in diamond crystal lattice, cause the color and are responsible for p-type conductivity.

In the same year a patent application was filled at Union Carbide to cover the Chemical Vapor Deposition process for diamond growth from the gas-phase. A hope was associated with the vapor growth for development of electronic quality diamond semiconductor films. Nevertheless, it took almost 36 years of research to grow single crystal epitaxial diamond films and to fabricate rudimentary electronic devices. The controlled growth of diamond films was the necessary condition for testing the feasibility of diamond electronics.

Before electronic diamond films became available, the research was focused on bulk natural diamond crystals. In this category, synthetic diamond crystals, grown by High Pressure/High Temperature (HP/HT) process were also explored. This process, disclosed in 1962 by General Electric, enabled doping diamond with boron during growth.

The start of diamond electronics research was not easy because scientific community was skeptical about reliable diamond growth from the gas phase. At the beginning of 80ties Russian and Japanese papers clearly described CVD processes yielding diamond films. The role of Penn State University was to confirm the process and dismiss the doubts. The announcement about this achievement in New York Times in 1986, made CVD process attractive for researches around the world. Penn State CVD data together with bulk semiconductor diamond crystals studies helped to design diamond electronics research program at the Office of Naval Research. The main goal of this wide scope program was making CVD diamond synthesis process practical, applicable to a variety coating applications, and testing feasibility of diamond electronic devices.

Electronic study of bulk semiconductor diamond single crystals was focused on the fabrication of prototype devices: point contact diode, high-temperature termistor, light-sensitive switch, optical radiation detector and ultrafast infrared detector. The first transistor on natural crystals was demonstrated in 1982 and on HP/HT crystals in 1987. Also Schottky diodes were fabricated on bulk crystals, they operated at elevated temperatures up to 700 $^{\circ}$C. At this point of the development of semiconductor diamond technology it has become evident that in order to make progress in active electronic diamond device engineering, significant improvements in diamond thin-film (or planar) technology must be accomplished.

THE FEASIBILITY OF DIAMOND ELECTRONICS

The support for ONR research program, among a variety of considerations, came from the calculation of Johnson figure of merit (JFM), which is a product of maximum allowable voltage and cutoff frequency:

$$JFM = E_c V_s / 2\pi$$

where: E_c is critical field (or the breakdown field) in excess of 10^7 V/cm
V_s is electron saturation velocity equal to 2.7×10^7 cm/s

JFM is used for comparison of semiconductor materials. Diamond has the highest JFM value, (for p-type diamond 32 times higher than for Si) among all semiconductor materials. This indicates diamond potential for power microwave application. The Keyes' figure of merit (KFM) in turn, considered for digital integrated circuits, combines three material parameters: thermal conductivity, dielectric constant and electron saturation velocity. Here again the value of KFM for diamond was the highest among all semiconductor materials. Based on these numbers, conclusions regarding potential of diamond in electronic device applications were very optimistic. Overall, diamond was considered to be a perfect semiconductor for high temperature, high frequency, and high power device applications. The low sensitivity to high-energy radiation only added to the image of diamond as an ultimate semiconductor material.

Following very promising predictions regarding potential of diamond as a semiconductor, major research programs on CVD diamond films were initiated in 1986. The ONR, NSF and other governmental and private organizations support for diamond research lasted for about 12 years. After 1997 the support for thin-film diamond research was substantially reduced in the USA, but continued in other countries.

CVD PROCESS

The up to date achievements of CVD diamond research can be summarized as follows:

* polycrystalline, black, free-standing plates up to 25 cm in diameter and 2 mm thick were
   grown.
* translucent (sometimes almost water-clear) polycrystalline, stress-free plates, up to 10 cm in
   diameter, are available ($100,000 per plate), as microwave or optical windows.
 * single crystals, in the shape of cubes, up to 1 cm^3 , were demonstrated.
* single crystal plates up to 4.5 mm across are available from Element Six Ltd.
* controlled homoepitaxy was used for successful fabrication electronic devices.

DIAMOND ELECTRONIC DEVICES

The following device-related studies were carried out as a part of the program:

*Ohmic contacts
Ohmic contacts have been successfully developed using well known ohmic metals. For example, Ti/Mo/Au layer showed no degradation for 400 hrs at 800 ^oC.

* Schottky diodes
The Au/Ti contact and Au gate contact to B-doped diamond homoepitaxial (001) films were used to fabricate Schottky diodes as a step leading to fabrication of rudimentary MESFETs. The diode operated at up to 600 ^oC. Considerable rectification was expected at 800 ^oC.

* <u>Field Effect Transistor</u>
MESFETs were considered as the first transistors to try because of unipolar behavior of diamond as semiconductor. The first transistor consisted of a p-channel (channel length 2 µm) B-doped layer deposited on intrinsic diamond crystal. Many devices were fabricated to achieve saturated ("pinch-off") I-V characteristics. The pinch-off characteristics and high transconductance were obtained for FETs with hydrogenated (with hydrogen atoms chemically bonded) diamond surface.

*<u>p-n junction</u>
Application of elaborate procedures for P-doping and established procedures for B-doping resulted in fabrication of p-n junction on (001) diamond surface. According to new measurements the P donor level is located at 0.58 eV. UV radiation is emitted by current-injection at room temperature.

CHALLENGES IN THE DEVELOPMENT OF DIAMOND ELECTRONICS

1. Shallow Doping

The most critical and at the same time the most challenging issue in the diamond program was the control over doping during film growth. Ion implantation and diffusion were also studied but the results were not satisfactory. The fundamental requirement for the success of diamond electronics is a possibility of introduction of dopant atoms, at the substitutional positions in the diamond lattice, in such a manner that they create SHALLOW LEVELS, p- or n-type, in the energy band gap. To make a device work efficiently these levels should be shallow enough to assure dopant activation at room temperature, where kT= 0.025eV. An example of shallow acceptor in Si is boron (B), its energy level is at 0.045 eV above the edge of the valence band. The shallow donor in Si is phosphorous (P) at 0.044 eV below the edge of conduction band. In diamond B level is at 0.36 eV. As a result of such high ionization energy of boron only 0.2 % holes are activated at room temperature. At higher temperature the device conductivity increases, but the mobility of holes decreases. This behavior limits performance of devices at high frequency. In the case of P situation is even worst, because the P donor is even deeper than B acceptor. The literature data for P donor spread over the range of 0.5 to 1.0 eV. The value of 0.58 eV was reported quite recently.

An unfortunate observation regarding diamonds electronics *status quo* is that the shallow dopants for diamond have not been found. This is a disappointing conclusion for the entire effort spreading over the decades of research. It means that it is not possible at this moment to fabricate diamond electronic devices similar to those made using doped Si or Ge.

The reasons, for which finding of the adequate shallow dopants for diamond is a very complex matter, is twofold. First, chemical bonding of carbon atoms in diamond structure is the strongest among all crystal phases. Incorporation of a foreign atom in diamond lattice creates a chemical bonding which is weaker than tetrahedral bonding between carbon atoms. The choice between the candidates for substitutional doping is limited for chemical reasons. Thus, the lattice energy fit to create a shallow dopant level is not possible within this group of elements that could possibly act as dopants. This conclusion was reached after an extensive research, which combined crystal chemistry approaches and first principle quantum mechanics calculations of binding energy of a foreign atom in diamond lattice. Phosphorus, lithium and sodium were among the candidates. None of these studies were successful.

The second reason is a disturbance of growth process caused by the presence of foreign atoms on the surface of the growing diamond film. The constructive role of the foreign atom is fulfilled when this atom is incorporated in the substitutional position in the diamond lattice as donor or acceptor. The foreign atom plays a destructive role when its involvement in crystal growth processes results in a creation of growth defects. Unfortunately, in the case of diamond growth minimization of the latter effect is very difficult. The specific situation appears when foreign atoms (or complexes) are active on growing diamond surface,

but they are not incorporated into diamond lattice. The important is behavior of nitrogen intentional addition to methane/hydrogen mixture. Such N addition at small concentrations (few atomic %) acts as "gas catalyst", it means, the growth rate of diamond increases about one order of magnitude. The opposite situation, in active participation, takes place at high concentration of N. The growth rate decreases comparing to pure methane/hydrogen mixture. The material obtained from such process has a distorted diamond structure, which depart from cubic diamond, according to Raman spectra and X-ray diffraction. It is better to name this phase: disordered tetrahedral carbon. Similar distortions of diamond lattice appeared during experiments on doping using P, S and O.

Experimental and theoretical study of n-type doping of diamond was the corner stone in the exploration of diamond electronics. Substitutional nitrogen (N) extra deep level lays 1.5 eV below the bottom of conduction band. The other N atoms create a series of complex defects. Substitutional P atoms create a deep level at around 1 eV. Also, the growth defects create traps inside the band gap, they accompany P doping process. The intensive study of doping with sulfur (S) was not successful, as sulfur was found to introduce a lot of growth defects. Other elements were also unsuccessfully tried. The shallow n-doping of diamond is a failure as we see it today. As such it is among key reasons for the lack of adequate progress in diamond electronics.

2. Growth Defects

Formation of growth defects during diamond Plasma Enhanced CVD (PECVD) processes is inherently connected to the interactions with hydrogen, silicon, and metal impurities from the plasma reacting with the wall of deposition chamber. The growth defects have a variety of forms, e.g. hexagonal stacking, twins: (111) and linear (001), interstitial atoms, hydrogen atoms, nitrogen atoms and complexes. They disturb periodicity of diamond lattice. Preserving lattice periodicity is the basic requirement for a scattering-free transport of carriers in semiconductor crystal. This lattice property is explained by Bloch theorem. The crystal lattice of PECVD diamond crystals depart far from strict lattice periodicity. There are areas where local symmetry differs from this of cubic diamond. This is a drastic disturbance of diamond lattice periodicity that affects carrier transport and decreases carrier mobility.

3. Homoepitaxy

Deposition of electronic quality diamond thin films for fabrication of devices works relatively well on single crystal diamond substrates. By definition, however, homoepitaxy requires as a substrate a defect-free natural or synthetic HP/HT diamond. Any structural defect in the substrate would have an adverse effect on the growth process. For example, inclusion at the surface can initiate growth of a hillock of polycrystalline disordered diamond. Such hillock (e.g. 10 μm across), during doping with B, will create a conductive channel locally introducing short-circuit in the transistor. In practice, homoepitaxial deposition plays a limited role in the research of diamond active electronics because of the difficulty in the reproducible growth, small area (4x4 mm) substrates, and their prohibitively high price. The additional cost is accrued when the growth needs to be carried out on disoriented (001) substrates. The selection of required off-angle substrates relies on a tedious and costly X-ray diffraction characterization performed on the large set of plates. The best results for step flow growth process were obtained when tilt from (001) plane is parallel to <110> direction. The alternative option for step flow growth mechanism is operation at the border of growth/etching, it means at very low methane concentration in hydrogen, (e.g. less than 0.1%). At such concentration the population of growth radicals on terraces on (001) surface is low and the choice of specific tilt is not critical. The novel approach is exploration of high temperature growth in respect to roughening transition temperature, which differs for basic crystallographic directions.

The second task for homoepitaxy is preparation of CVD substrates for future epitaxial depositions. Such substrates should be less costly than present natural and HP/HT products. A big step forward has been

made recently with the announcement by Element Six Ltd of the availability of CVD diamond plates (4.5 mm) for cutting tool applications. The hope for scaling up this process is reasonable.

4. Heteroepitaxy

Providing adequate quality diamond films are obtained, the heteroepitaxial growth could be a solution for active diamond electronics. The true diamond heteroepiaxy was demonstrated on B terminated (111) surfaces of cubic BN. These HP/HT bulk crystals are not easily available, and their size of 1-2 mm, make fabrication of commercial devices impossible. The exact (in the sense of semiconductor technology) macroscopic heteroepitaxy on other substrates was not achieved as yet. As an alternative, growth of diamond polycrystalline, oriented films was intensively studied. The most preferred choice was oriented growth on (001) Si. The growth of preferentially oriented diamond crystals (5-10 μm) was difficult to control. Approximately 90% of crystals have <001> orientation, the rest was arbitrarily oriented. Very local (100 nm) heteroepitaxial growth on (001) Si is documented using High Resolution TEM images. The largest uniform area of oriented growth was 25 mm in diameter, but it was smaller when grown in other labs. The diamond crystals in such films depart from cubic diamond structure. Silicon (etched by methane/hydrogen plasma) is incorporated into diamond lattice at interstitial positions as Si-vacancy complex. Si is easy to detect using electron microprobe and the complex is marked as strong luminescence peak. Such complex probably causes creation of local linear (001) twins. A new configuration of carbon atoms at the twin line introduces an intermediary sp2/sp3 bonding, which relates to non-diamond band in Raman spectra. The overall X-ray diffraction and Raman spectra data show lattice disorder, which decreases hole mobility. The devices fabricated on this material have inferior parameters comparing to these fabricated using homoepitaxial films.

The interest in heteroepitaxial deposition of diamond continues, following a limited success with nickel single crystal. At present, there is a push toward exploration of other single crystals of metals , e.g. iridium and related sandwiches, but the progress in this area is slow.

ACTIVE ELECTRONICS: CONCLUDING REMARKS

Realistic assessment of the progress in the field of active diamond electronics and photonics is that the intensity of R&D in this area did decrease significantly after 1995. Neither electronics nor photonic practical active devices have been successfully developed. Diamond is an indirect-gap semiconductor, and the efficiency of luminescence from light emitting diode made with diamond is very week comparing to the direct-gap GaN devices.

Research of single crystal growth was only in part motivated by the needs for substrates for homoepitaxial growth of semiconductor diamond films; other demands are coming from jewelry, high pressure research, where Bridgeman anvils need to be improved, single crystal tools like surgical knives or for cutting and etc., etc., etc…. The effort was not entirely in vain, as exemplified by the impressive progress in bulk diamond crystal CVD growth. At this moment single crystal growth is at the promising stage of development. 1 cm^3 cubes of diamond have been demonstrated at Carnegie Institution, and 4.5 mm plates are available from Element Six Ltd. Commercial availability of such wafers should be considered as an important breakthrough in diamond wafer engineering.

The increase of knowledge about defects in diamond resulted in enhanced capabilities regarding color manipulation. For instance, imperial red colored diamond crystals were obtained. While this is mainly a gemology domain, resulting improved understanding of defect engineering in diamond will certainly advance understanding of optoelectronic properties of diamond.

The overall good news is that despite of the discussed above difficulties the research on diamond active electronics is continued in many laboratories around the world. The issues of doping, heteroepitaxy and novel concepts for electronic devices, detectors, and sensors are still in pursuit. For example, the concept of monolayer B delta-doping (a pulse doping) for FET design has been reconsidered recently. Metallic type of conductivity can be obtained using B-doping. The wide range of diamond electrical conductivity, possibly achievable, makes applications like electrodes, resistors, and heaters seem realistic. It should be noted that the electronic band structure of diamond changes with a doping level. Optical spectroscopy has been used to study changes in the density of states in the band gap as a function of doping level. In particular, of interest was a determination which model better describes changes in the band structure when the concentration of B dopant increases: the Bardeen model, which involves changes in the position of the valence band, or the Mott model, which involves creation of electronic levels around the Fermi level and above the valence band. The results of the analysis indicate that the Mott model, which also can describes the transition to metallic conductivity, better represents physical phenomena involved.

Electron field emission from diamond films and tips was extensively studied during last decade. Negative electron affinity and ballistic-like electron transport in the conduction band have been considered as possible explanations for measured currents, which appear in cold cathode devices.

PASSIVE ELECTRONICS AND MECHANICAL DEVICES

While usefulness of diamond in active electronic and photonic device technology is still questionable, its key role in passive electronics and select mechanical device systems is unquestionable. This is because thermal conductivity of diamond is the highest among all solids and it also features exceptional mechanical properties.

Diamond crystal conducts heat through elastic waves running across its lattice. This is pure lattice conductivity. The numerical range of measured thermal conductivity is wide, depending on crystal lattice perfection. The highest values have been obtained for mono-isotope pure crystals. High crystallographic quality diamond crystals were grown by HP/HT method for C^{12}, C^{13} and intermediary composition solid solutions of C^{12} and C^{13}, using CVD starting materials. The thermal conductivity of these crystals exceeds thermal conductivity of pure copper 10 times. The thermal conductivity of CVD polycrystalline plates is 3 times higher and single crystal epitaxial films is 5 times higher than in copper.

Taking advantage of the exceptional thermal conductivity of diamond, a new concept of IC packaging is under study. Silicon on diamond (SOD) allows placing diamond heat spreader just under the heat emanating transistor. This approach requires deposition of Si active layer on diamond. The benefit is that in this configuration transistors in the circuit are in the immediate proximity of the diamond heat sink. The enhancement of thermal management in next generation ICs is the goal behind this project.

As far as mechanical properties are concerned it can be safely stated that diamond crystal is the world best spring. Exploiting elastic properties of diamond, membranes were fabricated by CVD process and applied to high performance speakers. These new generation speakers are available on the market now. Furthermore, the acoustic waves in diamond lattice are transmitted at the lowest attenuation in diamond crystal. This property was exploited for fabrication of high frequency surface acoustic filters. As the base in these filters polycrystalline CVD diamond plates were used.

Please direct comments and questions regarding this contribution to:
Andrzej Badzian <abadzian@psu.edu>