

NANODIAMOND: SYNTHESIS, TRANSPORT PROPERTY, FIELD EMISSION AND APPLICATIONS**Zishan Husain Khan and M. Husain***Department of Applied Sciences and Humanities & Department of Physics,
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ABSTRACT

Carbon nanostructure has an edge over other materials due to their wide range of applications. This is because carbon can form three well known allotropes that are distinguished by different types of electron hybridization viz. diamond, graphite and carbene with sp^3 -, sp^2 -, and sp^1 -, hybridization of carbon atoms, respectively. It has also a stable $\pi_n - \pi_n$ bonding which makes it useful for three to zero dimensional structures with a broad variety of attainable physical, chemical, electronic, optical and low temperature properties. Synthetic procedures of nano-diamond and diamond like carbon (DLC) are discussed with a brief history of their developments. The status of research on nanocrystalline diamond films during last ten years and its possible applications have also been focused in this review. Semiconductor to metal transition with change of film thickness, field emission and the appearance of superconductivity around 4.9K in DLC films incorporated with 60% tungsten (W) showed new road of research with DLC materials.

Key words: Nanodiamond, transport property, field emission.**INTRODUCTION**

Nanostructured materials are expected to make revolutionary impact on the upcoming technologies as they exhibit some unique properties (including semiconductor-metal transition and superconducting behavior). Carbon can form three well known allotropes that are distinguished by different types of the electron hybridization viz. diamond, graphite and carbene with sp^3 -, sp^2 -, and sp^1 -, hybridization of carbon atoms, respectively. It has also a stable $\pi_n - \pi_n$ bonding which makes it useful for three to zero dimensional structures with a broad variety of attainable physical, chemical, electronic and optical properties. All other known carbon modifications such as fullerenes, glassy carbons, diamond like carbon etc. are based on a combination of these types of electron hybridization. Meanwhile, there appears to be one more carbon allotrope that is referred to as nanodiamond, since many reflections in its electron diffraction pattern are similar to those of diamond. However, the electron diffraction pattern

of this phase comprises also of a number of strong reflections that are forbidden for diamond. Later on, it was suggested that this phase is a face-centered cubic (fcc) modification of carbon. The term "diamond-like" carbon describes a range of amorphous carbons, generally containing some hydrogen, which contain a mixture of sp^2 and sp^3 bonding. Diamond like carbon films, obtained by chemical vapor deposition, exhibit low friction coefficients, chemical durability and extreme hardness, which makes them excellent candidates for wear-resistant applications. Furthermore, a variety of electronic and optical applications have been reported. Diamond films have excellent thermal conductivities. Therefore, they may be used as heat exchangers on electronic components. The adhesion of the diamond films to the silicon surface can be improved by a previous deposition of a fullerene thin film, whereby Si-C bonds are formed. It has also been discovered that prolonged irradiation causes almost the whole onion to be transformed to diamond. The DLC films have a variety of properties in between those of diamond

and graphite. So diamond film can have both semiconducting and insulating behavior even at room temperature. The properties of DLC films vary with the concentrations of sp^2 and sp^3 carbon in the films. Recently, it has been shown that the properties of DLC films, such as hardness, optical transparency etc., approach the value of diamond with a high concentration of sp^3 carbon. The DLC films with high concentration of sp^3 carbon are termed as tetrahedral carbon, amorphous or *nanocrystalline diamond* (NCD).

This review presents the status of research on nanocrystalline diamond films during last ten years and its possible applications in different branches of science including low temperature physics.

Historical Background

Carbon in the form of charcoal or soot has been known for a long time. For more than 6000 years carbon materials have been used for the reduction of metal oxides. Nevertheless, only in the year 1779 graphite was discovered by Scheele to consist of pure carbon. Ten years later Lavoisier realized that carbon belongs to the family of chemical elements. Furthermore, he identified diamond with another allotropic form of carbon. All these old forms of carbon are formed either by nature or by artificial methods, under thermodynamically controlled conditions. At ambient pressure hexagonal graphite is the most stable carbon allotrope. Conclusively at temperature around 3000°C poorly ordered carbons are usually converted to well-ordered graphite materials. The rhombohedral graphite modification is slightly less stable than the hexagonal one¹. The conversion of graphite to diamond requires high pressure, as the density of diamond is higher than that of graphite². As diamond is a meta-stable phase, it is necessary to lower the temperature before releasing the pressure, in order to avoid decomposition to graphite. Carbon blacks are typically formed when carbon vapor is cooled down rapidly due to a limited mobility of carbon atoms. The size of the condensing graphite particles is very small. Therefore, carbon blacks consist of a conglomerate of nanocrystalline graphitic constituents. In contrast to the old forms of carbon, the new forms of carbon, for example the fullerenes, nanotubes and carbene-like one-

dimensional structures (CARBOLITES), are formed under kinetic control, starting from hot carbon plasma. In presence of noble gases, under various pressures, such plasmas are quenched to produce closed shell structures among other components.

Chemical Bonding

Carbon is unique among all the elements in the diversity of short, medium and long-range configurations it forms with itself and with other elements. Two crystalline forms of carbon (Fig.1) viz. graphite (sp^2 , three fold planar bonding), and (cubic) diamond (sp^3 , fourfold tetrahedral bonding) have been known and used by mankind for centuries, along with other less clearly identified carbon materials (coals). Hydrocarbons (oils) and organic materials have also been known for a long time. Diamond-like carbon (DLC), on the other hand, is a form of carbon produced for the first time 30 years ago in 1969 by Aisenberg and Chabot, pioneers for the use of energetic (hyperthermal) species for deposition. Following their work on epitaxial deposition of Si (producing Si ions by sputtering Si electrodes in an argon plasma), they used the same apparatus to sputter carbon electrodes and used the carbon ions (mixed with argon ions) for deposition of transparent, hard, insulating carbon films. These carbon films had many of the properties of natural diamond but were predominately amorphous and not crystalline. Professional caution prevented the use of the name diamond but it was felt that "diamond-like" would identify the properties as being similar to diamond without being presumptuous. In the wake of this work, a variety of deposition methods employing energetic species were used to deposit DLC films³⁻¹¹. The low deposition rate using carbon ions lead to depositions using hydrocarbon plasmas where the rate was increased by two orders of magnitude³. These new films, still hard and transparent, contain 20-50% hydrogen and are essentially very different from hydrogen free DLC but nevertheless are very often denoted as "DLC" without even monitoring their hydrogen content. More proper and appropriate names are "a-C:H (amorphous carbon hydrogenated)", "HDLC" (hydrogenated DLC) or "DLHC" (diamond-like hydrocarbon). In the 1980's, a lot of work on "DLC" involving hydrogenated films have been done in comparison to the DLC involving hydrogen free

films. The diversity of the deposition systems employed³⁻¹² and the host of characterization techniques used, led to an ambiguous nomenclature (DLC, a-DLC, a-C, a-C:H, ta-C, a-D, i-C, hard carbon etc.) where the same name is used for similar films. The most “presumptuous” terms (to use Aisenberg’s careful and clever definition) are “amorphous diamond” or “amorphous diamond” (a-D) which are as logical as amorphous crystal. The variety of both production methods and analysis have led to controversial data in the literature on issues such as the films structure, the optimal energy for the production of sp^3 rich films, the substrate temperature effect and the properties of the films. During the last 10 years more rigorous studies on

DLC deposition have been conducted¹³⁻²¹, mostly by using some kind of filtering so that the deposition parameters can be determined and controlled. These studies have led to a better understanding of the deposition processes and have also initiated several growth models²²⁻²⁸ and computer simulations of film growth^{23,29,30} and molecular dynamic studies^{24,31-33}. The work on hydrogen free DLC, which was extremely small in the 1980’s, has been constantly increasing. DLC will mostly refer to hydrogen free amorphous carbon with some sp^3 component in it. A predominantly sp^3 film ($sp^3 > 70\%$) with a tetrahedral local carbon configuration will be denoted as ta-C, amorphous or nanodiamond.

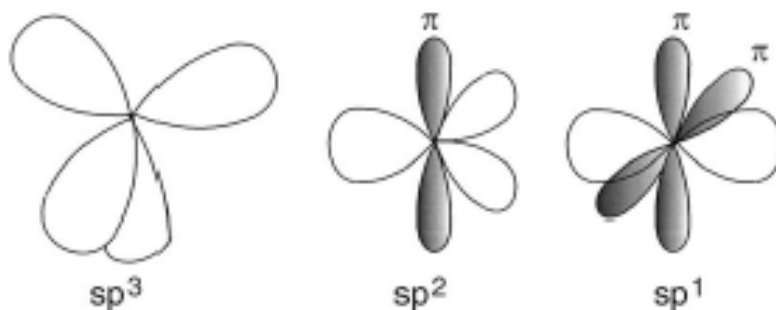


Fig. - 1: The sp^3 , sp^2 , sp^1 hybridized bonding

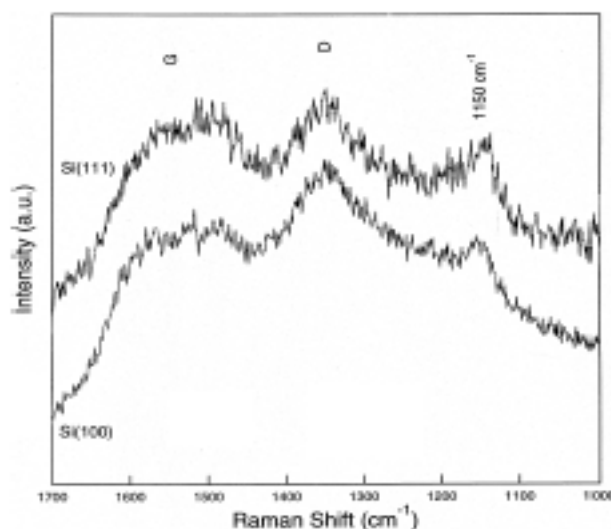


Fig. - 2 : Raman spectra of the films deposited on Si (111) and Si (100). The samples were excited by a 488-nm Ar⁺ laser. The three distinct bands near 1150, 1350 and 1550 nm correspond to nanocrystalline diamond, graphite D and G bands, respectively⁶⁹.

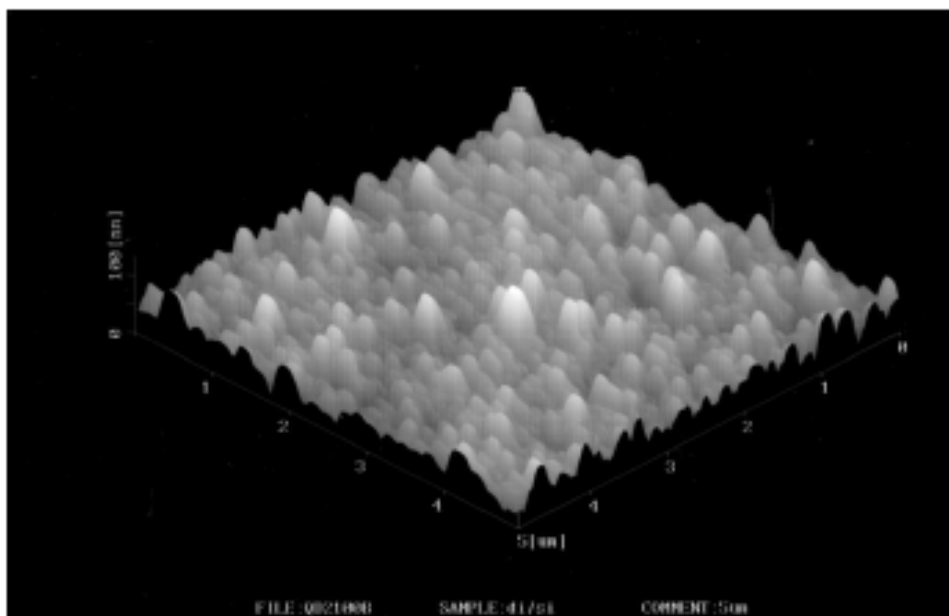


Fig. - 3: Three-dimensional AFM image scanned in an area of $5 \times 5 \mu\text{m}^2$ of the nanocrystalline diamond film grown on Si (100). The root mean square value and average roughness of the film were found to be 16.88 and 13.19 nm, respectively⁶⁹.

Nanodiamond Film Preparation and Current Status of Research

The formation of carbon nanotubes and nanodiamond films, and their properties and applications became the issue of interest of many research groups. Nano-crystalline diamond films have been recognized as an important class of structure in the family of diamond materials. In recent years, there is much attention involving the synthesis and characterization of nanocrystalline diamond films since the nanometer-sized films present several unique properties³⁴⁻³⁷, compared to that of the conventionally microcrystalline diamond films. Until now, most NCD films were grown in conventional hydrogen and methane plasma³⁸⁻⁴¹, which has already been widely used for diamond synthesis. Alternative carbon precursors, such as fullerene⁴² and camphor³⁵, for NCD film growth have also been reported. It is well known that the key parameter to obtain smooth NCD films is the primary nucleation density of diamond nuclei on the substrate. Nucleation densities exceeding 10^{10} cm^{-2} can be achieved by ultrasonically scratching the substrate surface with fine-grained diamond powder^{35,38-40}. A direct

relationship between the grain size of diamond powder and primary nucleation density on the substrates, and consequently the optical transparency, has been observed⁴⁰. Other parameters, such as the methane fraction in the source gas and the substrate temperature, also effect the morphology and the size of the crystallites. However, previous studies have only focused on the variation in grain size of the diamond powder, keeping in the source gas either constant or varying it over only a small range. The optimized value of the optical transparency at 700 nm and beyond used by previous workers was about 60% and the surface roughness was about 20 nm.

Researchers are interested to make films with reduced diamond grain size to achieve the desirable behavior needed to meet the practical applications³⁵. Various processes have been used to prepare nanocrystalline diamond films. Gruen *et al.*⁴³ deposited diamond films by magnetoactive chemical-vapor deposition (CVD). Chakrabarti *et al.*³⁵ produced nanocrystalline diamonds by introducing camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) into a specially designed CVD chamber. Orwa *et al.*⁴⁴ reported that

the diamond nanocrystals could be fabricated using ion implantation method. Jiang *et al.*⁴⁵ deposited successfully the diamond films with the average grain size of about 30-40 nm on Si substrates by conventional MPCVD using a high methane concentration. Deyan *et al.*⁴⁶ demonstrated the synthesis of nanometer diamond powder by explosive detonation.

A number of interesting results indicate that NDFs can also be grown from microwave enhanced chemical vapor deposition (MPCVD) chambers via fully replacement of hydrogen with argon. Conventionally, atomic hydrogen is thought to be indispensable for the growth of diamond in CVD methods. However, the discoveries of Gruen *et al.*⁴⁷ showed that in the hydrogen-depleted (Ar-C₆₀) microwave plasma, diamond films did deposit on Si wafers with their morphologies transiting from microcrystalline to nano-crystalline. A two-stage

method has been used by Bhusari *et al.*^{48,49} which produced a highly transparent NDFs. By using a CO₂ laser-induced plasma CVD method, nanodiamond films have been deposited on tungsten substrates with high deposition rates⁵⁰. A unique technique, in which a high-power pulsed laser in water etches a graphite target, has been employed in the deposition of nano-diamond films⁵¹. Zhang *et al.*⁵² demonstrated that the nanodiamond films can be deposited on Si substrates in a HFCVD chamber in which CH₄ and H₂ are used as reactant gases. Lin *et al.*⁵³ reported the transition of microcrystalline to nanocrystalline diamond films at high argon (Ar) concentration in a HFCVD system.

Bias-enhanced nucleation (BEN) appears today as the most promising nucleation technique for promotion of chemical vapor deposition (CVD) of diamond films growth. In this method a gaseous

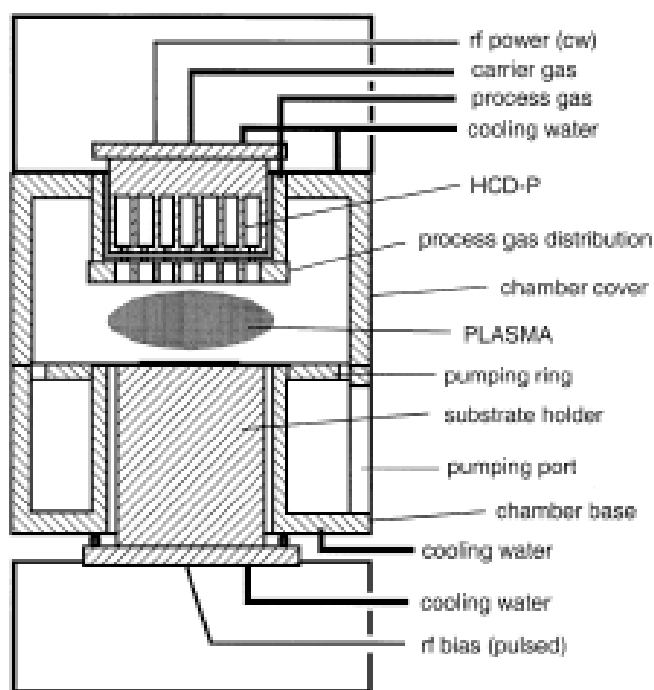


Fig. - 4: Systematic cross-section of the 13.56 MHz RF-RF system.

mixture, activated by microwave (MW) plasma or a hot filament (HF), reacts with negatively biased substrates to produce a carbonaceous precursor

to further grown poly-diamond [54-55]. BEN causes no damage to the substrate surface and this is the only method that resulted in hetero-epitaxial growth

of a diamond film on non-diamond substrate⁵⁴⁻⁵⁹. Several groups reported that the precursor for diamond chemical vapor deposition (CVD), formed by bias enhanced nucleation (BEN) process contains the nano-diamond phase⁵⁸⁻⁶². It has also been shown that the key step of BEN, at least in a high frequency (HF) CVD system, is the formation of stable dc-glow discharge in the vicinity of the substrate surface⁶³. Several groups have introduced the dc-glow discharge process as a novel, in situ surface pretreatment method for the formation of a precursor for diamond nucleation. The results showed that the promotion of diamond growth by this method is primarily due to the formation of nano-sized diamond particles during the pretreatment processes⁶³⁻⁶⁷. Heiman *et al.*⁶⁸ introduced a novel direct current (DC) glow discharge nucleation process where the reactive plasma is created by positive biasing of an auxiliary electrode without any additional gas activation⁶⁴.

As has been demonstrated, generation of a stable plasma in biasing process is a key step of DC-glow discharge assisted CVD. Under suitable conditions, the carbon precursor deposited during the DC-glow discharge process, is mostly composed of a nanocrystalline diamond-rich phase. In this method, a p-type boron-doped Si (001) wafer was used as a substrate. Prior to mounting in the reactor, the substrate was cleaned with acetone in an ultrasonic bath for 10 min. After insertion into the reactor a further cleaning step consisting of 5 min hydrogen plasma treatment was implemented before methane introduction. Substrate temperatures were varied from 800- 950°C as measured by optical pyrometer. The total pressure of the hydrogen-methane mixture was 10 Torr. The Mo-electrode was under a bias of +500 V during DC-glow discharge and the sample holder was grounded. This voltage generated stable glow discharge plasma and the measured current was 40-50 mA.

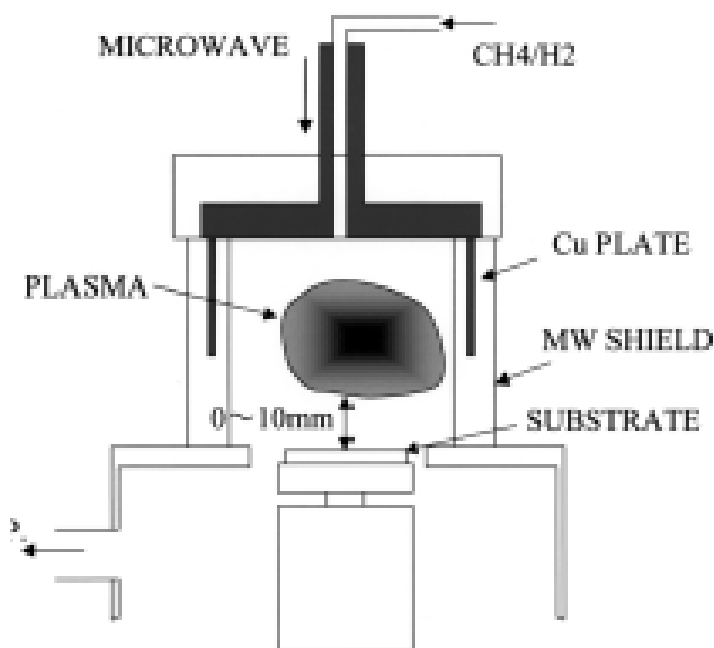


Fig. - 5: Systematic drawing of MPCVD system

Several groups have grown bias field enhanced NCD directly on a mirror polished substrate grown by MPCVD⁶⁹ as the ex situ processes consume much time and also the growth

rate on the scratched sample may be quite low⁷⁰. Yoshikawa *et al.*⁷¹ also reported the deposition of smooth nanocrystalline diamond films on Si substrates using microwave plasma CVD. All these

methods have their own advantages and disadvantages in producing high quality nano-diamond films. These films provide possibilities of fabricating economical NDFs in the near future. Figs. 4 to 5 show schematic diagrams and picture of some of the CVD systems, which are used to grow the nanocrystalline diamond films.

Kruass *et al.*⁷² reported the synthesis of phase-pure ultrananocrystalline diamond coatings by a novel microwave plasma technique using a unique C_{60}/Ar or CH_4/Ar chemistry. The morphology

and mechanical properties are ideally suited for MEMS applications in general, and MMA use in particular. Figure 6 shows the comparison of atomic microscopy images of the surfaces of micro-crystalline diamond and ultra-nanocrystalline diamond thin films. They also presented reported a series of SEM images of a 25-nm diameter Si tip emitter coated with a ultra-nanocrystalline diamond films with incremental coating thickness and two-dimensional ultra-nanocrystalline patterned films on Si(100) as shown in Figs. 7-10.

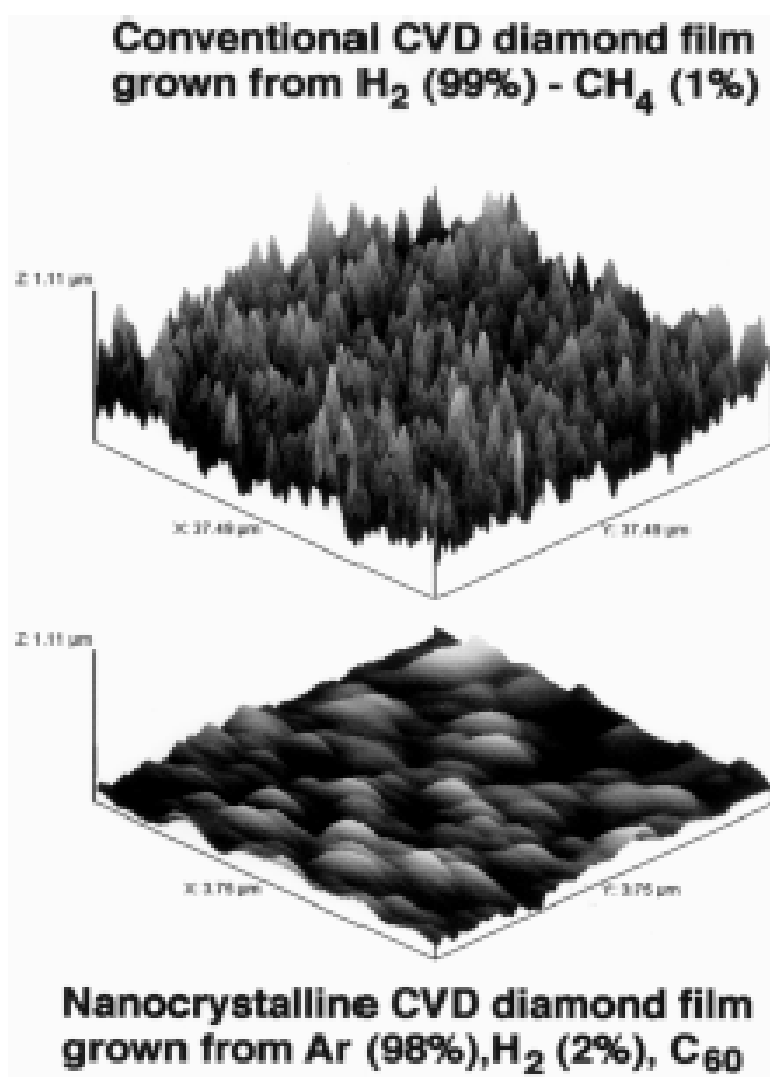


Fig. - 6: AFM comparison of the surfaces of micro-crystalline diamond and ultra-nanocrystalline diamond thin films⁷²

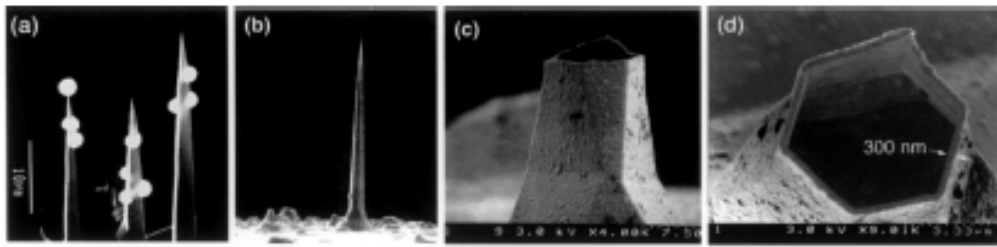


Fig. - 7: (a) Si microwhisker coated with conventional CVD diamond; (b) single Si microwhisker coated with ultra-nanocrystalline diamond, (c) base of fractured ultra-nanocrystalline diamond-coated Si microwhisker, (d) hollow ultra-nanocrystalline diamond three-dimensional hexagonal prism⁷²

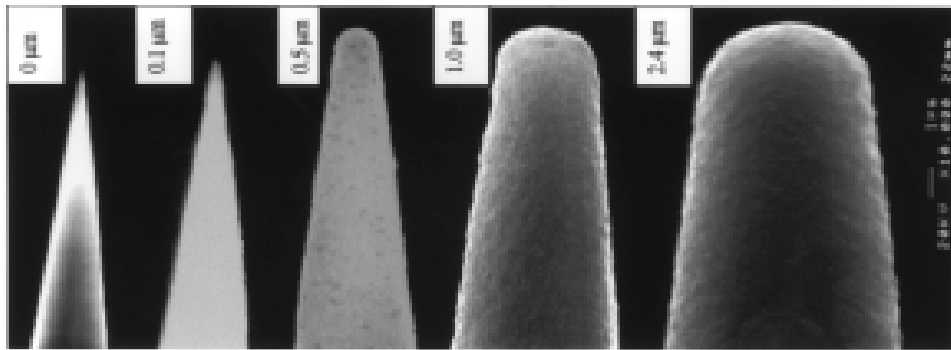


Fig. - 8: A series of SEM images of a 25-nm diameter Si tip emitter coated with a ultra-nanocrystalline diamond films with incremental coating thickness. The tip on the left is uncoated, while successive images to the right represent coatings ranging from 100 nm to 24 μm in thickness⁷²

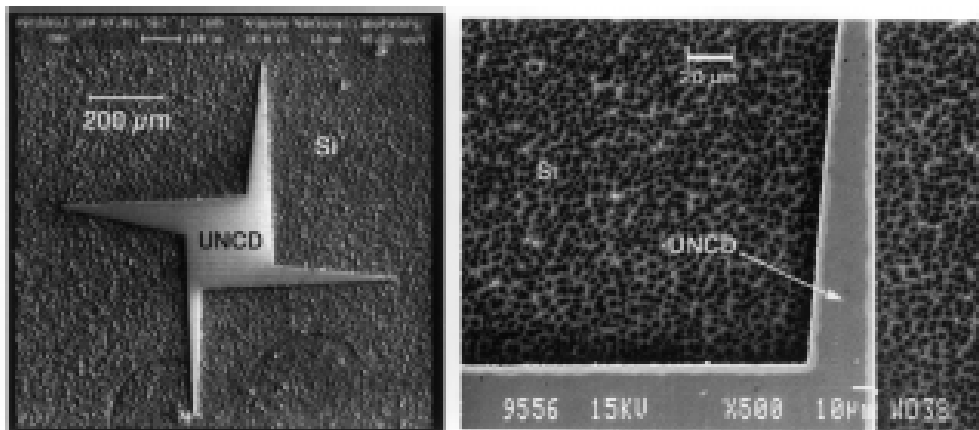


Fig.- 9: Two-dimensional ultra-nanocrystalline patterned films on Si(100)⁷²

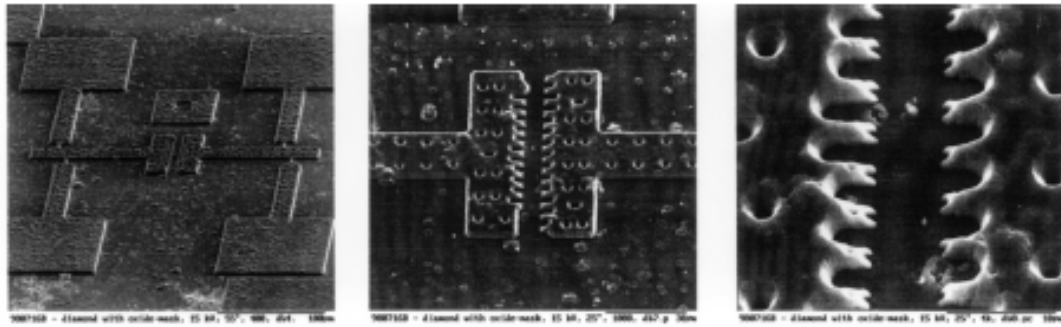


Fig. - 10: A ultra-nanocrystalline MEMS cantilever strain gauge produced by ultra-nanocrystalline diamond blanket film deposition and etching through a hard oxide mask N9⁷²

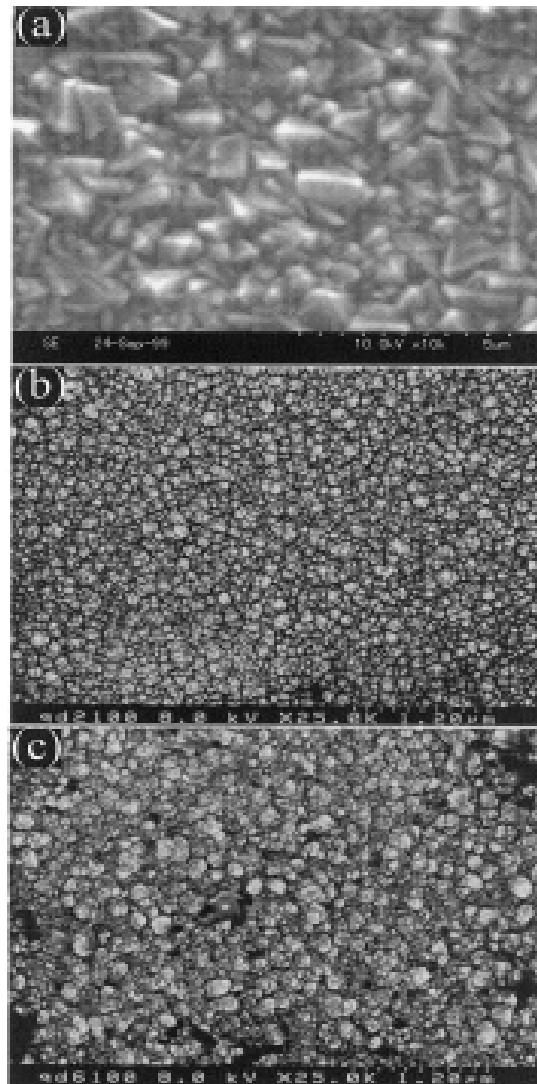


Fig. - 11: SEM of films (a) microcrystalline diamond, (b) nano-crystalline diamond grown at 600°C, and (c) nano-crystalline grown at 700°C⁷⁴

Yoshikawa *et al.*⁷¹ reported the synthesis of nanocrystalline diamond films using microwave plasma CVD. They synthesized the nanocrystalline diamond films by changing the position of the substrate from the plasma ball on the condition keeping the same methane concentration (CH_4/H_2 : 10%). As the position of the substrate was close to the plasma ball, the size of the diamond grains became smaller (<10 nm). NCD films synthesized by this technique had a very smooth surface (Rms : 1.3 nm) and showed the high hardness (Hv ; 82-99 Gpa) that is almost the same as natural diamond. Lopez *et al.*⁷³ reported the deposition of nanocrystalline diamond thin films by 35 kHz Ar-rich plasmas. They have observed non-uniform distribution of nano-diamond crystals in thin films grown on low temperature substrates (15°C) from decomposition of CH_4/Ar -rich plasma generated at 35 kHz. The concentration of the diamond nanocrystals on the samples is low i.e. about 10-20% of the amorphous carbon matrix and, consequently, the film hardness is also low (up to 15 Gpa, depending on the deposition conditions). Whereas the scarce amount of nanodiamonds detected in their films is associated to the low energy (i.e. out of the energy predicted by Lifshitz *et al.*^{21,23}) of the ions impacting the growing film, the non-uniformity of the nanodiamond crystal distribution is assumed to be due to the 35 kHz non-uniform ion energy distribution near the substrate.

Sharda *et al.*⁶⁹ deposited nanocrystalline diamond films by biased enhanced microwave plasma chemical vapor deposition. They found that substrate temperature plays a crucial role in the growth of NCD by BEG in the MPCVD system. Maximum concentrations of NCD, as observed by Raman and XRD results, occurs at 600°C. Hardness of the films also attains maxima at the same temperature. An increase in growth temperature may be responsible for a decreasing concentration of bonded hydrogen and increasing mobility of carbon atoms. Both factors help in developing NCD in the films grown at moderate temperatures with a concentration of sub-plantation mechanism, due to biasing, and a high concentration of H atoms in the gas-phase, typical of CVD diamond process. At higher temperatures, the implanted carbon atoms may be migrating back to the surface resulting in domination of surface processes in the

growth, which in turn should result in an increase in graphitic content of the films at such a high methane concentration and continuous biasing is used. Nanocrystalline or amorphous diamond, tetrahedral amorphous carbon (ta-C) and diamond-like carbon films, are much smoother, equally as hard as conventional diamond and can be grown at lower temperature⁷²⁻⁷⁶ and important for their application.

Optical transmittance of the film is found to be a strong function of the surface roughness but not the grain size of the NCD films. Ultra-smooth and highly transparent NCD films can be grown on either nm or mm-scratched substrates with either low or high methane fractions respectively. Contrary to prevailing knowledge, NCD films grown on substrates scratched with coarser diamond power can be more transparent than those on substrates scratched with finer powder under high methane fractions. An optical transmittance as high as 80-84% has been achieved by this *sample technique*. As this is a vast emerging research area due to its advantages over DLC films as well as a-C:H, a lot of research work is expected in this field in the coming years.

Some Important Properties

Chen *et al.*⁷⁰ reported the growth, characterization, optical and X-ray absorption studies of nano-crystalline diamond films. They found that the grain size of the NCD thin film can be varied between 4 nm and a few hundreds of nanometers via the methane fraction in the source gas and the substrate pretreatment. At low methane fraction, the grain size was comparable to the diamond powder used for substrate treatment. However, at high methane fractions, the grain size was virtually the same, independent of the substrate pretreatment. These observations indicate that the nucleation and growth mechanism may change at a methane fraction of about 15%. X-ray absorption spectra revealed mainly sp^3 -bonded carbon in the NCD films.

Raman spectra and atomic force microscopy image of the nano-crystalline diamond films deposited on Si (111) and Si (100)³⁹ are shown in Figs. 2 and 3, respectively. Raman spectrum of a good quality diamond presents single narrow line

at $\sim 1331\text{cm}^{-1}$ which may shift higher values depending on the deposition conditions, impurity etc. High sp^3 content gives a Raman peak at about 1332cm^{-1} . However, FTIR study of DLC diamond gives the sp^2 to sp^3 ratio in the film.

He *et al.*⁷⁷ studied the electron transport and electron field emission of nanodiamond synthesized by explosive detonation. They found that the conductivity of the nanodiamond coating as a function of temperature follows the Arrhenius relation at high temperature, but it diverges from the relation at low temperatures. The results may originate from the non-continuous network structure of the nanodiamond particles. The material has a good emission behavior and shows great potential as a cold cathode emitter. A progressive blue shift of the exciton state and conduction band edge was observed with the decrease of the grain size, indicating the presence of a quantum confinement effect.

A stable and reproducible emission current density as high as $\sim 95\text{ mA/cm}^2$ was obtained. It is suggested that the high emission might be due to the non-continuous network structure and the triple junctions composed of the surfaces of the nanodiamond particles, the crevice area and the vacuum. The detailed mechanism of the electron emission from the explosive detonated nanodiamond powders need to be further clarified before material can be used in vacuum microelectronics.

Itahashi *et al.*⁷⁸ studied the field emission of polycrystalline diamond films grown by microwave chemical vapor deposition and effect of p-type doping in diamond. The surface morphology of the B-doped diamond films was almost similar to that of the undoped diamond films of the same thickness. However, the quality of diamond films was improved by B-doping, and the resistivity was reduced significantly. The turn on field values as small as $8\text{ V}/\mu\text{m}$ were obtained for B-doped diamond. The turn on field of the B-doped diamond were independent of the film resistivity in the range $0.07 - 20\ \Omega\text{cm}$ and of the volume fraction of the non-diamond components, indicating that carrier transport in the B-doped diamond films was not controlled by the film resistivity or the quality of the

films. Also, the field emission values of the B-doped diamond were insensitive to the film thickness, which was not observed for the undoped diamond. From the potential distribution, they concluded that the emission efficiency was not significantly influenced by the surface morphology. The high efficiency of the electron emission in B-doped diamond films was believed to be due to the increase in the volume fraction of the conductive regions in the films and the density of emission sites on the surface.

Nanocrystalline diamond film grown at 700°C has a very high absorption coefficient ($>10^4\text{ cm}^{-1}$), though the film is smoother than that of the MCD film. NCD film grown at 600°C is much smoother than the MCD film with high transmittance ($\sim 78\%$) in the near IR region, which is close to that of diamond and, therefore, has the potential for applications as optical windows.

Sharda *et al.*⁷⁴ studied the structural and optical properties of diamond and nano-diamond films grown by microwave plasma chemical vapor deposition. They found that microcrystalline diamond (MCD) film is a high quality crystalline diamond film with low absorption coefficient in the whole spectral region from 200 to 2000 nm but with a surface roughness of 60 nm. SEM micrographs are shown in Fig.11.

There are also some reports about the photoconductive and photovoltaic properties of diamond films. In recent years, the potential applications of diamond films in opto-electronic devices have become more promising due to good electrical conductivity and opto-electrical responses of diamond films. The change in electrical conductivity of single crystal diamond after illuminating with photons of different wavelengths has been studied for many years. To generate an intrinsic photoconductive response requires absorption of light with a wavelength of less than 225 nm, which corresponds to the deep ultraviolet region of spectrum, since diamond has an energy band gap of 5.5 eV. The photoconductive properties of diamond films have been studied by a number of groups in order to gain some insight into the nature of the defects⁷⁹⁻⁸³. The physical form and commercial accessibility of this type of diamond enable it to be

considered for electronic device applications. The band gap energy, electronic properties and robust nature of diamond suggest that it is ideal for the provision of fast optoelectronic switches and high performance “visible blind” deep UV photo-detectors. This has provided the impetus for photoconductivity studies of diamond films.

Nahum and Halperin⁸⁴ were the first scientists to investigate the photoconductivity of natural diamond. They recorded a strong photoconductive response for a stone with a threshold of around 225nm originating from band to band transition. The presence of peaks in photoconductivity at longer wavelengths was found to be strongly affected by temperature (features present in a 300K spectrum were often absent when investigated at 80K). Indirect transitions to the conduction band by phonon interactions and thermal ionization of carriers from states in the band gap were suggested to be the cause of this difference. Denham *et al.*⁸⁵ studied the influence of the nitrogen content on photoconductivity. Photoconductivity associated with the population of states by longer wavelengths light (3.5 μm -350 nm) has also been characterized⁸⁶⁻⁸⁸. Conductivity stimulated by light with particularly sharp peaks within the spectral range 440-36 nm, is thought to be caused by the presence of vacancies and has been widely observed following high energy electron irradiation⁸⁹⁻⁹¹. The extrinsic photoconductivity displayed by free standing CVD grown diamond thin film has been studied by Allers and Collins⁹². *They found that the dominant photoconductive response in the near infrared and visible spectral regions was a broad band with a threshold of ~825 nm (1.5 eV), but it was not clear whether this was a donor or acceptor state.* The authors concluded that this defect was exclusive to diamond grown by CVD techniques. Gonon and co-workers^{92,94} studied 10mm thick diamond films supported on silicon. They found three distinct peaks; at 1127 (1.1 eV), 886 (1.4 eV) and 653 nm (1.9 eV) in the whole spectral region. The latter was believed to be acceptor states associated with bulk diamond. It was suggested that the 1127 nm feature was associated with ionization from acceptor states responsible for dark conductivity within the film, which was thought to be associated with disordered regions at the grain boundaries within the

polycrystalline film. Y Aikawa *et al.*⁹² investigated the photoconductive properties of a diamond optoelectronic switch made by CVD. They proposed a new configuration of the diamond gap to reduce the surface leakage current and avoid surface flashover. This technology made it possible to apply a static electric field with strengths up to 2×10^6 V/cm. The dependence of the mobility lifetime product $\mu\tau$ on the grain size was measured for a wide range of electric fields. The $\mu\tau$ value was found to be linearly proportional to the electric fields. Larger grain size samples had larger $\mu\tau$ values. The grain size dependence was attributed to the decrease in the mobility and lifetime inside the grain. The sensitivity to UV light was also measured and the value was 0.3 AW^{-1} at 150 nm. These results show the applicability of diamond films for UV photosensors. Pereira *et al.*⁹³ studied the electrical and photoconductive features of as-grown microwave-plasma-assisted chemical vapour deposited diamond films to correlate the magnetic results obtained from electron paramagnetic resonance (EPR).

The morphology of the as-grown film is analyzed by atomic force microscopy (AFM), showing $\langle 111 \rangle$ crystals with good uniformity of the deposit. The photo-response as well as the current-voltage features showed efficient photo-generation of carriers while the optoelectronic characteristics of the metal-diamond junction have an ideality factor of 1.6 together with a rectification ratio of about 10^4 at ± 2.5 V. It is also found that DLC films incorporated 60 at % W exhibit a superconducting property (with $T_c \sim 4.9\text{K}$)⁹⁴. Recently thickness dependent metal-insulator like transition has also been observed in DLC film prepared by Bhattacharay *et al.*⁹⁵. Therefore, the appearance of semiconducting, metallic and even superconducting behavior in DLC films is highly interesting and needs thorough investigation and analysis.

Applications of nanocrystalline diamond films

Diamond and related materials grown by chemical vapor deposition (CVD) and other techniques have enormous potential applications in areas such as hard coatings, optical windows, surface acoustic wave (SAW) devices, electrochemical electrodes for micro-mechanical systems and electron emitting surfaces for flat panel

displays. Currently uses based on the physical strength and hardness of diamond such as cutting tools, protective coatings and composite additives are in practice or in developing stage⁹⁶⁻⁹⁸. At the same time, in spite of intensive research, CVD diamond is not used widely for applications in thermal management and optical devices, coatings and electronics devices. Most of the above applications require smooth and defect free diamond films. For example, diamond is well suited for use as protective optical coatings but diamond films with high surface roughness cause attenuation and scattering of the transmitted signals restricting their use in optical coatings. In order to overcome the problem of surface roughness of diamond films either post-polishing should be adopted, or naturally smooth films should be grown without compromising their hardness and other useful properties. However, post polishing is expensive and time consuming^{96,99-99} and it would be better to concentrate on growing naturally smooth films⁹⁰⁻¹⁰².

Diamond films with nanometric sized crystallites have gained much attention because of their several outstanding properties. Studies on nano-diamond films were stimulated by the search for new protective coatings on mechanical tools, along with the antireflection coatings for IR optics which require low optical absorption in the IR region. Moreover, due to the smoother surface of nano-diamond alongwith the high band gap and hardness, it could be used as the transparent protective coatings on optical components. The field of application of nanodiamond varied widely e.g. from abrasives for semiconductors to lubricating material for hard disks. Nano-diamond films have also potential application in semiconductor devices related to the microelectronic industry. Recently it has been proved that nano-diamond is a promising material for the development of high performance MEMS devices and FEDs¹⁰³⁻¹⁰⁵.

The nanodiamond applications stem from its unique set of properties like

- high hardness and elastic modulus
- excellent wear resistance
- low friction coefficient
- high thermal stability
- chemical inertness

- bio-compatibility
- NDFs can be much smoother
- transparent in the IR region and to some extent also in the visible region
- high band gap material
- high resistivity and dielectric strength and
- good thermal conductivity

The lower friction coefficients and the higher hardness make nanometric diamonds better candidates as coating material for mechanical tools. The smoother surfaces and the wide band gap provide them the opportunity to act as an ideal transparent protective films on optical components⁹². Another very promising application of the nanodiamond lies in the field of fabrication of the effective cold cathode emitters. It has been shown that the electron emission efficiency of the nanometer-sized diamond films is much higher than that of the ordinarily microcrystalline films⁸⁷. The highly efficient emission properties of the nanocrystalline films were attributed to the presence of a large amount of grain boundaries which can increase the material's conductivity⁸⁸.

The intensive work on a-C:H at the 1980's which increased at the early 1990's yielded in the successful establishment of several industrial niches. The most important one is coatings for magnetic recording. Hydrogenated DLC coating on hard discs and heads eliminates adhesion of the disc to the head during stop-start events preventing catastrophic failure. It reduces friction and wear resistance on tape-recording heads and tape transport guides and prevents oxidation of a metal-film recording tape. A second successful application is wear protective and antireflective coatings for IR windows. The third application is wear protection of bearings and sliding/friction parts. A fourth one is precision gauges for the automobile industry. Efforts to enter to field of coating of machining tools were much less successful due to the limitations of a-C:H which include :

- oxidation at 250-350°C
- high friction coefficient in humid environment; and
- adherence problems to a variety of materials (especially steel), so that an interlayer is needed.

Attempts to enter the niche of biomedical coatings

(e.g. for joints and implants, taking into account the a-C:H biocompatibility) had only a limited success (some abrasive damage was observed in joints, as an example).

Extensive research has started for demonstrating the advantages of hydrogen free DLC films over a-C:H and other hard coatings including TiN and TiC, not only showing a much higher hardness but also exhibiting extremely low wear rates. Its main limitation is the high compressive stress, a substantial property of a-C and limits the available thickness to values of 0.1 – 2.0 μm depending on the substrate used. This problem can be partially overcome by reducing the sp^3 fraction to a value which still maintains good diamond-like properties but sufficiently lowers the compressive stress. Very recently it was shown that annealing the ta-C relieves stress without affecting other properties.

Field experiments not only proved that nanodiamond as a better material for most of the successful market niches of a-C:H (recording industry, protective and antireflective IR coatings, bearings/sliding parts), but also it provides very satisfactory solutions in applications where a-C:H failed. A good example is machining. Nanodiamond films can be successfully deposited with high adherence on a large number of materials without the necessity of an interlayer. Its excellent abrasive resistance can be used to prolong the tool life by 2-60 times, depending on the application. It can be used to mill and drill wrought aluminum, plastics, copper/copper alloys and wood. It can be used for wear protection of precision gauges in the automobile industry. It can be used in a humid environment and in liquid handling systems (e.g. moving parts of water pumps). An additional niche which utilizes the chemical inertness of nanodiamond as protective coating of optical fibers.

It should, however, be noted that contradictory to a-C:H and in spite of the technological success, nanodiamond have not yet entered the market. Recently Gillette has been marketing a new razor blade, MACH III, which is deposited by DLC and is claimed to have superior performance over conventional blades. As far as, this is first scale commercialization of a ta-C product.

In recent years, the potential applications of diamond films in opto-electronic devices have become more promising due to good electrical conductivity and opto-electrical responses of diamond films. The change in electrical conductivity of single crystal diamond after illuminating with photons of different wavelengths has been studied for many years. To generate an intrinsic photoconductive response requires absorption of light with a wavelength of less than 225 nm, which corresponds to the deep ultraviolet region of spectrum, since diamond has an energy band gap of 5.5 eV. The band gap energy, electronic properties and robust nature of diamond suggest that it is ideal for the provision of fast optoelectronic switches and high performance “visible blind” deep UV photodetectors.

Nanodiamond film is also a prospective candidate for its applications in solar cells as these films can be used as protective films on the solar cells to improve radiation resistance of space solar cells. The main reason for space solar cell efficiency degradation under the action of “solar wind” proton and electron irradiation as a reduction in carrier concentration of the base region, in addition to the decrease in the minority carrier lifetime¹⁰⁶. Another degradation factor in space is solar UV irradiation. Generally, the efficiency of InP-CdS or GaInP solar cells after proton and electron irradiation decreases less than in the case of Si or GaAs-based solar cells¹⁰⁷⁻¹⁰⁸. However, for long duration space solar cell application, solar cells must be protected by a cover glass or protective film¹⁰⁹. It is especially important for those Si-based solar cells, which have relatively low radiation resistance. The cover glass or protective film should be radiation protective. It should improve optical and thermal properties of the cell, thereby, making the cell radiation stable. Cerium-doped glasses¹¹⁰ are usually used to improve the cover glass radiation resistance, but the cover glass thickness is typically of about few hundred micrometers. However, it is very important to reduce solar cell weight, especially for interplanetary application. To achieve this aim, relatively thin protective film can be applied. Recently, it has been shown that diamond-like carbon (DLC) films are very promising antireflection and protective coatings for silicon solar cells¹¹¹⁻¹¹⁵ and for space solar cells¹¹⁵. The main advantages

of DLC films are high hardness, chemical and radiation stability as well as a possibility to change their optical properties under the variation of deposition conditions. These properties make it suitable to form multi-layer coatings which meet the requirements of optimal antireflection and protection of solar cells simultaneously. It is also found that the deposition of DLC films can substantially improve the efficiency and radiation stability of silicon solar cells.

Ma *et al.*¹¹⁶ reported the photovoltaic feature of metal-boron carbide-silicon (MCS) solar cell. They have prepared boron-doped diamond-like carbon thin film on n-silicon substrate using arc-discharge plasma chemical vapor deposition (PCVD) technique. The conductivity and the resistivity of the film were measured by Bio-Rad Hall5500PC system and found to be p-type semiconductor and 3-12 Ohm-cm, respectively. The boron content in the films was about 0.8-1.2%, obtained from Auger electron spectroscopy (AES), and some microcrystalline diamond grains (0.5-1.0µm) embedded in the mainly amorphous network were revealed through scanning electron microscope (SEM) and Raman spectrum. The performance of Au/C(B)/n-Si heterojunction solar cells has been given under dark *I/V* rectifying curve and *I/V* working curve (with 100mWcm⁻² illumination). A measurement of open-circuit voltage $V_o = 580\text{mV}$ and short-circuit current density $J_{sc} = 32.5\text{mAcm}^{-2}$ was obtained. Accordingly, the energy conversion efficiency of the device was tentatively determined to be about 7.9% in AM 1.5, 100mW/cm² illuminated. Huth *et al.*¹¹⁷ fabricated an inverted photovoltaic cell. This thin film cell consists of a p-n heterojunction in which the window layer is p-type and the absorber layer is n-type. They have demonstrated the feasibility of a new inverted p-n heterojunction p-diamond/n-CdTe solar cell. The non-optimized solar cell structure grown on semi-transparent p-diamond yielded an open circuit voltage of 0.23 V and a short circuit current of 1.54 mA/cm² when illuminated.

The electronic applications of nanodiamond are still in a very early stage. Some simple devices were produced, but there is still a long way to go for commercialization of these devices. The only study related to electronic

properties is that of field emission, attempting to reach the quality needed for the production of flat panel displays.

Field Emission Study

We have already discussed a little in Sec.4 about the field emission study. In this section an elaborate discussion about field emission is made. In order for an electron emitter to emit electrons without being heated to a high temperature, it is necessary to have the following features. (i) Effective mechanism is necessary for the electrons to be injected from an electrical contact or the substrate into the electron emitter, (ii) low resistance paths for electrons to be transported to the surfaces of the electron emitter, and (iii) electron emission sites with large field enhancement factors or a negative electron affinity. A large field enhancement factor can be achieved by filamentary electron conduction channels embedded in an electrically insulating coating, or tips, sharp peaks, and similar microstructures with a large aspect ratio without suffering from a severe electric field screening effect. Both a large field enhancement factor and a negative electron affinity allow electrons to escape from the solid surfaces of an electron emitter into the vacuum under the influence by a low applied electric field.

Since the flat-panel display technique became a very promising in late 90's, new techniques and materials for field emission have been widely explored. In the recent years, nanocrystalline diamond films and carbon nanotubes are becoming very popular candidates of electron emitter. In thermionic emission and photoemission, electrons are given energy to overcome the potential barrier at the metal surface. While in the field emission, the potential barrier is deformed so that unexcited electrons may also leak through it.

The electron emission mode in an intense electric field was first presented by Fowler and co-workers in 1928 [118]. The well-known Fowler-Nordheim equation is given by;

$$J(F) = \left(\frac{1.537 \times 10^{-2}}{t^2(y_o)} \right) \left(\frac{F^2}{\phi} \right) \exp \left[-6.83 \times 10^3 v(y_o) \left(\frac{\phi^{3/2}}{F} \right) \right] \text{A/cm}^2 \quad (1)$$

The plot $\ln(J/F^2)$ versus $1/F$, known as the Fowler-Nordheim (F-N) plot, is a straight line in a narrow region of field strength for typical field emission experiments. The slope of an F-N plot, according to Eq. (1) is given by

$$S_{FN} = \frac{d \ln(J/F^2)}{d(1/F)} = -6.83 \times 10^3 s \left(\frac{3.79 \times 10^5 F^{1/2}}{\phi} \right) \phi^{3/2} \quad (2)$$

It is found that extremely sharp tips can improve the field emission performance due to the enhancement of electric field (F). The local electrical field in a plane-to-plane anode-cathode configuration is defined as:

$$F = \beta F_o = \beta \frac{V}{d} \quad (3)$$

where F_o is the applied field, b is the field enhancement factor, V is the applied voltage, and d is the distance between the anode and cathode. Therefore, Eq. (2) becomes

$$S_{FN} = \frac{d \ln(J/F^2)}{d(1/F)} = -6.83 \times 10^3 s \left(\frac{3.79 \times 10^5 F^{1/2}}{\phi} \right) \left(\frac{\phi^{3/2}}{\beta} \right) \quad (4)$$

The field enhancement factor is regarded as the aspect ratio r/h , where r is the radius and h is the height of the tip respectively.

Recent studies show that the nanocrystalline diamond films have much higher electron emission efficiency than that of the ordinary microcrystalline diamond films and for this reason, diamond has attracted interest as a cold cathode material as it has chemical stability and low-onset fields for electron emission. Yonhua *et al.*¹¹⁹ reported the electron field emission from chemically vapor deposited polycrystalline diamond, nanocrystalline diamond, and glassy carbon coatings. Figure 13 represents SEM images for diamond coatings deposited at 800°C substrate temperature by microwave plasmas using 1% methane diluted by hydrogen for 2 hr, 1% methane diluted by hydrogen for 18 hr, and a mixture of methanol and ethanol with a ratio by weight of 100: 5. Electron field emission I-E characteristics for diamond coatings

deposited under same conditions, mentioned above, are shown in Fig. 13. They studied the effects of hydrogen-rich or oxygen-containing CVD precursors on electron field emission from CVD carbon coatings. It was found that the surface conductivity and negative electron affinity resulting from hydrogen termination of crystalline diamond promote electron field emission for discrete diamond particles and non-continuous diamond films but not for high quality and continuous diamond films as well as nanocrystalline diamond and glassy carbon coatings containing conductive graphitic carbon. Graphitic carbon in nanocrystalline diamond coatings and glassy carbon coatings provided additional conduction paths for electrons and allowed more effective injection of electrons into electron emitters. Nanocrystalline diamond coatings deposited by methanol/ethanol plasmas contained more graphitic carbon than that deposited by hydrogen/methane plasmas resulting in lower turn-on electric field and higher electron field emission current. Glassy carbon coatings deposited by both processes exhibited excellent electron emission characteristics. Low turn-on electric field, i.e., 1 V/ μm , for electron field emission was achieved for diamond and glassy carbon coatings deposited under optimized conditions. Among these three classes of carbon coatings, glassy carbon deposited at elevated substrate temperatures were found to exhibit the best electron field emission properties.

Kock *et al.*¹²⁰ have investigated high sp^2 content intrinsic and sulfur doped nanocrystalline diamond films to study field emission properties by electron emission microscopy operated in different modes. Electron emission microscopy enables real time imaging of the electron emission from a surface with a lateral resolution of ~ 15 nm. The nanocrystalline intrinsic diamond films exhibit electron emission at room temperature from localized emission sites with weak temperature dependence, and a density of $\sim 10^3$ to $10^4/\text{cm}^2$. In contrast, sulfur doped diamond films show similar emission characteristics at room temperature, but at elevated temperatures the emission significantly increases from the localized regions and a thermionic component is identified in the I/V dependence. They have also discussed the role of S-donor states to explain the enhanced emission

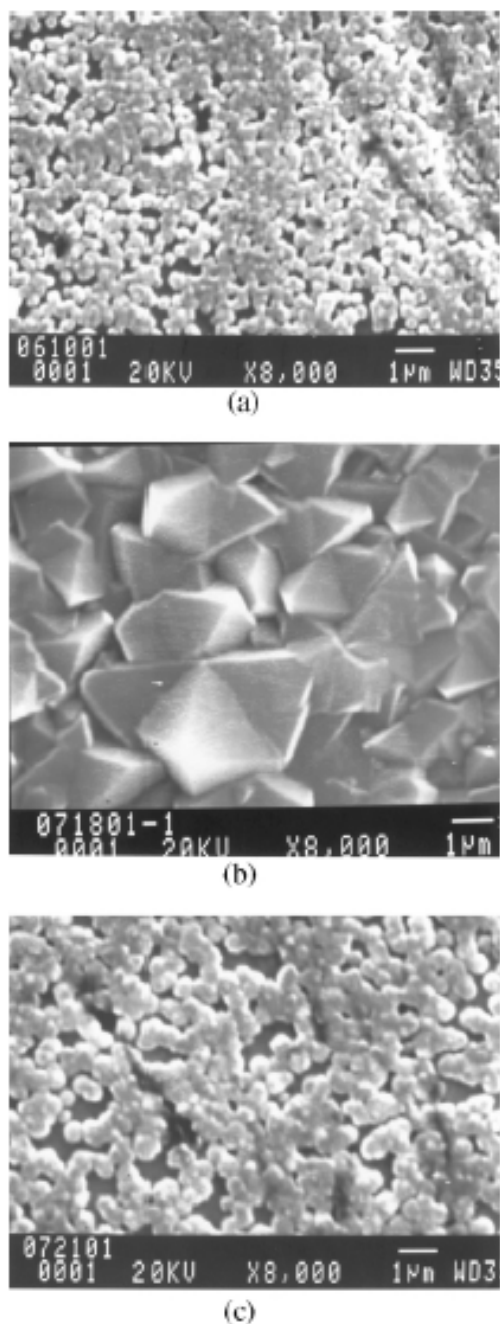


Fig. - 12: SEM photographs for diamond coatings deposited at 800°C substrate temperature by microwave plasmas in (a) 1% methane diluted by hydrogen for 2 hr, (b) 1% methane diluted by hydrogen for 18 hr, and (c) a mixture of methanol and ethanol with a ratio by weight of 100: 5 ¹¹⁵

of the S-doped nanocrystalline diamond. Frolov *et al.* ¹²¹ presented the results on a complex study of field electron emission (FEE) and structural correlations for nanocrystalline diamond and nitride. It was found that all the samples studied showed similar dependences of the Fowler Nordheim work function and effective emitting area on the threshold emission field. Besides it was generally observed that FEE occurred at nanosized regions on the boundary of high and low conducting areas, and peaks of the emission intensity were associated with a lowered surface electron potential. Based on the experimental data, the following mechanism of low-FEE from the materials studied can be supposed. Electrons are transferred from the conducting channel into a vacuum through the low dimensional region where the emission probability is high due to the quantum well effect. A physical model of the electron escape from a quantum well was analyzed. As follows from the estimations, the quantum size effect, being combined with a moderate field enhancement (the field enhancement factor 10 to 100), allows us to explain the observed variation in the energetic parameters for the samples studied. The function of the insulating grains is mainly to support the conducting channels in the sample body. Also, the grains can fulfill an additional function of the heat sink.

Field emission displays (FED) are a modern version of the traditional cathode ray tube, which still dominates today's display technology. They are flat, compact and promise superior picture quality with improved power efficiency. The manufacturing technology of FED is based on the use of microtips, but reliable and reproducible fabrication of such microtips over large area is still very difficult and expensive. The use of materials with low electron affinity could allow the production of FED without microtips, thus dramatically reducing the manufacturing cost. Diamond is a very suitable candidate for FED application. An electron field emission (FE) from nanocrystalline diamond has attracted many researchers to develop these materials as the key elements of cold cathodes for field emission display (FED). To manufacture FEDs, the development of emitters with low turn-on electric field, high emission current and excellent thermal stability is essential. The nanodiamond-based emitters have been expected to satisfy these

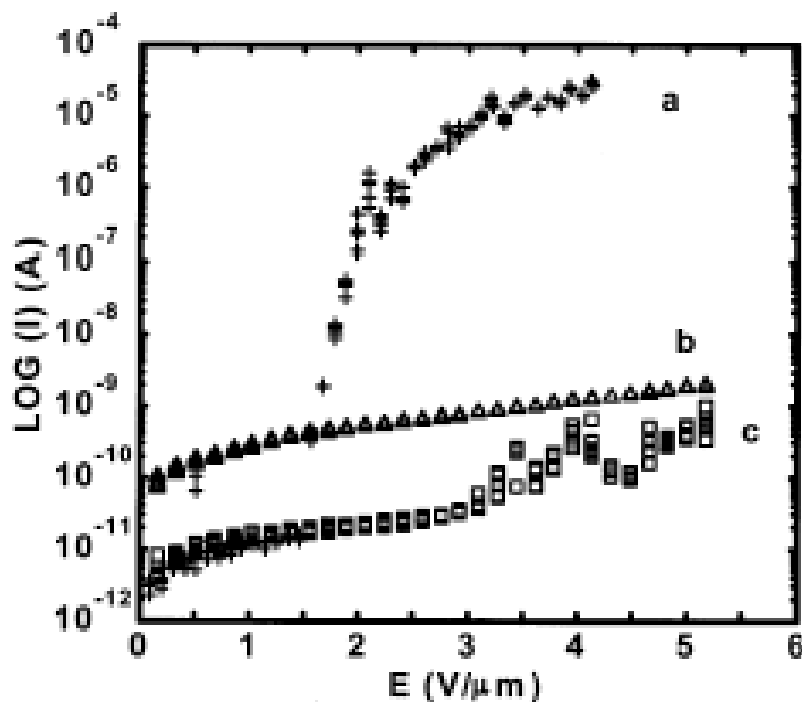


Fig. - 13: Electron Field emission I-E characteristics for diamond coatings deposited at 800°C by microwave plasmas in (a) 1% methane diluted by hydrogen for 2 hr (cross), (b) 1% methane diluted by hydrogen for 18 hr (triangle), and (c) a mixture of methanol and ethanol with a ratio by weight of 100: 5 (square)¹¹⁹

requirements, because diamond has negative (or small) electron affinity and high chemical stability and thermal conductivity.

Conclusions

During last few years, extensive research on nanodiamond films are being made. The major impetus has been given on field emission properties and MEMS. The work related to the photoconducting, photovoltaic properties and morphological observations through microscopy have also appeared in some literatures. The potential applications of using nanodiamond films in real life applications are huge ranging from UV-sensors, solar cells, MEMS and FED's. It is dependent on how to utilize fully the extraordinary properties of nanodiamond in different applications. Significant progress has also been made in the understanding and control of DLC films using a variety of different deposition methods. MSIBD or filtered arc systems demonstrated the capability of fine-tuning the properties of DLC films to meet specific requirements. The sp^3 fraction in DLC films

deposited using a variety of techniques was significantly increase (up to ~ 80-90% i.e. nanodiamond films), pushing the film properties closer to those of diamond (e.g. elastic modulus of 800 Gpa, an optical energy gap of 2.5 eV). This article briefly reports recent developments related to nanodiamond films. After grouping up all concluding remarks from literature, it has been found that there are still a numerous problems that should be solved before putting these advanced materials in to a real life. For an instance, the efforts dedicated to approach sp^3 fractions of 100% should be made. Decrease of the sp^2 fraction to only a few percent (compared to >10% at present) will very likely lead to mechanical properties similar to diamond and increase the optical band gap to the theoretical value of 3.9 eV. Decrease of the sp^2 fraction to very low values will increase their potential as electronic materials. The better doping capabilities needed for semiconductor applications may be achieved in such films. How to control shape and size of the nanodiamond crystals during the synthesis has great impacts on the design and

fabrication of devices based on nanodiamond. It is still a challenge to apply these capabilities to commercially available deposition systems where the processes could be industrialized and scaled up. The approach of direct growth of nanodiamond into ordered structures on surfaces is a promising route to approach nanoscale problems and create novel molecular-scale devices with advanced physical and chemical functions. Gaining further control on the nanodiamond growth will continue to open new possibilities in basic and applied sciences and real world applications. It is an ultimate goal for growth to produce nanodiamond with perfect crystal shape and size in larger quantity by

simple and efficient methods, gain control over various growth parameters and be able to direct the growth of nanodiamond films (sp^3 rich) from and to any desired sites.

In future, there is no doubt that the nanotechnology will be one of the emerging technologies that will play a significant role in developing compact and low cost devices. The development of a new manufacturing process of nanodiamond with geometrical identity, productivity and low cost is an important factor in bringing the nanodiamond to be more acceptable to the modern society.

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