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Cold Plasma Processing for some Novel Material Development

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Abstract. Versatility of cold plasma processing has made its deployment in numerous fields possible and is now seen as a vehicle for creation of wealth. In this paper we show how it has been successfully used in high rate deposition of device quality amorphous Hydrogenated Silicon thin films, stress relived Diamond Like Carbon (DLC) films, as also in growingGem quality diamondfilms

INTRODUCTION

Versatility of cold plasma processing can hardly be overemphasized. In an important publication (Tata McGraw-Hill) entitled 'Plasma Sciences and the creation of Wealth', Prof. P.I John has succinctly outlined what all can be done to create wealth using plasma processing. Cold plasma processing deals with ion/electron densities in the range of $1x10^9cm^{-3}$ to 10^{11} cm^{-3} and electron temperature in the range of 1-3 eV. For Glow discharge deposition , i.e. PECVD/PACVD , Rf frequency of 13.56 MHz is the normally allowed frequency .In recent time VHF plasma processing (27 ,40,60 MHz) has gained importance for high rate growth of amorphous Hydrogenated Semiconductors for solar cell fabrication . For Electron Synchrotron Resonance (ECR) deposition & etching 2.45 GHz is the allowed frequency range .Inductively Coupled Plasma(ICP) reactors (electron densities in 10^{11} -$10^{13}cm^{-3}$) with the BOSCH licensed process is being increasingly used for MEMS fabrication .Free standing Diamond for Gyratrons, Gem quality Diamond, Nano diamond, CNT, Graphene and DLC ,all these carbon forms are now commercially produced by innovation in plasma processing .Plasma polymerization is again an area which is seeing much development in textiles as well in interface design of Biosensors.

Authors of this paper were once coworkers at the National Physical Laboratory, New Delhi in its erstwhile " Plasma Processed Material group" and had many opportunities to work at the then emerging interfaces of Plasma Science and technologies [1-6]. Drawing from their experiences they present in this paper an experiential account of the following technological problems they set out to understand and find solutions,

1. High rate deposition of device quality Amorphous Hydrogenated Silicon films by PECVD, specifically for PV and various sensor applications.
2. High built up stress in PECVD produced Diamond like Carbon films and its containment for Thermal imaging and other related applications.
3. Issues related to Gem quality Diamond production by PECVD.

   We now briefly discuss each of above 3 tasks undertaken. While doing us we refer to our numerous publications and related other works in published literature for those interested in depth study.

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High Rate deposition of device quality Amorphous Hydrogenated Silicon films

The low deposition rate (typically close to 1 Å/sec) of device quality hydrogenated amorphous silicon (a-Si:H), grown using conventional RF plasma enhanced chemical vapour deposition (PECVD) at 13.56 MHz, has been identified as one of the problems the photovoltaic and other industries based on this material have been encountering. This is because, a-Si:H obtained at higher deposition rates, by applying significantly high RF power to a conventional PECVD reactor has been found to possess inferior opto-electronic properties due to incorporation of higher silane radicals , as compared to the device quality material (Photoconductivity/dark conductivity about 5 order, low microstructure factor, Urbach energy in the range of 45-50 meV).

Hence, the primary concern has been to enhance the deposition rate without compromising the opto-electronic properties of the material. In this connection VHF Plasma processing has been vigorously pursued worldwide for the manufacturing of PV devices by Oerlikon, UniSolar, FZK Julich and others. There exits great interest in adopting this process for poly-silicon based TFT arrays with mobility round 20 $cm^2/(V\cdot s)$.for driving pixels of AM-OLED displays, thereby avoiding the present use of lasers in such manufacturing.

Analysis of VHF discharge by M. Meyyappan et al . [7] and others indicate the following,

i) High density plasmas can be generated in a capacitively coupled system at frequencies above the industry standard of 13.56 MHz
ii) Total power absorbed per electron decreases with an increase in frequency
iii) At a given pressure, the power spent on accelerating the ions in the sheath decreases with an increase in frequency and an increasing fraction of the supplied power goes into generation of electron-ion pairs
iv) Sheath thickness, ion energy, ion flux, rates of inelastic processes, all scale favorably with frequency
v) Plasma and ion characteristics are uniform across even large area electrodes except near the edge.

However, for large area reactors VHF Plasma processing poses problems due to what is known as finite wavelength effect. Pulsing the VHF discharge can possibly obviate such deleterious effect. However, if silane plasma is completely extinguished during the pulse off period, silicon bearing dust settles on the growing films. Authors have innovated a Modified Pulse plasma Deposition (MPPD) technique (since patented), which has shown marked improvement on deposition rates achievable while retaining good photoconductivity of the films so grown.

MPPD can be thought of as a discharge where sheath electric field never vanishes, rather switches between a very high to a low value almost in a similar fashion as that of the power variation. In such environments negative ions and/or particles are rather forced to stay outside the growth zone i.e. in the vicinity of the substrate.

In this novel pulsed plasma growth process, deviating from earlier such experiments, a non zero low power condition is maintained instead of 100% modulation. In our studies, a-Si:H films were deposited at 10 W (100 mW cm^{-2}) CW condition and at 2 Hz modulation with different high power levels (HPLs75 and 60 W) and dwell times (Fig. 1). The low power level (LPL) was maintained at 10 W. The flow rates were 24 sccm for 0.3 Torr and 40 sccm for 0.1 Torr for pure silane discharges. For dilution studies carried out at 0.3 Torr, 8 sccm of hydrogen or helium was added to 24 sccm silane. The growth rates defined as the thickness (measured using Talystep profiler, Rank-Taylor-Hobson make) of the film deposited divided by the total deposition time. Film thickness was approximately 1 micron. Time resolved optical emission spectroscopy (TROES) studies were carried out for SiH*, H*, and Si*. The films were characterized by optical bandgap estimation (from reflectance–transmittance measurements) and the dark and photoconductivity were measured in a coplanar geometry, at 100 mW cm^{-2} intensity and AM1.5 spectrum. Hydrogen-content, C and microstructure factor, R were estimated from IR absorption spectra recorded using a Nicolet 510P FTIR spectrometer. By creating a large number of reactive species during the high power condition and by sustaining the glow discharge by using a low power for the remaining part of the cycle it was anticipated that higher deposition rates for a-Si:H will be achieved.

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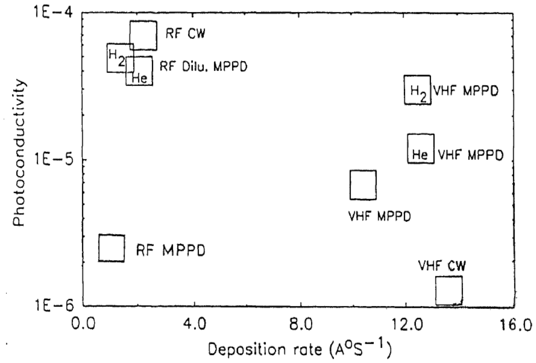

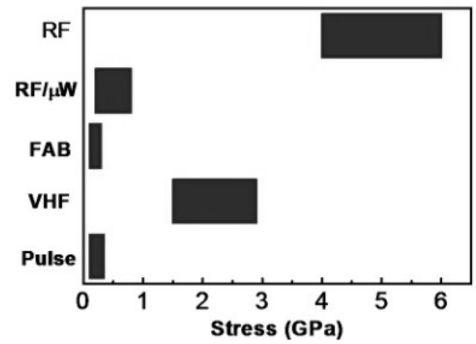

FIGURE 1. Summary of NPL efforts to achieve high rate deposition of device quality a-Si:H (details in Ref 6).
FIGURE 2: Stress management in DLC films at NPL by various approaches: Dilution of the feed stock (like nitrogen), Deposition at Very High Frequency (VHF, 100 MHz), Separation of plasma generation and bias application (dual frequency, RF/μW), Pulse plasma decomposition and saddle Filed Fast Atom (FAB) beam source.

We find VHF excitation of a silane discharge has been now adopted for the tandem MICROMPRPH thin film Silicon Solar cell processing. In VHF MPPD, the beneficial effects of ion bombardment are only realized when it is optimized for right energy (dependent on high power level), right duration (dependent on dwell time) and right flux (dependent on pressure). Thus, the favorable sheath characteristics of VHF discharges provide an edge to VHF pulsed discharges over RF pulsed discharges. The observed increase in rd after H2 dilution would have been possible because of the following reasons:

i) Higher dissociation of silane due to enhancement of ne (electron density) and ŧe (dwell time) compared to undiluted silane discharges, during both HPL & LPL21.
ii) The suppression of gas phase secondary plasma reactions due to hydrogen dilution, mainly during HPL, may have lead to enhancement of the arrival rate of a-Si:H film forming precursors to the substrate and thereby contributing to useful film growth. In fig our effort to enhance growth rate of a-Si:H has been summarized.

DLC films have also been grown by VHF plasma processing by our group at NPL [8-9].

High built up stress in PECVD produced Diamond Like Carbon films and its containment for Thermal imaging and other related applications

DLC films contain tetrahedral diamond like sp^3, trigonal graphite like sp^2 and even sometimes linear sp^1 phases of carbon in its structure [10, 11]. By varying the proportion of sp^3 and sp^2 hybridized carbon present in DLC films, the electrical, optical and nano-mechanical properties can be tailored. The a-C:H films with high sp^3 / sp^2 ratio exhibit highly diamond-like character, like hardness and hence, referred to as diamond-like carbon (DLC).
Despite of excellent properties, DLC films have certain issues. For example, DLC film deposited using plasma enhanced chemical vapor deposition (PECVD) technique has been considered to be the moderate hard with the hardness in the range 15-25 GPa. So increment in the hardness of PECVD deposited DLC films is an important area of research. DLC films exhibit high residual stress that leads to poor adhesion of films to the substrates resulting in complete delamination at higher film thickness. Under reference 1 we have given in certain detail various causes leading to such delamination and its mitigation.

At NPL, New Delhi innovative R & D has been carried out successfully to contain residual stress less than a GPa. Figure 2 summarizes our efforts in containing residual stress in DLC films that allowed us to grow DLC based AR coatings on Ge optics for thermal imaging meeting varies MIL specifications as also coatings on razor blades, inside of beer bottles etc.

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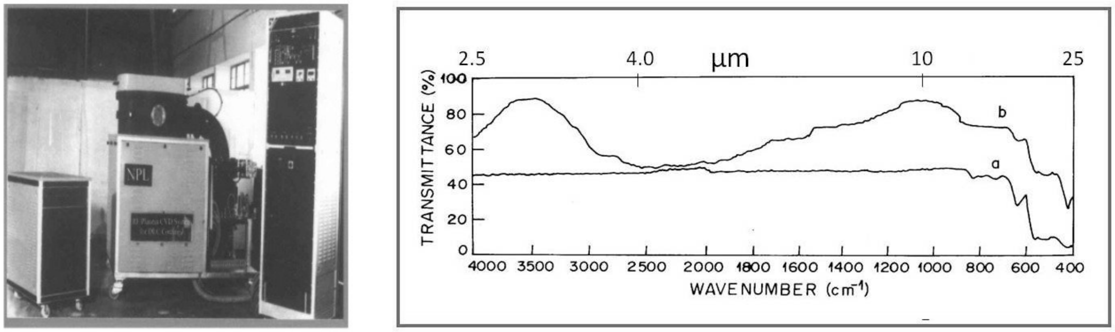


(A) (B)

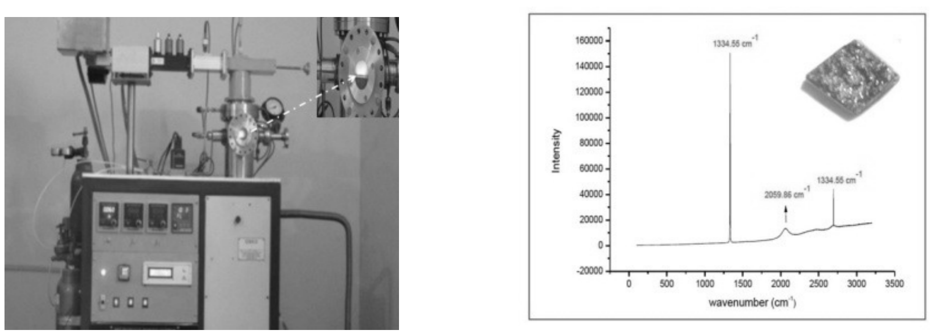
FIGURE 3. (A) Photograph of RF plasma reactor developed at NPL for DLC deposition for Ge optics (B) Infrared transmittance of (a) Ge substrate (b) Quarter wave thick DLC films on both side of the Ge substrate.

Specifically, it is found that adopting Pulse PECVD and FAB techniques, and more importantly choice of suitable precursors and fluent, appear to have the capability to produce low stress (less than 1.0 GPa) DLC films, which is otherwise found to be very high (7-10 GPa), if grown using conventional RF-PECVD technique. Authors' erstwhile group at NPL, New Delhi had designed and developed many Plasma reactors. A photograph of such a reactor developed at NPL, New Delhi for DLC deposition as protective & antireflection coating for Ge optics meeting various MIL specification is shown Fig. 3(A). Infrared transmittance of quarter wave thick DLC films grown in this system on both side of the Ge substrate are shown in Fig. 3(B). These DLC coatings met all stringent acceptance test for thermal imaging application.

Gem Quality Diamond Films by Microwave PECVD

In this process a mixture of Methane and Hydogen (6-8%) is subjected to intense mirowave discharge (10 kW and more applied power) at relatively high pressure of about 100 Torr. The gas mixture is weakly ionized - i.e. some of the atoms have lost an electron. These electrons are very hot indeed, about 20,000 degrees. The presence of hydrogen atoms is thought to be very important to the growth of diamond on Silicon substrates, which are kept at about 900- 1100 centigrade.

A microwave PECVD system has been designed and fabricated/developed by Omicron scientific equipment Co, New Delhi. The photograph of system is shown in Fig. 4(A) which is suitable to grow single crystalline & polycrystalline diamond layers on diamond seeds, nano-diamond, graphene, carbon nano-tubes etc. A typical Raman spectra of diamond grown in this system is shown in Fig. 4(B). Under reference no 12 the state of art on Large Area Single-Crystal Diamond Synthesis by 915 MHz Microwave. Plasma-Assisted Chemical Vapor Deposition has been presented.



(A) (B)

FIGURE 4. (A) Photograph of microwave PECVD system developed at Omicron scientific equipment co. for diamond growth (B) Typical Raman Spectra of diamond grown (inset shown diamond layer).

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CONCLUSION

In this brief report we have tried to summarize years of our sustained efforts, while we were at NPL, to understand the intricacies of various plasma CVD processes to tailor Silicon and Carbon films for meeting some exacting specifications. The acquired understanding of plasma processes enabled us design and fabricate many plasma reactors for different applications involving vacuum equipment manufacturers in the country.

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