PLASMA
PROCESSING UPDATE

A newsletter from the

Facilitation Centre for Industrial Plasma Technologies
Institute for Plasma Research

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Contents

Editor's Note

Solar energy is an affordable, in-exhaustible, and clean source of energy. This energy can be harnessed as long the Sun shines upon us. Solar energy can be converted into electrical energy through photovoltaic technology. Many types of absorber layers/materials, to form the solar cells, have been developed over a period of time. However, most of these materials are either cost intensive, scarce, or hazardous. Hence, efforts are on, all over the world, to develop new absorber materials which are affordable, abundant and non-hazardous; even if the efficiencies are low to start with. CZTS is one of such absorber materials and an efficiency of 19% (max. on lab scale samples) was already achieved. A program to develop CZTS based solar cells is being initiated at FCIPT and Mr. Sagar Agrawal has explained in detail.

Editor : *Dr. S. Mukherjee*

Co-Editor : *A. Satyaprasad*

Conference Presentations from FCIPT

Name of the Author	Topic	Date	Place	Conference
J. Alphonsa	Effect of Plasma Nitriding on Duplex coated AISI M2 Steel	13 – 17 September 2011	Harbin, CHINA	17th international conference on Surface Modification of Materials by Ion Beams (SMMIB-2011)
J. Alphonsa	Nitriding of welded joints of AISI 304 steels	19 -22 September 2011	Dalian, CHINA	8th Asian-European international conference on Plasma Surface Engineering (AEPSE-2011)
J. Alphonsa	Plasma based coatings for automobile components	3 – 4 November 2011	Indore	Invited talk at Two day intensive course on Surface Engineering in Automotive Industry
P. M. Raole	A perspective on requirements and developments of Fusion Reactor Materials	10 – 11 November 2011	KIIT University Bhuvaneshwar Orissa	Invited talk at national workshop on Plasma Processing for Thermonuclear Fusion and Industrial Applications (PPTFIA-2011)
J. Alphonsa	Low pressure Plasma Technologies for industrial applications	10 – 11 November 2011	KIIT University Bhuvaneshwar Orissa	Invited talk at PPTFIA-2011
Suryakant B Gupta	Applications of non-thermal plasma in biological science	10 -11 November 2011	KIIT University Bhuvaneshwar Orissa	Invited talk at PPTFIA-2011
Suryakant B Gupta	Development of power supplies for plasma based surface engineering & Bio-electrics applications	25 – 27 November 2011	Kottayam, Kerala	First International Conference on Plasma Processing of Organic Materials and Polymers (PPOMP 2011)
Vadivel P Murugan	Safe Disposal of Biomedical Waste using Plasma Pyrolysis Technology	2 – 4 December 2011	M.S.Ramaiah Medical College, Bengaluru	Indian Society of Hospital Waste Management Conference (ISHWMCON2011)
J. Alphonsa	Surface Modification using Plasma Nitriding Process	7 – 9 December 2011	Bengaluru	Invite talk at Society of Surface Protective Coatings (SSPC-2011)
Suryakant B Gupta	An introduction to plasma technology	8 – 10 December 2011	Nirma University, Ahemdabad	2nd International Conference on Current Trends in Technology (NUiCONE-11)

About FCIPT

Facilitation Centre for Industrial Plasma Technologies

The Institute for Plasma Research (IPR) is exclusively devoted to research in plasma science, technology and applications. It has a broad charter to carry out experimental and theoretical research in plasma sciences with emphasis on the physics of magnetically confined plasmas and certain aspects of nonlinear phenomena. The institute also has a mandate to stimulate plasma research activities in the universities and to develop plasma-based technologies for the industries. It also contributes to the training of plasma physicists and technologists in the country. IPR has been declared as the domestic agency responsible in INDIA to design, build and deliver advanced systems to ITER (International Thermonuclear Experimental Reactor), to develop nuclear fusion as a viable long-term energy option.

The Facilitation Centre for Industrial Plasma Technologies (FCIPT) links IPR with the Indian industries and commercially exploits its knowledgebase. FCIPT interacts closely with entrepreneurs through the phases of feasibility study, incubation, development, demonstration and delivery of technologies. Complete package of a broad spectrum of plasma-based industrial technologies and facilitation services is offered. Some of the important areas in which FCIPT has worked or has been working on, include Plasma Surface Engineering, Plasma Pyrolysis/ Gasification/ Energy recovery, Plasma Diagnostics, Plasma based Nano Patterning and Nano Synthesis, Plasma based Thin film Deposition, Plasma Material Interaction, Plasma based High Heat-flux Source Development, Space Plasma and Stealth technologies, Textile Engineering, Solar Cell Development etc. The Centre has process development laboratories, jobshops and advanced material characterisation facilities like Scanning Electron Microscope, X-ray Diffractometer, Microhardness testing facilities, which are open to users from industry, research establishments and universities. For further information, please visit our website.

This newsletter is designed to update the readers with the latest developments in the important field of plasma processing and plasma based technology development, and to look for new industrial opportunities. We would be very happy to have you write to us on ways of improving this service.

Please visit our website: *http://www.plasmaindia.com* *or* *http://www.ipr.res.in/fcipt*

Path towards the Development of Multilayer Thin Films for Photovoltaic Application

Sagar Agrawal

Photovoltaic (Solar Cell) is the technology that converts solar power in to electrical power. As long as sun light is shining on the solar cell, it generates electrical power and when the light stops, the electricity stops.

Solar cells are made of materials called semiconductors, which have weakly bonded electrons occupying a band of energy called the valence band. When energy exceeding a certain threshold, called the band gap energy, is applied to a valence electron, the bond is broken and the electron is somewhat free to move around in a new energy band called the conduction band where it can conduct electricity through the material. Thus, the free electrons in the conduction band are separated from the valence band by the band gap (measured in units of electron volts or eV). This energy needed to free the electrons can be supplied by photons (or in simple language - light). There, a specially made selective contact that collects conduction band electrons, drive such electrons to the external circuit.

Silicon (Si), one of the most abundant materials in the Earth's crust, is the semiconductor used in crystalline form (c-Si) for 90% of the photo voltaic (PV) applications today. Although c-Si is well established for PV applications, there is an intense need to develop a totally different semiconductor technology to achieve lower cost and improved manufacturability at larger scales than that could be envisioned for Si wafer-based modules. The main problem with the c-Si based PVs is that c-Si wafers are expensive and slow to grow and c-Si requires the greatest thickness (~300µm) to absorb sunlight, among all the other absorbing semiconductors due to its unique optical properties. Overall goal of the PV research is to reduce the manufacturing cost (use less semiconductor material by making thinner solar cells, use less expensive semiconductor materials and increase the material utilization by reducing the wastage of material in semiconductor and cell fabrication) and improve the performance. Thus, it is recognized that other semiconductors are better suited to absorb the solar energy spectrum. These other materials are in development or initial commercialization today. Some are called thin film semiconductors, of which amorphous silicon (a-Si), copper Indian gallium diselenide or disulfide ($Cu_2(In_xGa_{1-x})(Se,S)_2$ or CIGS), cadmium telluride (CdTe) and recently copper zinc tin sulfide (Cu_4ZnSnS_2 or CZTS) receive most of the attention. When they are fabricated into useful devices, they are so thin that they must be deposited on a foreign material called a substrate like glass, thin metallic foil for mechanical support. Of late, study on the development of low cost thin film solar cells based on Cadmium Telluride (CdTe), Copper Indium Gallium Diselenide ($CuInGaSe_2$, also known as CIGS), and Copper Indium Disulphide ($CuInS_2$, also known as CIS) have attracted much attention and a lot of work has been carried out. These solar cells have shown higher conversion efficiencies (16.7%, 19.5%, and 11.4% respectively) and high optical absorption coefficient (typically of the order of $5x10^4$ cm^{-1}). Typical structure and thickness of this kind of solar cell is shown in the fig.1, which is a multilayer thin film device.

All the layers are deposited on glass. Bottom-most layer is a back contact layer which is a conductive metallic layer, which acts as one electrode of the device. Above this layer there is an absorbing layer, which is made of semiconductor material to absorbs the sunlight and produce the charge particles. Above this layer there is a buffer layer, which forms a pn-junction with the previous layer and helps to reduce the recombination of the opposite charge particles and thus enhances the separation of charge particles, hence the efficiency. Top-most layer is the transparent conducting oxide (TCO) layer, which is highly transparent for the visible spectrum in sun light to allow the sunlight to reach the absorbing layer and is conducting in nature to work as the other electrode of the device. There are various choices of materials as shown in figure 1 for different layers.

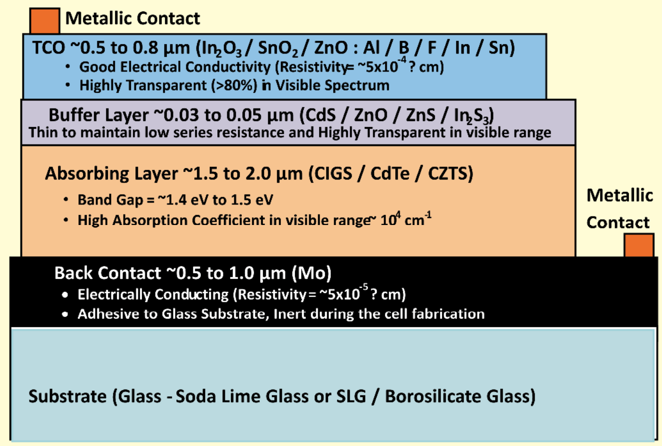

Fig.1: *Typical Structure of Multilayer Thin Film Compound Solar Cell.*

However, these absorber coatings have certain limitations too. In the case of CIGS coatings, the scarcity of the rare element Indium (In) is the major shortcoming. On the basis of abundance of Indium in the earth crust (0.049 ppm only) and current consumption rates, it is estimated that Indium reserves will get exhausted in a short time period of only thirteen years. In the case of Cadmium based absorber coatings such as CdTe, the important drawbacks are concerned with the toxic nature of Cadmium, and the extremely short abundance of the Tellurium. Therefore, the disposal and long term safety of CdTe is a known issue in the large-scale commercialization of CdTe solar panels. Hence, there is a great necessity for the development of thin film absorber coatings, free from Indium and Cadmium.

Copper Zinc Tin Sulfide (CZTS) is one of the promising materials as an absorber layer in thin film solar cells because of its excellent material properties. It has a direct band gap of ~1.45eV, which is very close to the optimum band gap of the semiconductors used for PV solar energy conversion and has a high absorption coefficient (10^4 cm^{-1}). Various research groups all over the world are working on this new material and demonstrated up to 9.7% efficiency, which proves the great potential of this material to develop a commercial technology for the solar energy in future.

FCIPT has also started an activity with the ultimate aim to develop a multilayer thin film solar cell device using Physical Vapour Deposition (PVD) technique. In the initial phase of the activity, bottom most layer of Molybdenum (Mo) back contact and the top most layer of TCO (ZnO:Al) has been studied and further experiments are going on.

We have deposited the Mo thin film on soda lime glass using DC magnetron sputtering technique and achieved a low resistive (ρ~3x10^{-5} -cm) and adherent to glass ~500nm thin film of Mo, which is suitable to use as a back contact electrode for the thin film solar cell. Figure 2 shows the SEM images of cross section and surface of the film. Figure 3 shows XRD results, which indicate that film is polycrystalline and Mo is formed in bcc phase.

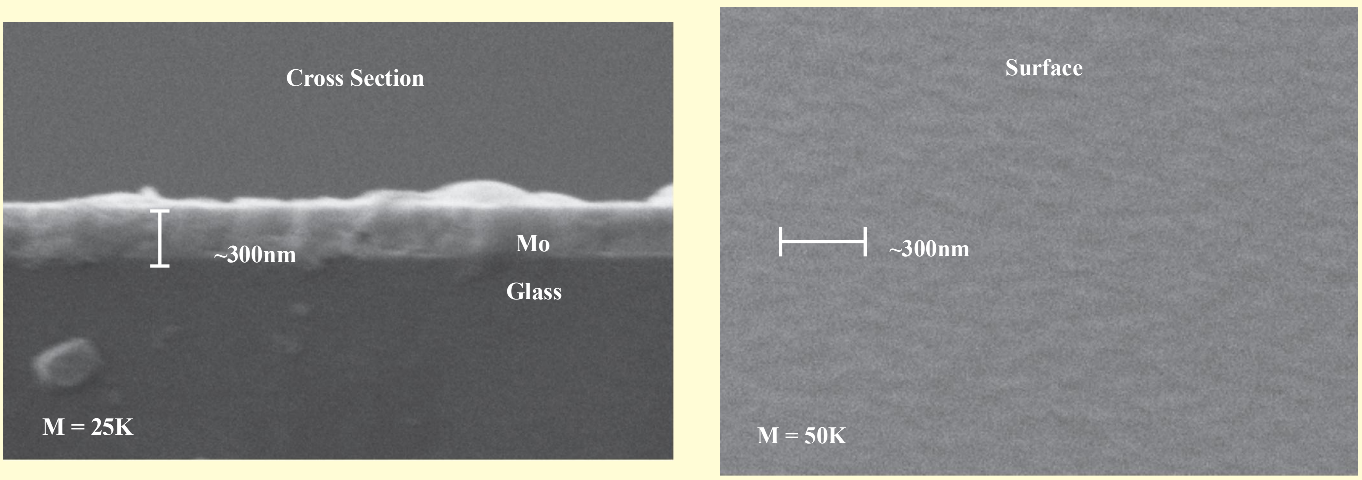

Fig. 2: SEM Images of the Mo Thin Film deposited on glass

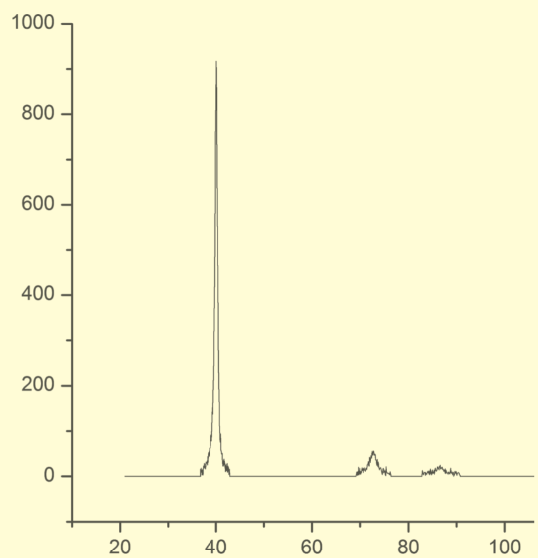

Fig.3: XRD results of Mo on glass thin Film

We have also deposited Aluminum doped Zinc oxide (ZnO:Al) thin film on glass using DC magnetron sputtering with pure Zinc and Aluminum targets in a gas environment of Argon and Oxygen. We have achieved ~1µm thin film with more than 80% transparency in visible range and 1 -cm resistivity with 4% Al doping. Further experiments are going on to achieve the lower resistivity. Figure 4 shows the SEM cross section and surface images of the film. Figure 5 shows the film deposited on glass (red circle), which is transparent as the letters beneath the glass are clearly visible.

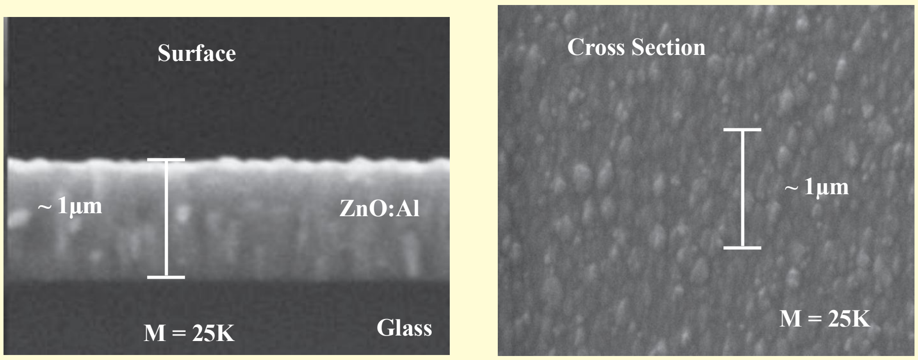

Fig. 4: *SEM Images of the ZnO:Al thin film deposited on glass*

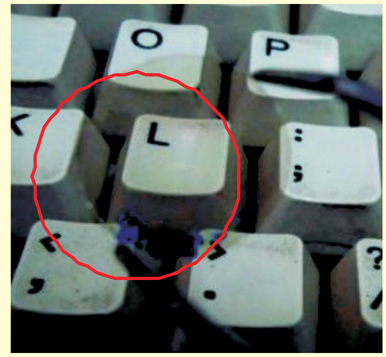

Fig.5: *Transparent ZnO:Al thin film*

However, all the layers have to be studied individually and then the complete multilayer thin film solar cell has to be developed. However, these are the preliminary results and a detailed study is underway.

Deposition & Characterization of Dielectric Films by PECVD Method

Purvi Kikani

Polymer films deposited by PECVD method are widely used in dielectric and photonic applications such as high/low *k* films for dielectric devices, high performance capacitors, AR coatings, band gap filters, wave guides etc. The *k* of a material is defined as the ratio of material's permittivity to the permittivity of vacuum. It is a measure of the relative amount of polarization induced by an electric field applied. A low *k* dielectric is a dielectric that has low ability to polarize and hold charge. Low *k* dielectrics are good insulators for isolating signal carrying conductors from each other. Thus low *k* dielectrics are a necessity in very dense multilayered ICs wherein coupling between very close metal lines need to be suppressed to prevent degradation in dielectric performance. A high *k* dielectric on the other hand has high permittivity. Because high k dielectrics are good at holding charges, they are preferred dielectrics for capacitors. They are also used in memory cells that store digital data in the form of charge [1]. Polymer materials such as fluorocarbon, polyamide, Siloxane, Silazane, hydrocarbons, silicon dioxide, silicon nitride, silicon oxy nitride etc. are promising candidates for their use in microelectronic applications as a dielectric material [1, 2, 3, 4, 5, 6].

Dielectric films can be deposited by various methods such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD) and by Plasma Enhanced Chemical Vapour Deposition (PECVD). In CVD, the deposition of the film and its properties are controlled by the temperature of the substrate and the deposition process takes place under thermodynamic equilibrium and the film has a well-defined structure and is usually crystalline (single crystal or polycrystalline).

In contrast to CVD, the PECVD method is a non-equilibrium technique, where the process is controlled mainly by the energy of the electrons in the plasma. As a result, the plasma dissociates the molecules in the gas phase into a variety of radicals, which recombine on the substrate to form a solid film comprising a variety of different bonds. The films deposited by PECVD are usually amorphous materials. The substrate temperature may affect the properties of the deposited film, but it is typically lower than the temperature that is required for depositing a film from the gas phase by thermal CVD.

Recently, considerable work has been undertaken to fabricate polymeric dielectric and photonic thin films using PECVD techniques due to its room temperature, solvent free and versatile operation. Many organic precursors can be selected to prepare thin polymer films with a wide range of compositions and chemical functionalities. Plasma polymerized (PP-) films, exhibiting highly cross linked structures have been targeted for optical and dielectric applications such as waveguides, anti-reflection coatings, and band gap filters for integrated optics, high performance capacitors and dielectric devices [1].

Siloxane based films prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD) consist of Si-O-Si and Si-CH_3 bonds that are chemically stable, resist thermal decomposition and feature low moisture absorption. These films have been widely used in variety of industries [7].

In the present work we have deposited plasma polymer dielectric film using Hexamethyldisiloxane (HMDSO) and Oxygen gas mixture at different ratios by PECVD method on metal substrate. In this study, a-$SiO_xC_yH_z$ films were deposited in a cylindrical stainless steel process chamber having dimensions of 60 cm diameter and 30 cm height. Plasma was generated by Radio Frequency (RF) power source at a frequency of 13.56 MHz. Silicon wafers, polished Aluminum round samples, and polyethylene sheets were used as substrates for deposition in a parallel plate configuration. Gas mixture was introduced via shower-head cum top electrode for uniform gas distribution. Schematic of the system used is shown in figure 1.

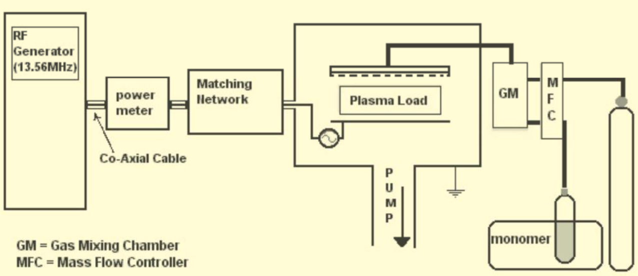

Fig. 1: *Schematic of PECVD Deposition System*

Film was deposited at a constant operating pressure of 0.1 mbar with variable oxygen concentration from 10 – 90 % in the gas mixture. Deposited films were tested for wettability and surface chemistry by means of Contact Angle Goniometer and Fourier Transform Infra-Red (FTIR) Spectroscopy respectively. It was found that the wettability increases with increased oxygen content in the gas mixture as shown in the figure 2 below.

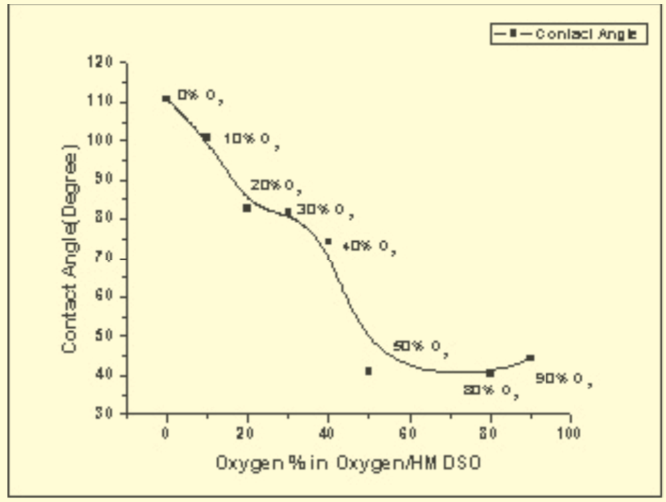

Fig. 2: *Oxygen % vs. Contact Angle*

FTIR results also confirmed the presence of hydrocarbon species at 0% Oxygen, their gradual reduction with increasing oxygen concentration in the gas mixture, and very minimal at 90 % Oxygen as shown in figure 3 (a) and figure 3 (b) respectively.

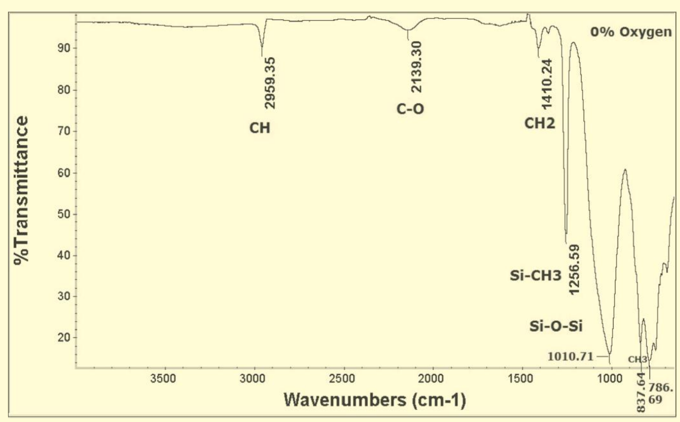

Fig. 3(a): *FTIR Spectra at 0 % Oxygen*

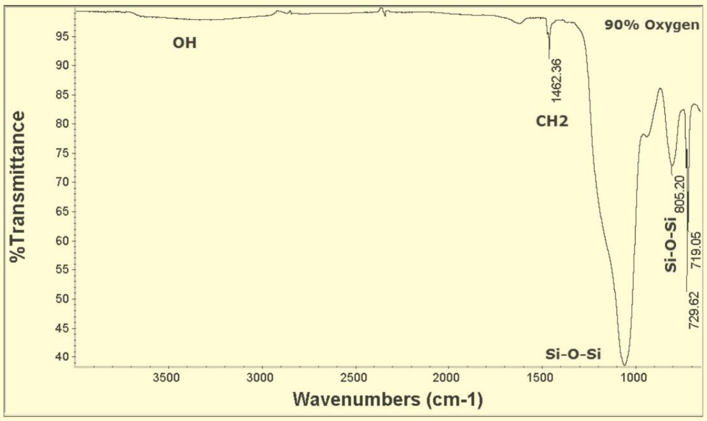

Fig. 3(b): *FTIR Spectra at 90 % Oxygen*

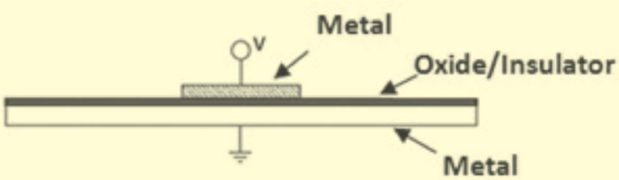

Fig. 4(a): *MIM Structure*

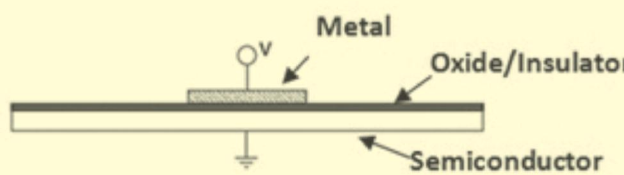

Fig. 4(b): *MIS Structure*

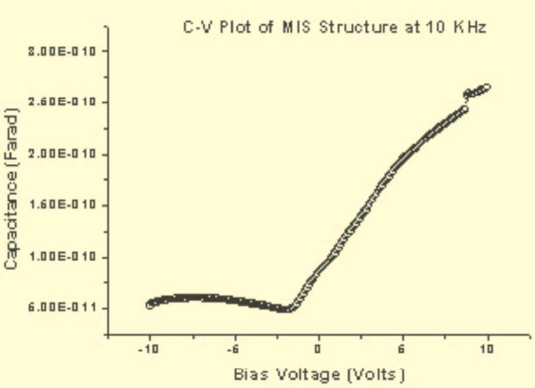

Fig. 5(a): *C-V Plot at 10 KHz*

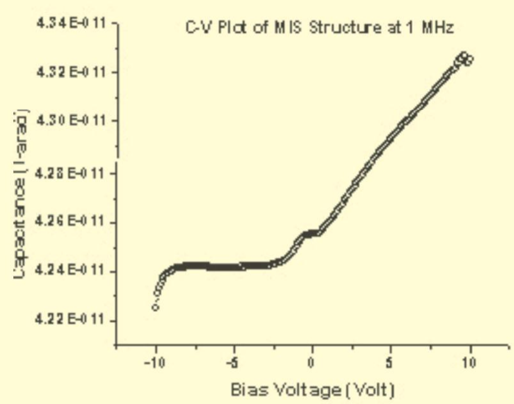

Fig. 5(b): *C-V Plot at 1 MHz*

In order to measure the dielectric constant of the deposited films, Metal-Insulator-Metal (MIM) and Metal-Insulator-Semiconductor (MIS) sandwich structures were fabricated as shown in figure 4a and 4b respectively.

Top metal contacts for MIM and MIS structures were deposited using thermal evaporation method. Capacitance-Voltage (C-V) characteristics were measured for MIS structure at 10 KHz and 1 MHz frequency as shown in figure 5 (a) and 5 (b) respectively.

We can see that the capacitance of dielectric film reduces with increasing frequency. This describes poor dielectric properties of deposited material at high operating frequencies. This generally happens due to high concentration of free radicals in the film. These radicals react with oxygen and form polar groups. Dielectric constant calculated for low and high frequency is 1.5 and 0.21 respectively for deposited film.

References

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[3] Surface & Coating Technologies 169-170 (2003) 600 – 603

[4] Micro Electronics Journal 35 (2004) 571 - 576

[5] Materials Science in Semiconductor Processing 7 (2004) 295 - 300

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[7] Materials Science in Semiconductor Processing 5 (2003) 279 – 284

Development of Tube based RF Power Supply with Matching Network

Vishal Jain

Institute for Plasma Research (IPR) has vast knowledge and expertise in developing radio frequency (RF) power supplies of high power rating. At Facilitation Centre for Plasma Technologies (FCIPT), with the technical inputs from IPR, a tube based RF power supply was developed for operating on plasma loads for various industrial applications.

The power supply comprises of a high voltage full bridge converter system for supplying 5 kV DC to anode of the tube, a Hartley oscillator based tank circuit to provide a high frequency signal input to the grid of the tube, a heating system for cathode heating at 20A and 6V, filter system for filtering low frequency and high frequency signals using low pass and high pass filters respectively at appropriate place in the circuit, measuring and controlling system etc. The mode of operation was chosen to be as class AB amplification for which the grid was kept at slightly negative voltage. RF supply up to 1kW power is very much suitable for applications like plasma enhanced chemical vapour deposition (PECVD), plasma based physical vapour deposition (PVD) etc. Hence, the RF supply of 600W, 13.56 MHz was developed at FCIPT, to test its suitability for plasma applications, along with the suitable matching network.

Figure 1 shows the basic topology of the RF power supply including DC supply, tank circuit, tube etc. and also shows the Hartley oscillator circuit which is essentially a configuration that uses two series-connected coils and a single capacitor to comprise a tank. In the Hartley oscillator the tuned LC circuit is connected between the plate and grid of the triode. The advantages of the Hartley Oscillator are:

(1) The frequency may be varied using a variable capacitor

(2) The output amplitude remains constant over a frequency range

(3) Either a tapped coil or two fixed inductors are needed

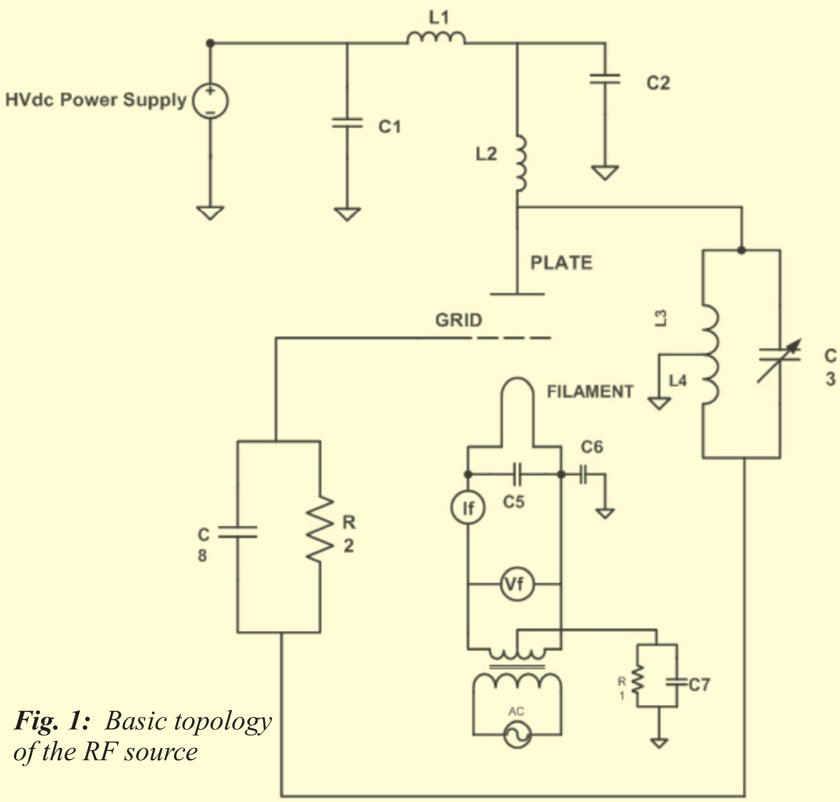


Fig. 1: Basic topology of the RF source

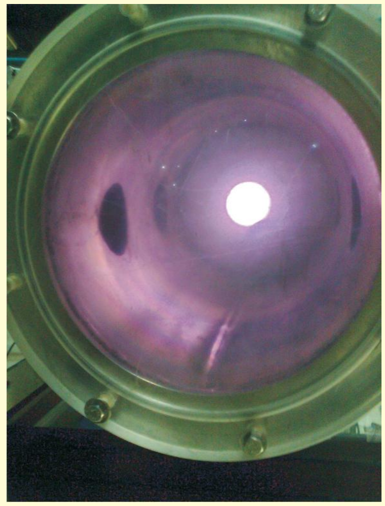


Fig. 4: Magnetron RF plasma

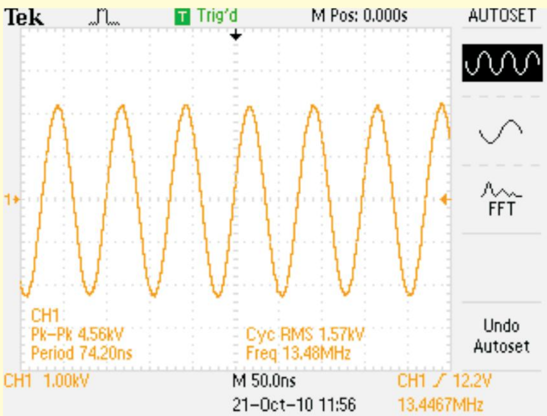


Fig. 2: RF output Wave-form

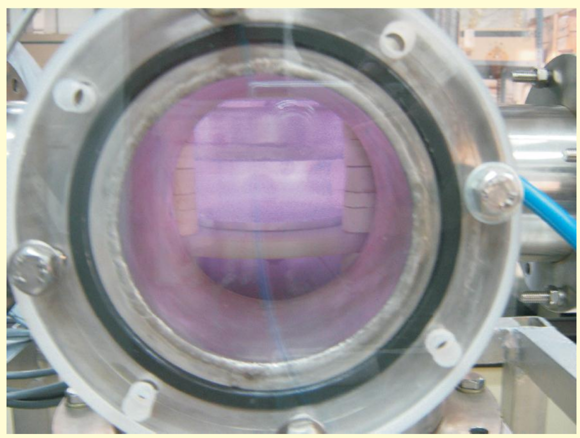


Fig. 3: Capacitively coupled RF PECVD Plasma

Figure 2 shows the RF output voltage waveform across 50 Ohm resistive load and the power supply has been successfully tested with plasma load as well. Figure 3 shows the photograph of the capacitively coupled plasma load and figure 4 shows the photograph of a magnetron plasma load operating with a RF power source.

Development of Matching Network

The plasma load is a complex load and hence, in order to draw maximum power from the source for better efficiency, the load and source should be coupled through a network which compensates the reactive part of the load. This ensures that the voltage and current are in phase with each other depicting a resistive load. Such networks are known as matching networks. To design a matching network, knowledge of complex load parameters is essential. A lot of literature is available suggesting on how to find the complex impedance of the plasma load under certain operating conditions. We designed the matching network for a magnetron which has 100 gauss permanent magnetic field. For this kind of plasma, the load parameters were selected from the literature and then we identified the suitable network, which is L type network, and we also ensured that the Thevnin's impedance across the load is a complex conjugate of the plasma load impedance. We also validated the network parameters by using an equivalent component across the plasma load and observed that the net power transferred to the plasma is increased.

We observed an L type network with an inductor of 0.7 to 0.9 micro Henry and a capacitor of 500 to 3000 Pico Farad, can suitably increase the net power transferred to the plasma load. The advantage of a tube based power supply is its ability to withstand high power, which is the sole limitation of solid state techniques for RF power generation.

Plasma Torch Activities

Dr. G. Ravi

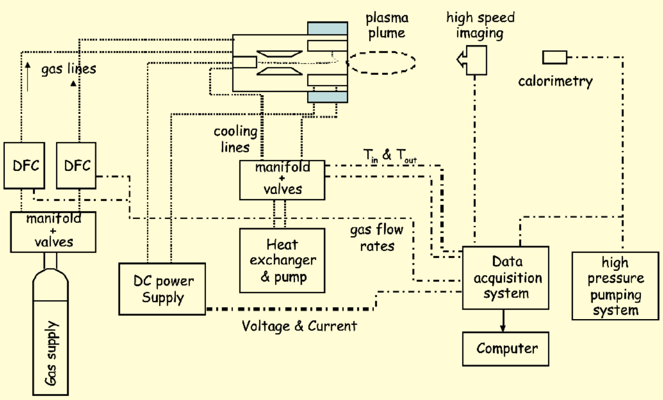
Since thermal plasmas are of great technological interest, industrial thermal plasma systems are in use in variety of applications ranging from plasma spraying & waste treatment, to metal melting, smelting, & spacecraft re-entry simulation. Facilitation Center for Industrial Plasma Technologies (FCIPT) has been involved in developing many thermal plasma technologies for over a decade. Graphite electrode based torches have been used successfully for pyrolysis of medical and plastic waste, involving thermal disintegration of carbonaceous material in the absence of oxygen. Non-expendable electrode based torches have also been developed and used in variety of applications e.g. spherodization of irregular alumina, dissociation of Zircon sand etc. A new program for development of high power (100 - several 100's of kW) non-transferred plasma torches for use as high heat flux sources has now been initiated, keeping in mind several high-end applications such as fusion, metallurgical, space and defense applications. The program comprises of two main activities:

(i) Development of higher power torches

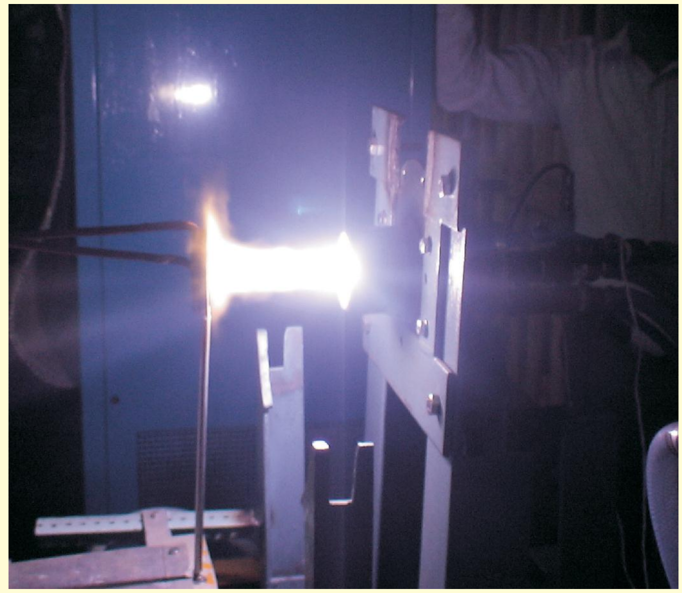
(ii) Fundamental studies on the thermal plasma inside the torch

To start with, a low power torch (~ 25 kW) with all three stabilization mechanisms i.e. wall, gas & magnetic field has been designed, and subsystems such as cooling & gas supply, voltage probes, magnetic coil power source & high pressure system for calorimetric diagnostics, have been put into place. A new data acquisition system for simultaneous sampling of data has also been set up; it can be controlled remotely by a computer via fiber optic link. Control system for torch operation, high speed imaging and calorimeter are being incorporated and will soon be put into use. Exhaustive experimentation was carried out on the low power torch to understand its electrical and thermal characteristics and influence of the experimental parameters on its operational stability and efficiency. Arc voltage and plasma torch electro-thermal efficiency were measured and calculated, respectively, as a function of different controllable experimental parameters. Many more experiments are underway to generate an exhaustive experimental database. Activities related to the design and development of higher power torches (~ 100 kW) are in full swing.

Schematic of plasma torch system



For the investigation of fundamental processes inside the torch, new torch designs have been worked out to incorporate and accommodate simple diagnostics inside the torch body itself. Interesting results have emerged pertaining to the role of external applied magnetic field on the torch characteristics and its efficiency. More experiments are underway to unravel the physical processes occurring inside the torch. This will help in identifying the key experimental parameters for process stability & repeatability. Also, it will help the plasma torch designer for scale-up to higher powers. In order to complement the experimental efforts, computational studies based on finite element & fluid dynamic approaches have also been initiated. It is envisaged that all the above three activities will go hand-in-hand and result in a vibrant plasma torch program.



Photograph of plasma torch in operation

OTHER NEWS

Ph. D. Thesis Submission

A Ph. D. thesis was submitted to Homi Bhabha National Institute, Mumbai, on "Plasma Response to Transient High Voltage Pulses", by Satyanand Kar under the guidance of Dr. S. Mukherjee; in the month of December 2011.

Facilitation Centre for Industrial Plasma Technologies

Institute for Plasma Research,
A-10/B, Sector-25,
GIDC Electronics Estate,
Gandhinagar, Gujarat - 382 044
INDIA

Phone *(079) 23269000/ 23269002*
23962000
Fax *(079) 23269001/ 23962001*
E-mail *fcipt@ipr.res.in*
Website *www.plasmaindia.com*
www.ipr.res.in/fcipt