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Optical thin films of silica and titania deposited by plasma polymerisation process: System design and fabrication

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Plasma polymerization provides a very versatile and cost-effective technique for the deposition of a wide variety of dielectric films, in particular optical thin films of silica (silicon dioxide) and titania (titanium dioxide) that are widely used as low and high index films in optical multilayer coatings for a variety of applications. The deposition of these films is often carried out using toxic and corrosive precursors–silane gas for silica and titanium tetrachloride liquid for titania – that are expensive and difficult to handle. The use of non-toxic organic liquid precursors, that are cheaper and safer and easier to handle, has been reported for the deposition of these films. In order to develop indigenous expertise in such deposition processes, a plasma polymerization deposition system that uses non-toxic and safe organic liquid precursors for the deposition of optical quality silica and titania films has been designed and fabricated in-house and successfully made operational. The problems that arise in this deposition process, the methods adopted to overcome them, the precautions that must be taken, have been studied in detail. Optical quality silica and titania films with satisfactory refractive indices and extinction coefficients have been deposited using this home-made deposition system.

Key words: Optical thin film, Plasma polymerization, Silica, Titania, Precursor

Plasma polymerization is a process, in which organic or organometallic gaseous monomers get stimulated through plasma and condense on a substrate as high cross-linked layers forming a thin film. Plasma polymerization has been recognized as a unique method for preparing high quality thin polymeric films[1-5]. Plasma polymerization process is nothing but the well known plasma enhanced chemical vapour deposition (PECVD) process, but with liquid organic or organometallic precursors. However, plasma polymerization process is a specific type of plasma chemistry, which involves reactions between plasma species, between plasma and surface species, and between surface species. Conventional plasma polymerization requires that the precursor should contain chain-producing atoms like C, S, etc. However, one can use this process to deposit inorganic films as well, by removing the H and C content from the films. This is especially important in the deposition of optical thin films that make use of inorganic oxide materials like silica (silicon dioxide) and titania (titanium dioxide).

The plasma polymerization process is often more versatile than physical vapour deposition and also offers several advantages over conventional polymer synthesis[5]: (i) The starting feed gases used need not contain the type of functional groups normally associated with conventional polymerization. (ii) Such films are often highly coherent and adherent to a variety of substrates, including plastics, glasses and metals. (iii) Polymerisation is a dry process and may be achieved without the use of solvents. (iv) Plasma polymer films can be easily produced with thicknesses of 50 nm to 1 µm. (v) Ultra-thin, pinhole-free films can be deposited. (vi) Through careful control of the polymerisation parameters, it is possible to tailor the films with respect to specific chemical functionality, thickness and other chemical and physical properties.

Plasma-polymerised films have received a great deal of interest due to their extensive applications in the fields of mechanics, electronics and optics. Applications include chemical, physical and biological sensors, microelectronic devices, non-linear optical and molecular devices. Thin film optical coatings, which hitherto used dielectric thin films deposited mainly by physical vapour deposition, are also utilizing dielectric-like polymeric thin films for various applications like antireflection coatings and filter coatings[5].

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Silica and titania films are most commonly used films for optical applications. Instead of the commonly used precursors like gaseous silane (for silica films) and liquid $TiCl_4$ (for titania films), which are toxic, inflammable or corrosive, expensive and difficult to handle, non-toxic and safely handled liquid precursors like TEOS (tetraethoxysilane) and HMDSO (hexamethyldisiloxane) for silica films, and TIPT (tetraisopropyl titanate or titanium isopropoxide) and TBOT (tetrabutyl orthotitanate or titanium tert-butoxide) for titania films, have been used, whose vapours can be easily carried into the reaction chamber by a carrier gas like argon since they are quite volatile even at 50-60°C. The plasma polymerization deposition system has been designed and fabricated in-house, incorporating several key safety features and precautionary measures, and operated successfully to deposit optical quality silica and titania films.

Deposition Process Chemistry

Silica (SiO_2) films

The main advantage of using silane (SiH_4) is that it is an inorganic precursor with weak Si–H bonds, so that in the presence of oxygen it is easily dissociated and SiO_2 is formed, along with water vapour. One can deposit high quality SiO_2 films at quite low temperatures and with reasonable growth rates[6]. However, silane is highly toxic and inflammable. It can react with traces of moisture and form silica particles that can clog gas lines and mass flow controllers. Further, silane produces reactive radicals in the plasma that can react and produce particles in the gas phase, causing voids in the deposited film[4]. Special precautions have to be taken to avoid these problems. An attractive alternative is the use of non-toxic and cheap organic liquid precursors in PECVD deposition processes. The most widely used organosilicon precursors are TEOS [$Si(OC_2H_5)_4$] and HMDSO [$(CH_3)_3SiOSi(CH_3)_3$]. This is because precursors with a larger number of alkoxy groups require less excited oxygen radicals for deposition of good quality SiO_2 films, and while SiO–CH_3 bonds are easily broken, even without oxygen, the breaking of Si–CH_3 bonds requires oxygen radicals[6]. Nevertheless, oxygen is introduced into the deposition chamber along with TEOS or HMDSO vapours, to minimize the incorporation of carbonyl (C, OH or CH) groups into the deposited films, which may increase optical absorption in the films[5].

Titania (TiO_2) films

As in the case of silane for SiO_2 films, the use of titanium halides like $TiCl_3$ and $TiCl_4$ for the deposition of TiO_2 films has the advantage of weak Ti–Cl bonds and thus the possibility of deposition at lower temperatures and at high growth rates. However, the disadvantages are the incorporation of chlorine in the deposited film (which increases optical absorption) and the production of HCl vapours from the hydrolysis process, necessitating the use of corrosion-resistant deposition chamber and exhaust lines. Non-toxic and safe organometallic liquid precursors are an attractive alternative[6]. One possible precursor is TEOT [tetraethoxy titanate or titanium ethoxide, $Ti(C_2H_5)_4$], whose vapours are carried into the deposition chamber along with oxygen for formation of TiO_2. However, the titanium tetra-alkoxides like tetraisopropyl titanate TIPT [$Ti(OC_3H_7)_4$] and tetrabutyl orthotitanate TBOT [$Ti(OC_4H_9)_4$] are more often used. This is because an alkoxide contains four O radicals, and so there are, in principle, enough oxygen radicals present to form TiO_2 without additional oxygen being needed. Nevertheless, further oxygen is usually used to minimize the incorporation of carbonyl groups into the deposited films, which may increase optical absorption in the films[5].

Deposition System: Design and Fabrication

Plasma polymerised films are grown in a variety of reactor configurations[4]: (i) internal electrode reactors, (ii) external electrode reactors and (iii) electrodeless microwave (MW) or high frequency (HF) reactors. The most common reactor with internal electrodes is the bell jar type reactor with parallel plate metal electrodes between which a RF power (usually at 13.56 MHz) is applied for excitation of the plasma.

A plasma polymerisation deposition system has been designed, fabricated in-house at NPL for the deposition of optical thin films of silica and titania. The overall deposition system consists of the following component sub-systems, as shown schematically in Fig. 1:

i. Deposition chamber (or plasma reactor chamber) consisting of pumping ports and gas/vapour inlet ports, electrode assembly, substrate heater etc.
ii. Pumping system comprising a chemical pump (special rotary pump), Roots blower, diffusion pump / turbomolecular pump and various valves, as well as an automatic pressure controller (APC)

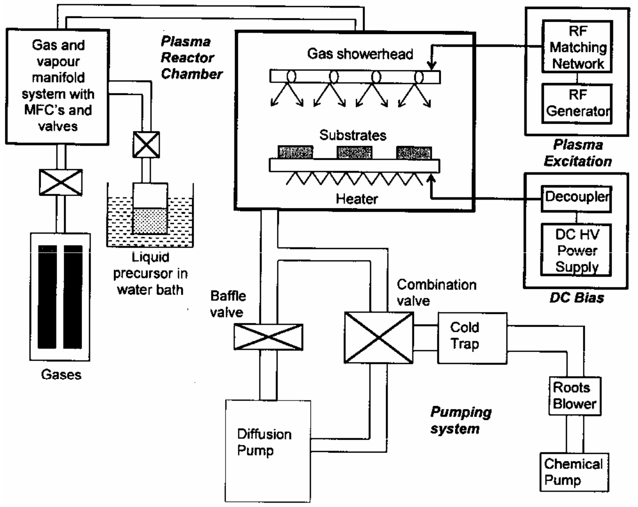

Fig. 1—Schematic diagram of the plasma polymerization thin film deposition system

and a specially designed cold trap to trap liquid precursor vapours reaching pumps.

iii. Gas and vapour manifold system, to deliver gases and vapours of the precursor to the deposition chamber, comprising gas cylinders with regulators, precursor vapour delivery system, stainless steel (S.S.) tube delivery network with various types of valves, mass flow controllers (MFC's), etc.
iv. RF generator and RF matching network to apply RF power to the electrode system, for plasma excitation
v. DC power supply to apply a DC bias voltage to the electrode system as required.

The basic features of these sub-systems are described below:

Deposition chamber and electrode system

The deposition chamber consists of a 20 cm diameter glass bell-jar, with Viton L-gaskets and S.S. base plate and top plate for vacuum sealing. The electrode system basically consists of two electrodes in the form of circular parallel S.S. plates, each about 150 mm in diameter. The electrical power (RF, 13.56 MHz) is applied to the upper electrode. The substrates to be coated are placed on the lower electrode, which is connected to ground. This is done for safety and convenience in substrate loading, but since RF power is applied to the upper electrode, appropriate insulation has to be provided to the gas supply system so that parasitic discharges do not occur in the gas feed lines to the chamber. The process gases/vapours are introduced into the reactor chamber through appropriate inlet tubes.

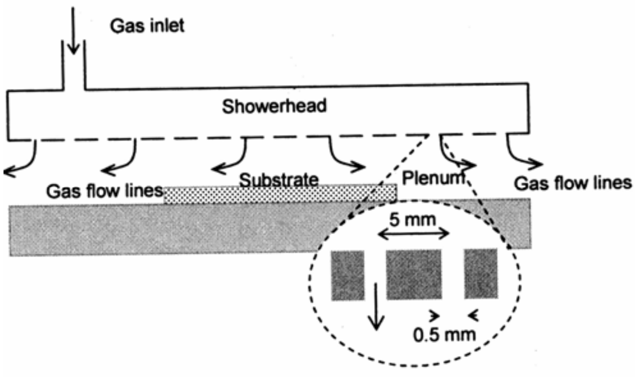

Fig. 2— Schematic diagram of showerhead arrangement

In order to ensure uniform distribution of the process gas in the space between the two electrodes, a showerhead system is used, which is incorporated into the powered upper electrode itself. The showerhead uses a perforated plate to inlet the reactant gases and make them flow more or less uniformly over the substrates, placed on the lower planar parallel electrode surface. This configuration provides very uniform film deposition on one or more substrates. A schematic diagram of the showerhead arrangement is shown in Fig. 2. The "hole" configuration of the showerhead is important in determining the uniformity of thin film deposition. Operation at high pressures (greater than a few torr) requires that the holes be small, as otherwise a localized hollow cathode discharge may occur in the holes, causing localized heating and erosion. A hole diameter of about 0.5 mm can usually prevent this discharge, in view of the Debye length in the gas discharge. Further, since the precursors used are liquids at room temperature, the showerhead is heated to above ambient temperature with a flat heater to prevent the precursor from condensing inside the holes of the showerhead and blocking them. A similar flat heater, insulated and sealed inside a S.S. box, is also used to heat the lower electrode, on which the substrates are placed, up to 400°C, if required.

A very important electrode design parameter is the electrode gap. Changing this electrode gap has several important effects: the chamber volume and thus the surface-to-volume ratio is modified, affecting the residence time in the discharge zone, the consumption time, and the radial velocities of the gases/vapours. Changes in the residence time strongly influence the extent of gas phase reactions. Therefore, it is useful to be able to change the electrode gap easily. Adjustable mounting has been provided for the lower electrode, to enable an adjustable gap between the two electrodes. Teflon insulation has also been provided to enable application of substrate bias.

Pumping system

A low pressure environment is required to generate plasma. The vacuum pumping system generates this low pressure environment in the deposition chamber. The components of the pumping stack have been selected to allow the desired level of vacuum to be achieved in a reasonable time, based on the effective pumping speeds determined from the pump specifications and the chamber conductance. But since the major gas load almost always consists of vapour, pump down times are limited by the vapour pumping speed of the system. The pumping system employs a chemical pump – a special rotary pump using 'Fomblin oil' that is more resistant to attack by reactive vapours of the organic precursors used than regular rotary pump oil. A diffusion pump is used to evacuate the deposition chamber to an initial base pressure of about 10^{-5} torr. During the deposition process, which occurs at a chamber pressure of 0.01 – 1 torr, a Roots blower is used to provide the high pumping speed required for the appreciable flow rates (several tens of sccm) of the reactant gases/vapours into the deposition chamber. However, it is found that even with the use of a chemical pump the exhausted gases contained enough reactant vapours to form powdery deposits inside the rotary and diffusion pump oils, rendering them inoperable unless cleaned and the oils replaced – a very laborious, time-consuming and expensive task. Inbuilt line filters are available commercially, but they decrease the pumping speed and make the pumping system bulky. Therefore, cold traps have been designed and fabricated and fitted into the pumping line at the exit point of the deposition chamber, to prevent the exit reactive vapours entering into the vacuum pumps from the deposition chamber. A cold trap provides a low temperature surface on which the vapour molecules can condense, and also improves pump down by one or two orders of magnitude.

Further, the pressure in the deposition chamber during deposition is controlled and maintained at a pre-set value by incorporating an automatic pressure controller (APC) in the pumping line at the entrance port of the chamber. The APC used here is an exhaust throttle valve with high speed motor/gear assembly (Model 653B, MKS Instruments, USA) that is set to maintain the chamber pressure at 0.01 – 1 torr during deposition.

Gas/vapour delivery system

Many precursors like TEOS, HMDSO, TIPT and TBOT are liquids at room temperature and even at about 60°C. If the vapour pressure is less than the pressure in the chamber, the precursor vapours cannot be transported to the chamber like a gas, by themselves. A common solution to this problem is to use a bubbler to deliver the vapour. A bubbler is a closed vessel containing the liquid whose vapour is to be delivered, with two or more tubes attached. One tube extends below the level of the liquid and generally delivers an inert carrier gas like argon. The other tube extracts the mixture of carrier gas and vapour from the space above the liquid. A typical bubbler assembly is shown schematically in Fig. 3. Bubblers rely for their operation on the formation of small bubbles of the carrier gas in the liquid, in which the vapour quickly attains an equilibrium pressure as the bubbles come up to the liquid surface. A cap with many small perforations is sometimes attached to the end of the tube dipping into the liquid, to ensure the formation of small bubbles and fast attainment of equilibrium conditions. The operation of the bubbler is dependent on the liquid level, which can be visually monitored in bubblers made of quartz or glass. The amount of vapour delivered depends on the vapour pressure and thus the temperature of the liquid. Temperature control is therefore essential for accurate

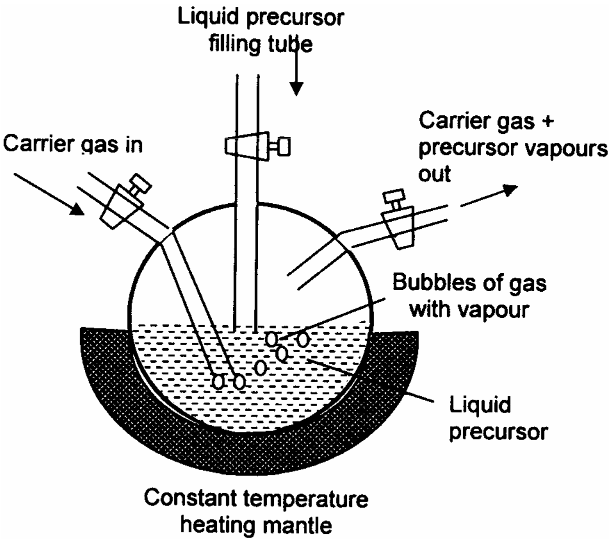

Fig. 3—Schematic diagram of the gas bubbler system for transport of precursor vapours

vapour delivery, even when the liquid is at approximately room temperature. Therefore the bubbler vessel is kept in a constant temperature heating mantle (or a water bath). Since the bubbles agitate the liquid, its temperature stays reasonably constant. If the vessel is made small to minimize the time required for heat transfer to the liquid, it will need to be refilled frequently, and then variations in the liquid level will change the temperature response and vapour saturation may occur in the space above the liquid. The better option is frequent small refills to avoid changes in the liquid level during operation. This can be done through a third tube attached to the bubbler vessel.

The gas/vapour delivery line manifold comprises a network of ¼” S.S. tubes, fitted with ferrule joints and incorporating S.S. two-way and three-way valves and metering valves to direct the pumping paths and flow of carrier gas and vapours to the deposition chamber as required. A very important and essential feature of the vapour delivery system is that heating tapes must be wrapped around the delivery lines and valves along the vapour paths, to keep them at a temperature of about 80–100°C, in order to avoid condensation of the vapours in the lines, which can lead to the choking of valves (especially metering valves) and tubes and will necessitate complete dismantling and thorough cleaning of the entire delivery system. Provision is made for oxygen to be carried into the deposition chamber as well, to ensure that the silica and titania films deposited are free of carbonyl groups that can lead to increased optical absorption. The flow rates of the gases are regulated with mass flow controllers (MFC’s) [Model GPC, Aalborg USA], calibrated for argon and oxygen gas flow at pre-set sccm (standard cubic cm per min) rates.

RF power supply

A RF generator (13.56 MHz, 600W), model Cesar136 and RF matching network, model Dressler 600A [Advanced Energy, USA] are used to apply RF power for plasma excitation.

External dc bias and decoupling circuit

It is known that when RF power is applied to the upper electrode a negative voltage will be developed near the lower electrode (normally the substrate holder), which is called self bias and is applied to the substrate. Due to this negative substrate bias, the positive ions in the plasma gain energy and get accelerated towards the substrate and bombard the surface of the growing film, due to which multiple mechanisms come into the picture[7], viz., sputtering, atomic mixing, densification, enhanced migration of adatoms and field-enhanced diffusion via charging and restructuring. The ionic bombardment by the energetic ions on the growing film leads to the creation of various metastable states/structures due to thermal spike. Thus the substrate bias plays a vital role in determining the structure of the deposited films. In our earlier studies[8,9] we have deposited diamond-like carbon (DLC) films of different structures by PECVD at room temperature, just by varying the applied substrate bias.

The self bias voltage depends on the electrode geometry, electrical power and frequency, and deposition pressure. Both the ion flux and self bias vary with the applied electrical power, so it is practically not possible to have independent control over both the ion flux and the self bias. But in order to avail the obvious advantages of the substrate bias, it is desirable to have independent control over substrate bias. One simple way of achieving such independent control is to adjust the substrate bias externally by using an additional power supply. In the present case we have used an external dc power supply (Aplab Model 7323) to control the substrate bias. When RF power is applied for plasma generation, it is necessary to decouple the RF power from the applied DC bias through a decoupling circuit, which is a simple π-section filter containing inductor-capacitor combinations.

Results and Discussion

The silica and titania films have been deposited on silicon [Si(100), p-type] and ophthalmic glass substrates. The substrates have been cleaned following the standard cleaning procedures before loading into the deposition chamber. Prior to each deposition run, the substrates have been exposed to argon plasma at –400 V bias for 5 min, to clean their surface.

Silica films

TEOS or HMDSO are the widely used precursors for the deposition of SiO_2 films[10-14], and these precursors have been used in the present work as well. Several deposition runs were carried out to deposit SiO_2 films on glass and silicon wafer substrates.

The vapours of the TEOS liquid precursor have been carried into the reaction chamber by argon as the carrier gas (flow rate about 10 sccm), with the heating