New Approaches to
Titania and Silica CVD

by Michael L. Hitchman and Sergei E. Alexandrov

The companion article by Mark Allendorf[1] highlights the importance of on-line CVD coating for flat glass manufacture. Two smaller, but fast growing, markets are those of precision optics and telecommunications. Both these markets are driven by the rapidly developing requirement for high throughputs. Current deposition methods rely on PVD techniques that are augmented with cumbersome tooling to move the complex geometries and thereby achieve time-averaged deposition over whole surface areas. Such techniques limit throughput and usually give a non-uniform deposit on parts of the coated sample, necessitating special alignment within an optic system and thereby incurring significant costs. The non-line-of-sight attribute of CVD makes the technology ideally suited for coating complex lens and fiber geometries that are used in optical telecommunication

transmission and distribution systems and for other precision optics. The coatings of interest are usually oxides other than SnO_2, such as TiO_2 and SiO_2. This article considers some aspects of the CVD of these materials. In particular, it describes a novel process for the deposition of the rutile form of titania at low temperatures and new approaches to thin film formation of silica by plasma enhanced CVD (PECVD) without the need for the use of a vacuum.

Thin Film Growth of Titania

Titanium dioxide (TiO_2) thin films are used in a wide variety of applications because of their outstanding physical and chemical properties. In particular, the high refractive index of the material and its excellent transmittance in the visible and near-IR spectral regions has led to extensive applications for antireflection coatings and waveguides. Titania

exists in three crystalline forms—anatase, rutile, and brookite—with rutile having the highest refractive index of the three (2.61 – 2.90). Rutile is therefore the most interesting for many optical applications. It is also the most thermodynamically stable form at all temperatures, but interestingly it is the anatase form which grows preferentially at the lower temperatures that are often required for film formation on thermally sensitive substrates. So, for example, TiO_2 films produced by a range of techniques from low technology processes (such as sol gel deposition and thermal oxidation), through PVD methods (such as reactive sputtering and ion assisted deposition), to a variety of CVD systems, are invariably either amorphous or crystalline anatase at temperatures below 400°C.[2,3] Reported temperatures for the anatase to rutile transition range from 700 to 1100°C[4] and while the direct CVD growth of rutile has also been described,
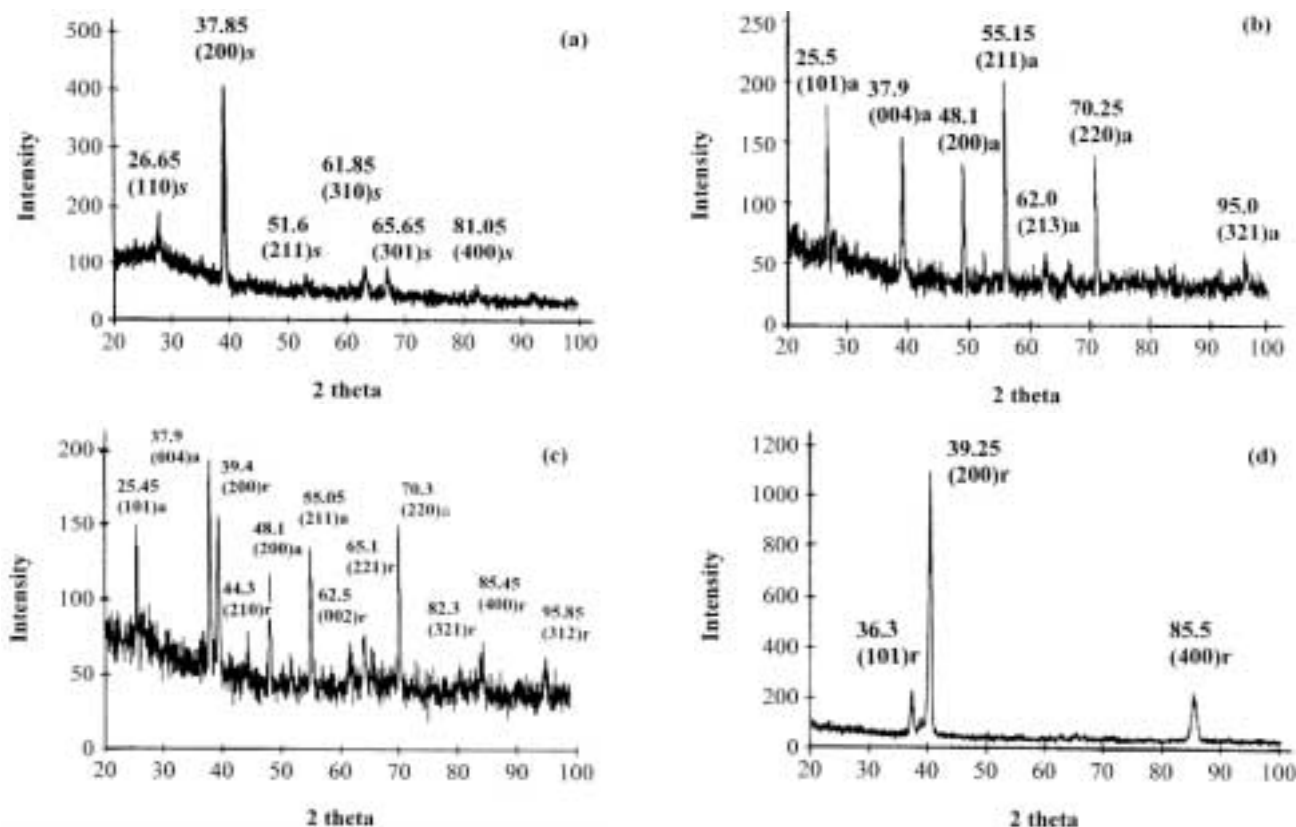

FIG. 1. XRD patterns for (a) SnO_2 coated glass and TiO_2 films on SnO_2 coated glass at (b) 257°C; (c) 268°C; and (d) 300°C.

it is usually for deposition temperatures in excess of 500°C.[5] Therefore while rutile is energetically the most favored form of titania, the fact that anatase is formed at lower temperatures implies that there is a higher kinetic activation barrier for rutile than for anatase. This is unfortunate because many optical applications for TiO_2 require low thermal budget processing to avoid the introduction of stress or damage to temperature sensitive substrates.

A Serendipitous Discovery

A recent serendipitous discovery has led to the first low temperature CVD formation of rutile with growth of this crystalline form on a number of different substrate surfaces at 300°C.[6,7] This surprising result came about during a study of CVD titania growth at low temperatures for photocatalytic applications.

These applications usually require anatase, particularly with a controlled degree of crystallinity. So a number of CVD precursors were investigated for their influence on crystalline quality. The most widely reported precursors are titanium halides (*e.g.* $TiCl_4$, $TiCl_3$, TiI_4) and titanium tetra-alkoxides (*e.g.* ethoxide, iso-propoxide and the tert-butoxide). The halides have the disadvantage of producing hydrogen halide gases as by-products from the hydrolysis process, so the alkoxides are an attractive alternative. Because an alkoxide contains four oxygens, there is, in principle, enough oxygen to form TiO_2 without additional oxygen being needed. Often, though, further O_2 is used to minimize carbon incorporation into the deposited layers. An alternative oxygen source is H_2O, which has the additional feature of lowering the reaction temperature. This combination of an alkoxide, the tert-

butoxide, and water led to the unexpected discovery of a low temperature CVD rutile process.[6,7] There is nothing out of the ordinary about the type of deposition system required, with standard gas handling facilities and a conventional hot-walled reactor with a typical operating pressure of about 1 Torr. What is remarkable is the transition from amorphous material to anatase to rutile as the substrate temperature increases from 200°C through 250°C to 300°C. The XRD patterns in Fig. 1 show this variation for TiO_2 deposited on tin oxide coated glass; this is a preferred substrate for photoelectrochemical applications. Of course, SnO_2 has a rutile structure itself and it could be argued that this is influencing the crystallization of the CVD layer. However, as the Raman spectra in Fig. 2 show, rutile can also be grown on such disparate materials as steel, aluminum, sapphire and glass, as well as silicon (not shown). On other substrates such as copper and magnesia, though, the CVD layers grown at 300°C are anatase (Fig. 2). This phenomenon of low temperature CVD rutile growth appears to be unique to the combination of titanium tetra-*t*-butoxide and water since investigations under similar conditions with the ethoxide, *iso*-propoxide, n-butoxide and *sec*-butoxide all yield either anatase or anatase/rutile mixtures. The reasons behind this unexpected result are still not clear. The rupture and formation of Ti-O bonds is known to be the rate determining step in the anatase-rutile phase transformation and can be promoted by impurities.[8] One could speculate that this is perhaps facilitated in the deposition process from the *t*-butoxide by more carbon-containing impurities being present in the layer than when other precursors are used; β-hydrogen elimination with the resulting formation of stable hydrocarbons on the surface is likely to be more complex and have a higher activation energy for a *t*-butoxide than for less branched alkoxides. However, further studies on this point are needed. The role of the substrate is also puzzling because the materials that promote rutile growth have a range of different structures; *e.g.* an hcp octahedral structure for sapphire and possibly for native oxides on iron and aluminum, while silicon is tetrahedral. There seems little likelihood of any epitaxial effect with those structures, although one must remember that surface reconstruction could alter the surface energies significantly. Glass clearly has no well-defined structure, but it may be able to catalyse the anatase to
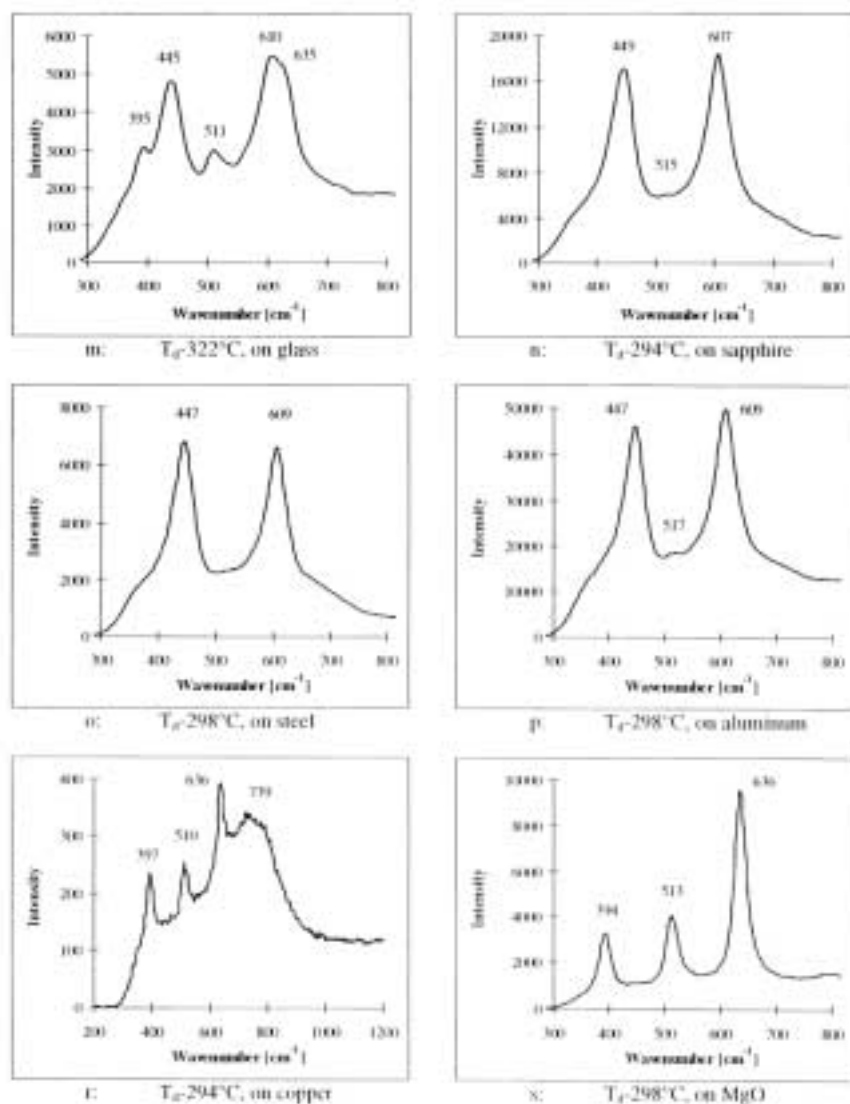

FIG. 2. Raman spectra of LPCVD TiO_2 films deposited on different substrates. Expected frequencies/cm-1: Anatase: 194, 397, 515, 637. Rutile: 144, 235, 448, 612.

rutile transition.[9] Whatever the reasons for the low temperature growth of rutile from titanium tetra-*t*-butoxide and water vapor, two issues are clear. First, while theoretical considerations are of value and importance for understanding and predicting CVD chemistry, there are still unexpected discoveries to be made. Second, low temperature rutile growth has considerable potential for the production of high refractive index coatings on thermally sensitive substrates. We are currently exploiting the new process for such applications.

Thin Film Growth of Silica

Like titania, thin films of silicon oxide have interesting physical and chemical properties that make them attractive for a wide range of applications in microelectronics, optics, for the protection of metals and polymers, and particularly as a component of multi-layers and graded-index coatings. As mentioned earlier, for the latter applications, thermal budgetting is critical. As a result, PECVD techniques have attracted considerable interest as they can provide the possibility of deposition of silicon oxide films at substrate temperatures as low as 100 to 300°C.[10] However, it has been shown by many workers that a conventional, or direct, PECVD approach, in which a mixture of reactant gases is introduced directly into the plasma region, has a number of disadvantages. Thus, process parameters such as the total pressure, RF power, gas composition, and gas flow rate are all interdependent and can be difficult to control individually. Also, complex reactions can arise as a result of the simultaneous production of many different reacting species, some of which can participate in the film formation process, leading to films with unpredictable composition. In particular, there is likely to be intrinsic doping of films deposited by direct PECVD. So, for example, films deposited using silane as a precursor generally contain large concentrations of contaminants,[11] such as SiH_x (x=1-3) and OH groups.

A great deal of research of the PECVD of various materials, and especially of silicon oxide films, has been directed toward overcoming some of the drawbacks of direct PECVD processes. One approach, known as remote PECVD, is to separate the discharge generation region and the deposition zone in space and to introduce only some of the initial gases into the discharge generation region for excitation (Fig. 3).[12] The other reagents, usually the less stable precursors, are introduced downstream from the discharge generation region. The results of a comparative analysis[13] of the main features of direct and remote PECVD show that the remote technique provides less interdependence for many process parameters and so there can be better control. For example, growth of SiO_2 films by remote PECVD has been shown to yield layers with remarkably low concentrations of contaminants because of this better control of the plasma phase composition.[12] Therefore, the technique of remote PECVD is a very promising one for thin film technology.

However, the use of low-pressure PECVD, whether it is direct or remote, for very large quantities of optical materials is not a particularly appropriate technique because of the high cost of volume vacuum equipment. Because of this economic drawback, some relatively new CVD processes based on the use of various types of electrical discharges sustained at atmospheric pressure have attracted considerable interest.

Atmospheric Pressure PECVD

Several attempts have been made to use non-thermal plasmas generated at atmospheric pressure for oxide CVD processes.[14-16] One example is the successful use of a plasma jet that operates at atmospheric pressure and near room temperature for plasma deposition of silicon oxide films.[14] The plasma jet was fed oxygen and helium between two coaxial electrodes that were driven by a 13.56 MHz RF generator at 40-500 W. Tetraethoxysilane (TEOS) was mixed with the effluent of the plasma jet and directed onto a substrate located 1.7 cm downstream. The highest registered deposition rate of 300 ± 25 nm min^{-1} was achieved with a TEOS partial pressure of 0.2 Torr and an RF power of 400 W. It was shown that the properties of the deposited films were comparable to those of thermally grown SiO_2 films.

A similar idea based on the use of an RF plasma torch has been developed for the enhancement of CVD growth of silicon oxide films using tetramethoxysilane (TMOS) as a precursor.[15] The reactive cold plasma was generated between coaxial electrodes with an RF source of 13.56 MHz and an applied RF power of 80-100 W. With this cold plasma torch, silicon oxide films were deposited on various substrates with growth rates higher than 600 nm min^{-1}. The carbon content in the deposited films was rather high, though, being in the range 1-7 atomic percent.

Some more basic work has been done on film formation from TEOS and hexamethyldisiloxane (HMDSO) in an atmospheric pressure glow (APG) discharge (15 kHz, 50 W) by studying the emission spectra.[16] The spectra of the APG discharges ignited in either a TEOS-He-O_2 mixture or a HMDSO–He-O_2 mixture were very similar. For both precursors with He, but without O_2, emission lines corresponding to He, CH and H were observed while with O_2 additional lines for OH, CO and O appeared. The intensity of the He line decreased in the presence of either precursor or O_2. No emission lines related to Si or Si-containing species were detected. In fact, the species observed to be present from the spectra were very similar to those found in conventional low pressure PECVD. This led the authors to suggest that the deposition mechanism involving precur-
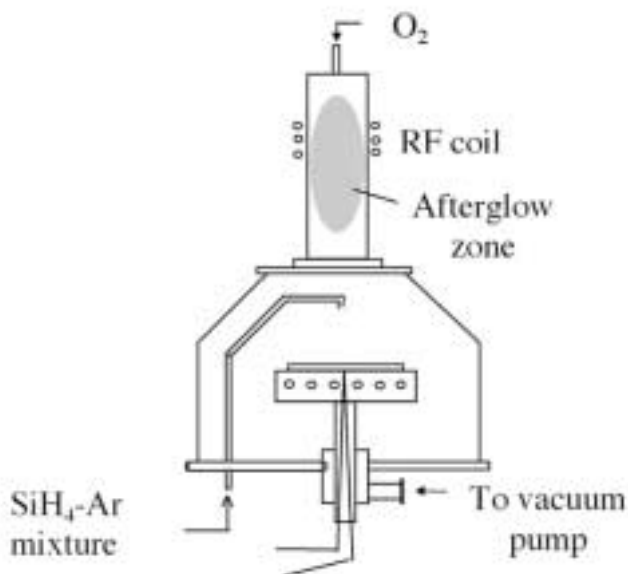
FIG. 3. Schematic diagram of a remote PECVD reactor with inductively coupled RF power.

sor molecules in the two discharges are the same, although for the APG discharge O_2 and the precursor are dissociated by energy transfer from metastable He atoms by a Penning mechanism.

Remote PECVD has been successfully used for deposition of various coatings at atmospheric pressure (AP). Recently we have developed a remote AP-PECVD system for deposition of silicon oxide films based on the use of HMDSO as the silicon-containing precursor. Argon and oxygen were passed through a region where barrier discharge was sustained with the use of high voltage supply operated at a frequency of 50 Hz. HMDSO vapor was carried to the deposition zone by argon and was introduced downstream from the discharge genera-

tion region. With this technique, high quality, silicon oxide films have been deposited at 400-500°C with reasonable values of growth rate (8-10 nm s^{-1}).

Another promising approach to atmospheric pressure PECVD coating of glass substrates in the open atmosphere is flame assisted CVD, or so-called combustion CVD (CCVD). A flame is a type of plasma that is characterized by quite low values of electron energies (less than 0.6 eV), electron densities (10^7-10^8 cm^{-3}) and degrees of ionization ($<10^{-10}$). The flux of heat released by the occurrence of various exothermic reactions is the source of energy for sustaining the plasma. There are two main types of CCVD processes. One type uses a liquid fuel containing the dissolved precursor

required for film formation. The other type uses gaseous fuel and the precursors are introduced into the flame either in gaseous form or as a mist. A number of different oxide materials including silica,[17] but also Al_2O_3[18] and CeO_2,[19] have been deposited using this process. For example, amorphous silica coatings were deposited at a temperature of 750 ± 50°C using a liquid fuel of ethanol containing 0.0025 M TEOS as the silicon containing precursor.[17] The layers were deposited with growth rates of about 0.8 μm h^{-1} and were shown to be suitable for protection of metal alloys against high temperature corrosion. While the deposition temperature is somewhat high for glass substrates, the results of CCVD studies have,[17-19] nevertheless, suggested that, despite the high energy flux directed to the substrate (a few kW cm^{-2}), the technique could be a versatile, inexpensive, atmospheric thin film deposition method for large scale manufacturing applications such as coating glass samples. The flame supplies the heat necessary to promote chemical reactions on the substrate surface which must be exposed in the "flame environment" only for short periods of time (typically a few seconds) in order to prevent overheating of the surface. This then means that for a CCVD process, deposition should be characterized by a high growth rate. Thus one has the concept that the flame must act as the reaction chamber in which the highly reactive species required for film formation are formed from the precursors. Therefore the choice of suitable precursors and the provision of a favorable temperature distribution in the flame are important problems to be solved for the development of such a process.

Precursor Chemistry

Precursors should be stable in an oxidative atmosphere and at elevated temperatures as well as participating in reactions resulting in the formation of active species required for the deposition process. So with CCVD, because there is a sharp temperature profile in a flame, the positioning of the injection nozzle for the introduction of the precursor is of critical importance. This is of particular concern for the case of silicon oxide CCVD based on organosilicon precursors because of the very low thermal stability of these compounds. This instability can be illustrated by the results of thermodynamic calculations for the Si-C-O-H system when HMDSO and O_2 are used as the initial reactants (Fig. 4). As can be seen, silicon oxide is
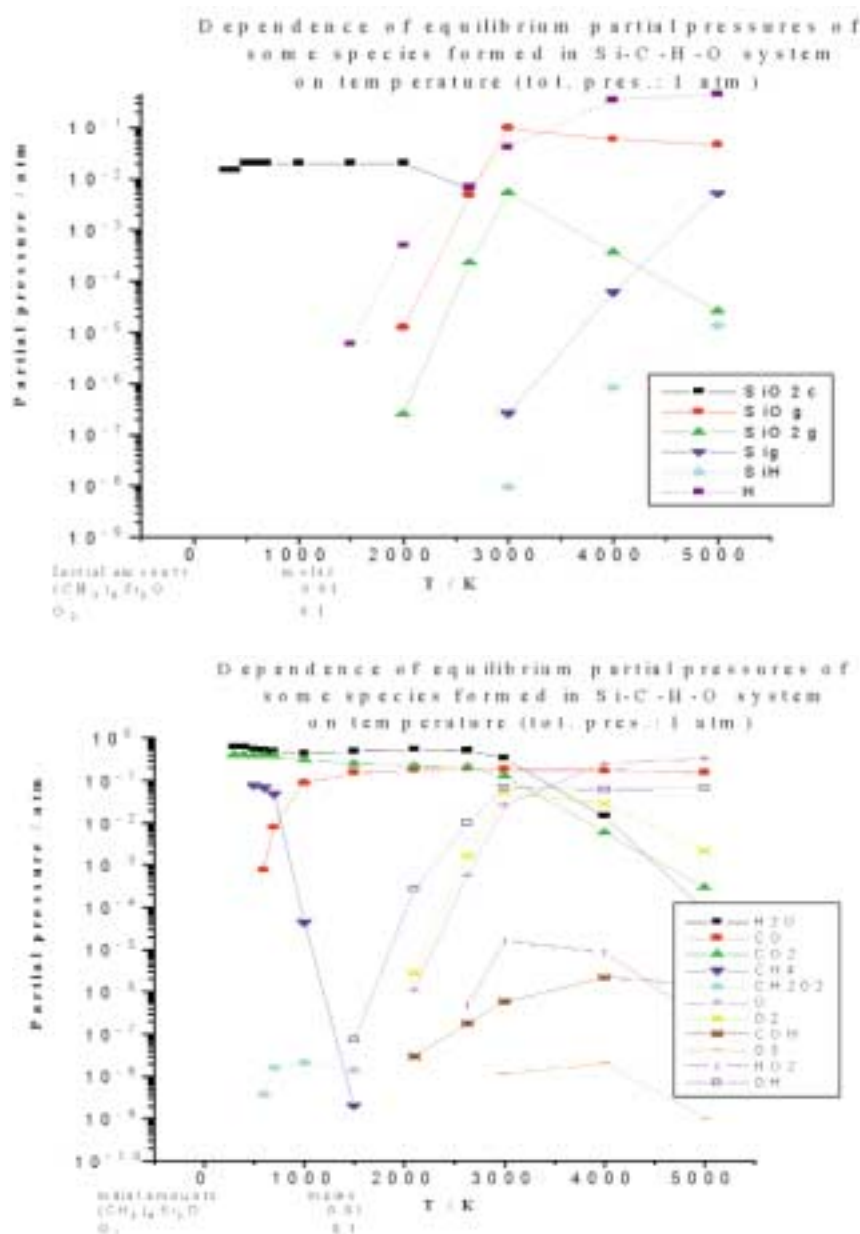

FIG. 4. Equilibrium gas phase composition in the system Si-C-O-H.

the thermodynamically stable phase at temperatures below 2000 K. At higher temperatures silicon monoxide and atomic silicon prevail over other silicon containing species. The concentration of methane—one of the most stable hydrocarbons—sharply decreases with increasing temperature above about 500 K. One can also note the increase in concentrations of the elements in atomic form and of radicals (OH, HO_2) with temperatures above 3000 K. Most significantly, the equilibrium concentrations of silicon-hydrogen and silicon-oxygen-hydrogen species are negligible at temperatures higher than 1000 K.

For CCVD, molecular chemistry is obviously a major factor in choosing the precursor. This can be equally true for other PECVD processes because of the complex reactions that occur either in the plasma or downstream from the discharge region. As a result, one of the main research directions for the CVD of silicon oxide films has been to find the best silicon containing precursors to provide higher growth rates and improvements in film quality. Silicon containing precursors for PECVD of silicon oxide can be divided into two major groups: silicon containing inorganic compounds (*e.g.* silicon halides, chlorosilanes, and silane)[10-12] and silicon containing organic compounds (*e.g.* organosilicon monomers such as hexamethyldisiloxane (HMDSO),[20] tetraethylorthosilicate (TEOS),[21] and tetramethylsilane (TMS).[22]

The main advantage of silane as an inorganic precursor with weak Si-H bonds is that there is the possibility of depositing high quality silicon oxide layers at quite low temperatures and with reasonable growth rates. However, for an atmospheric pressure PECVD system, the design has to take into account the high flammability and explosive nature of silane. Therefore, for CVD of silicon oxide films based on the use of a thermal plasma or with combustion CVD, for non-electronic applications, such as the coating of glass substrates, silicon halides and chlorosilanes are probably the most promising precursors, especially from an economic point of view.

Several groups of the most generally used organosilicon precursors can be identified. Group 1: alkyl silanes such as tetramethylsilane, $Si(CH_3)_4$; group 2: disiloxanes such as hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$ and tetramethyldisiloxane (TMDSO), $(CH_3)_2HSiOSiH(CH_3)_2$); group 3: methoxysilanes such as tetramethoxysilane (TMOS), $Si(OCH_3)_4$, methyltri-

methoxysilane (MTMOS), $H_3Si(OCH_3)_3$, and trimethylmethoxysilane (TMMOS), $(CH_3)_3SiOCH_3$); group 4: ethoxysilanes such as tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$, ethyltriethoxysilane (ETEOS), $C_2H_5Si(OC_2H_5)_3$, dimethyldiethoxysilane (DMDEOS), $(CH_3)_2Si(OC_2H_5)_2$, and trimethylethoxysilane (TMEOS), $(CH_3)_3SiOC_2H_5$).

A comparative study of the use of plasmas for oxygen/organosilicon precursors representative of groups 2-4 above has been made for remote PECVD.[23] The mechanisms of deposition are not known and seem to be extremely complex. In order to compare the various precursors, the dependencies of conversion ratios per substrate area on the so-called Remote Composite Parameter (RCP) [$W\ cm^{-1}$] has been studied. This parameter reflects the combination of the microwave power absorbed in the plasma and the distance of the substrate from the center of the plasma source. It can be interpreted as the critical flow rate of excited oxygen species coming from the discharge generation region for complete reaction with the monomer.[23] A monomer molecule that needs more oxygen atoms for a high conversion ratio should show a higher RCP. It was shown that there was an increase of RCP with decreasing number of alkoxy groups:

$$RCP_{critTMOS} < RCP_{critMTMOS} < RCP_{critTMMOS}$$

$$RCP_{critTEOS} < RCP_{critETEOS} < RCP_{critDMDEOS} < RCP_{critTMEOS}$$

Other authors[24,25] have found as well that precursors with a high number of alkoxy groups require less excited oxygen species for deposition of good quality silicon oxide films. It has also been shown that while $SiO-CH_3$ bonds are easily broken, even without oxygen, the scission of $Si-CH_3$ bonds requires oxygen radicals; this conclusion is consistent with the comparative bonding energies. Because of this, TMS is not widely used for PECVD of SiO_2 films and, in particular, it is not a promising precursor for remote PECVD. Thus, the results of the RCP studies demonstrate that alkoxy groups have improved reactivity compared to alkyl groups and that monomers with ethoxy groups form silicon oxide films more readily than those with methoxy groups. The RCP studies also showed that the transfer of excited oxygen species from the discharge generation region to the substrate surface can be identified as the rate limiting step in the remote PECVD

of silicon oxide films. It is thus clear why TEOS and HMDSO are the most widely used precursors for PECVD of silicon oxide films.

Conclusions

CVD is currently not extensively used for coating optical components. As the market demands grow, though, and costs need to be kept down one can expect to see an increasing use made of CVD in order to take advantage of the non-line-of-sight possibilities it offers for increasing deposition throughput and also for coating complex substrate geometries. In addition, one must never forget the C in CVD and the potential that has for developing novel processes. The further feature of deposition at low temperatures by the introduction of plasma sources and the economic attraction of not having to use vacuum systems by exploiting atmospheric pressure discharges strongly suggests that CVD will make a significant contribution to the burgeoning areas of telecommunications and precision optics. ■

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