General Plasma, Inc.
546 East 25th Street
Tucson, Arizona 85713
tel. 520-882-5100
fax. 520-882-5165

Deposition of Silicon Oxide, Silicon Nitride and Silicon Carbide Thin Films by New Plasma Enhanced Chemical Vapor Deposition Source Technology

M. George, P. Morse, J. Morris, H. Chandra* and J. Madocks

General Plasma, Inc., Tucson, Arizona, USA

* University of Arizona, Department of Materials Sciences and Engineering, Tucson, Arizona, USA

General Plasma's innovative Plasma Beam Source (PBS) offers a new technology for plasma enhanced chemical vapor deposition (PECVD) of dielectric thin films of silicon dioxide, silicon nitride and silicon carbide. The PBS source overcomes previous PECVD problems associated with electrode coating and enables dense, uniform, adherent films at temperatures compatible with many plastics. The source design is linearly extendable for large area in-line or roll-to-roll coating applications such as barrier coatings, encapsulation, thin film solar cells and anti-reflective coatings. We present a summary of the thin optical properties, hardness, uniformity and adhesion of PECVD thin films of silicon dioxide, silicon nitride and silicon carbide.

Introduction

General Plasma is continuing to develop an array of large area thin film coating processes utilizing an innovative linear source for plasma enhanced chemical vapor deposition (PECVD) source[1].   The new source overcomes prior technical hurdles, that limit the use of PECVD as a large area coating process. Advantages to the new technology include exceptional deposition rates, dense, high quality films and the ability to deposit on low temperature substrates.

PECVD is routinely used in semiconductor processing[2] and large area flat panel displays[3]. However, it is less common in large area applications with more demanding economics such as roll-to-roll web and in-line glass coating. One problem limiting use of PECVD for these applications is excessive coating of reactor electrodes. For instance, in a parallel plate RF reactor, the powered electrode is exposed to the PECVD process and receives a large portion of the deposition. In semiconductor and flat panel display applications this is countered by routine plasma etch back cycles. A similar problem exists for recently developed linear microwave PECVD technology. The microwave waveguide dielectric, where the plasma intensity is the highest, receives substantially more coating than the substrate. Frequent removal of the quartz waveguide tubes is

required. In continuous processes like web or in-line coating, frequent etch back cycles or higher frequency maintenance periods are not practical. For these applications it is important that electrodes remain free from thin film build-up over the length of process runs that often exceed 3 weeks of 24/7 operation.

Beyond electrode coating, the ability of the source to operate at pressures compatible with magnetron sputtering is important. A powerful process advantage is gained by the ability to run in-line processes that leverage both PECVD and sputtering technologies. A PECVD source operating at pressure of 10's of millitorr has the additional advantage of easily avoiding higher pressure process conditions where gas phase particle generation is problematic[4].

The demanding optical applications for which many roll-to-roll and in-line applications are targeted requires excellent film uniformity. It is common for the uniformity requirements to be better than ± 5% over large area. Conventional RF and linear microwave PECVD sources struggle to meet this demanding requirement for source widths and lengths longer than several hundred millimeters.
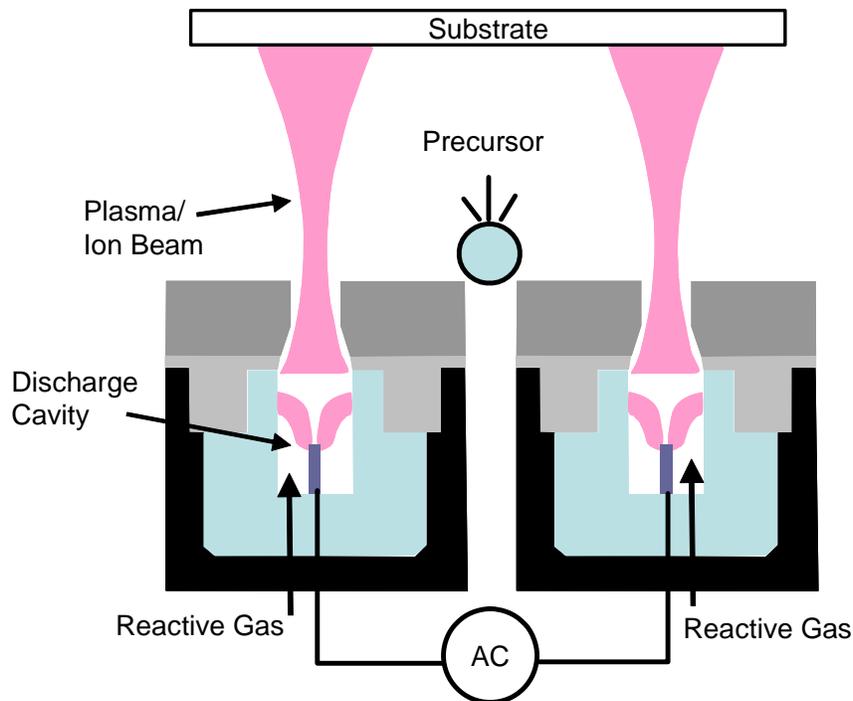

Fig. 1 Arrangement of PECVD source showing the discharge
cavity, ion beam, precursor delivery site and substrate

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Plasma Beam PECVD Technology

The Plasma Beam Source™ (PBS™) for PECVD technology was introduced in 2002[5] and applied to plasma cleaning in 2003[6]. This patent pending plasma source is a linear source that implements an internal magnetron cathode in a discharge cavity. Figure 1 shows a section view of the PECVD source arrangement highlighting discharge cavity, plasma beam, location of reactive and precursor gas delivery and the substrate.

Inside the discharge cavity the magnetron cathode forms a linear, uniform high density electron source where non-condensable reactive gas is introduced. Here, the high density plasma efficiently dissociates the reactive gas into radicals and ions.

The dense plasma exiting the discharge cavity into the chamber volume is used to dissociate the precursor. The thin film precursor is delivered outside the discharge cavity.. This has two advantages; first the precursor is dissociated outside the discharge cavity eliminating contamination of the source electrodes. Second, the reaction zone is in the chamber volume where there is high pumping speed. Precursor fragments generated by the plasma chemistry will have a low residence time in the reaction volume reducing contamination of the growing thin film.   With low residence times and low operating pressure deleterious gas phase nucleation of particles is eliminated. The uniform, collimated nature of the emanating plasma beam is clearly seen in Figure 2.
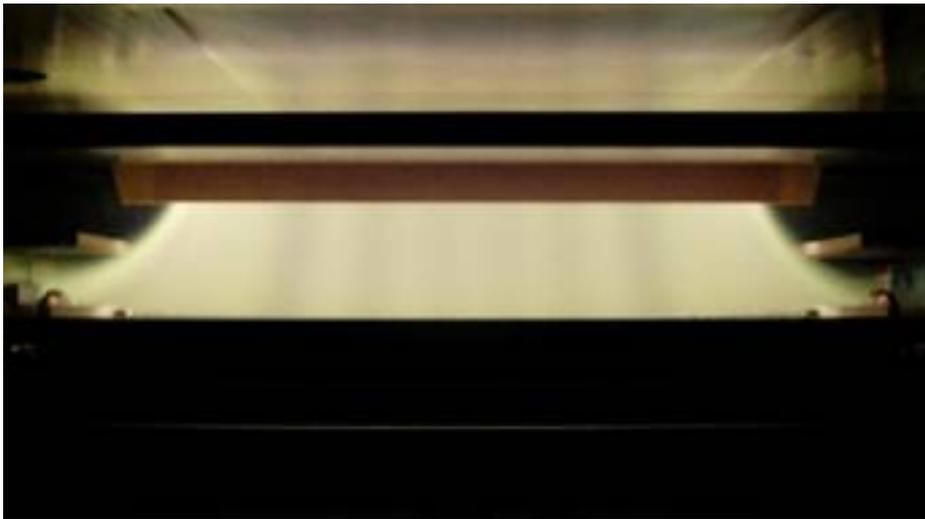

Figure 2. Plasma Beam emanating from a source
operating with Oxygen in the discharge cavity.

When two PBS™ sources are combined across a mid-frequency AC power supply like the configuration shown in Figure 1, large area PECVD processes are particularly enhanced. Figure 3 shows an example of a dual PBS™ in operation.
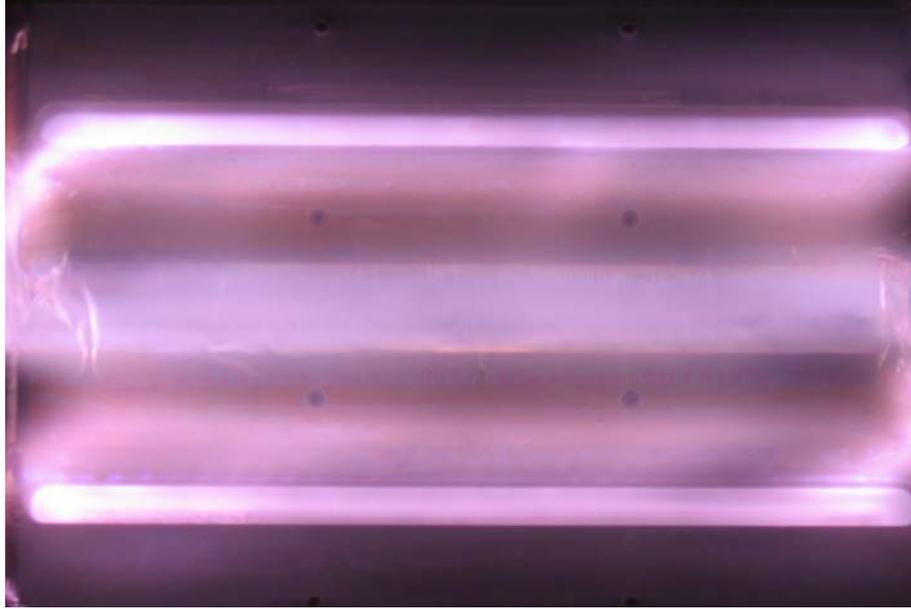

Figure 3. Dual PBS™ in operation observed through a PET film.

In the arrangement shown in Figures 1 & 3 each source alternates as the cathode and anode of the AC circuit. As the cathode, the source is a uniform, linear plasma source. During this half cycle, the opposite source is the anode.

Electrons leaving the cathode source must reach the anode source to return to the power supply. As the electrons attempt to enter the anode source, they encounter the mirror magnetic field emanating out of the source. This impedes electron flow and generates an electric field. When gas atoms leaving this source encounter these impeded electrons some are ionized and these ions experience the accelerating electric field. The ions exhibit relatively low energies, between 20 and 70 eV. Ions with this energy range are ideal for modification of growing surfaces, but below the energy threshold to cause sub-surface damage[7]. The action of these ions results in thin films that are adherent, dense and modestly compressively stressed.

Thin Film Applications

SiO$_2$ Thin Films

For hard coats we have developed a process chemistry based on hexamethyldisiloxoane (HMDSO) and O$_2$. Our hard coating process has been successfully applied to PET, Trogamid, Polycarbonate and PEN[8]. The ratio of O$_2$: HMDSO utilized in our processes is of importance to balance thermal expansion matching and adhesion to these varied substrates. Analysis by FTIR shows that there are important thin film compositional differences as the O$_2$ ratio is increased. Figure 4 highlights these thin film changes as the process gas composition is changed from a low to high ratio of O$_2$:HMDSO.

Of particular note is the decrease in the methyl (CH$_3$) groups and the increase in Si-Si bonding and Si-O bonding as the proportion of O$_2$ in the process increases. The hardness of these films improves as the O$_2$ ratio increases and the methyl groups decrease. The low O$_2$:HMDSO films have pencil hardness of 2H while that of the highest O$_2$ ratio has a typical hardness of 8H. Utilizing this feature of the O2:HMDSO chemistry we have successfully applied SiO$_2$ coatings up to 20 microns thick on plastic substrates.
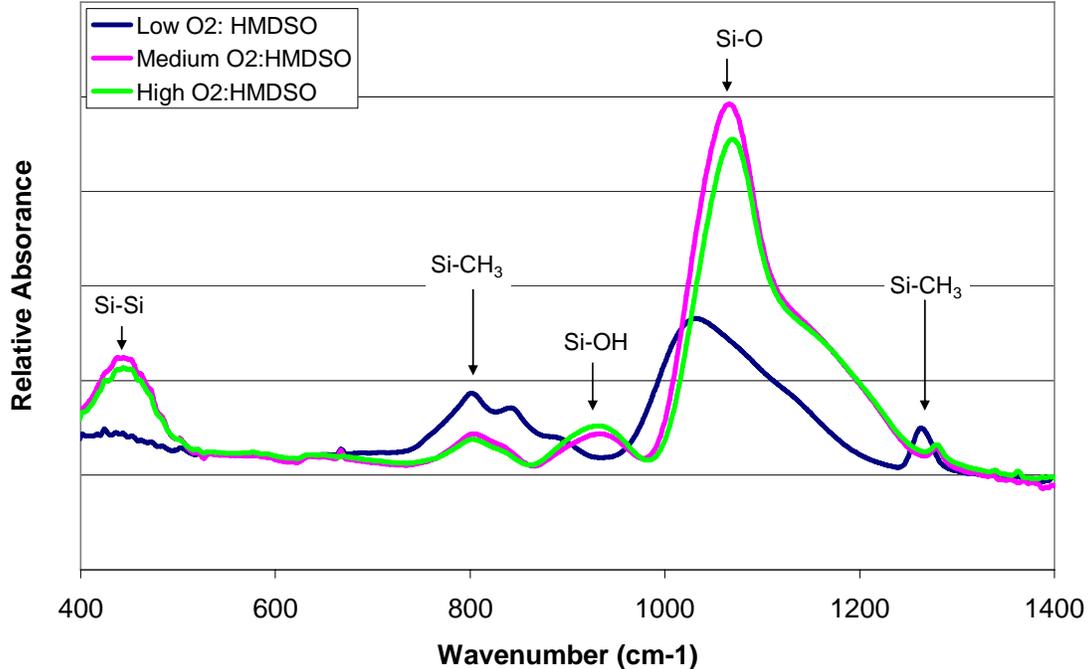

Figure 4. FTIR spectrum of several SiO$_2$ coatings deposited from different ratios of O$_2$ and HMDSO.

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Silicon Carbide

The utility of silicon oxide coatings is limited by its applicability for good barrier properties. There appears to be a fundamental limit to how effective SiO_2 thin films can be to water vapor transport[9]. Silicon carbide, in this case, has superior performance as a barrier to water vapor as compared to SiO_2. For example, PECVD of silicon carbide by RF parallel plate reactors has resulted in films with exceptional barrier properties to KOH, which is used as a test for encapsulation of MEMS sensors against attack by hydroxyls[10]. This property would have applicability for protected aluminum reflective surfaces if the film could be made optically clear, hard and flexible. Thin films of silicon carbide have an absorption band edge at approximately 500 nm making them somewhat yellow in appearance. However, only several hundred angstrom thickness of silicon carbide is required for this coating application, which mitigates the effect of the optical absorption.

Analysis of the films deposited by FTIR and XPS reveals that there is between 20 and 30% of oxygen incorporated in the deposited thin film. A representative FTIR spectrum is shown in Figure 5. The spectrum clearly shows the formation of high quality Si-C bonds along with Si-O bonds.   A small amount of methyl groups from undisassociated precursor is retained in the films. The presence of the Si-O bonds helps to explain the lower index of refraction of our films compared to the published values of 1.85 to 2[10]. These films also have a lower optical absorption which would enhance its use for optical applications. While oxygen was not included in the process gas chemistry, oxygen arises most likely from either background water that is emanating from the plastic substrates and outgassing from chamber walls.   Even given this relatively uncontrolled oxygen availability, the deposited films on an aluminum substrate still provide an excellent resistance to aqueous 10% KOH.
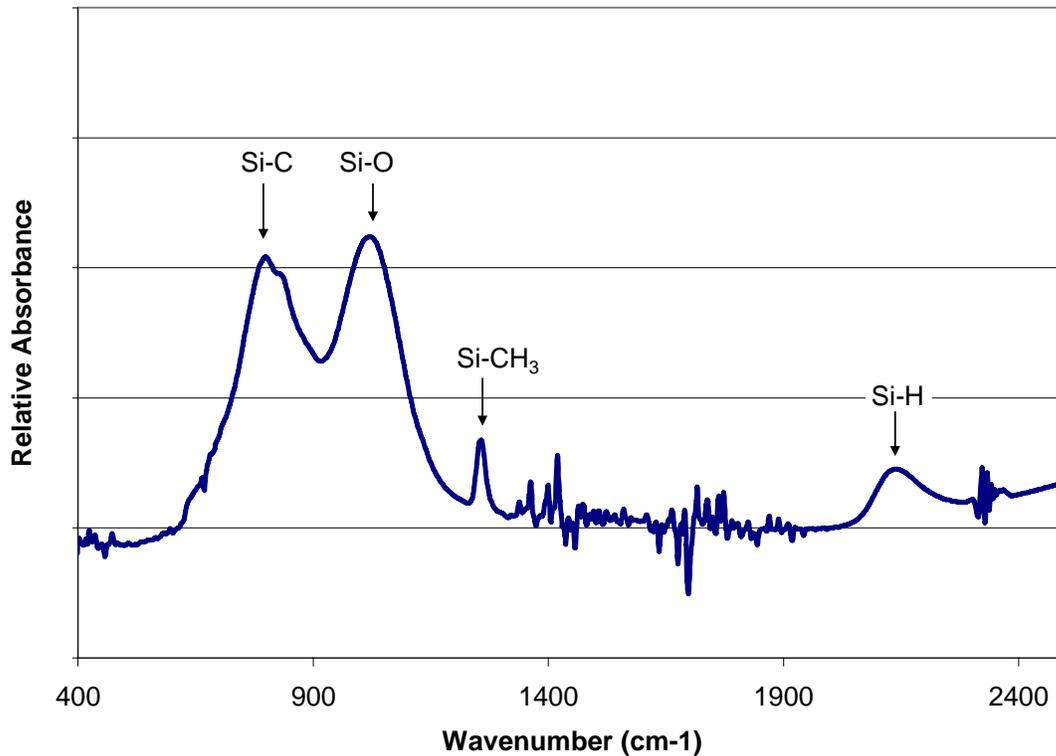
Figure 5. FTIR spectrum of SiC thin films deposited from the plasma beam source.

Silicon Nitride

PECVD silicon nitride films were recognized several decades ago by the semiconductor industry as an effective diffusion barrier and etch stop[11]. These properties of silicon nitride were not lost on the large area coating industry and several examples of sputter deposited SiN encapsulants and barriers exist. Unfortunately sputter deposited silicon nitride has a low dynamic deposition rate, therefore its use is limited to only a few higher value added applications. One of the important challenges is to bring the excellent material properties of PECVD silicon nitride to a more economical state for large area applications. General Plasma has developed two different PECVD chemistries one for the photovoltaic industry based on a highly hydrogenated silicon nitride material without carbon contamination. This chemistry relies on the well known combination of SiH_4 and NH_3 which prevails in the semiconductor and flat panel display industries. A second chemistry is under development for barrier applications utilizing an organic amide silane precursor. Compositional differences resulting from these different chemistries deposited at 80 ^oC are shown in the FTIR spectra of Figure 6.

The hydrogenated Si-N film exhibits a large concentration of N-H bonds relative to Si-H bonds, making it potentially attractive for passivation of p-type silicon semiconductor surfaces. The organic amide silane thin film is characterized by approximately 50% C-N bonds and 25% Si-N and 25% Si-NH bonds. The appearance of the CH_3 is an indication that the precursor was not fully dissociated by process conditions selected for this film.
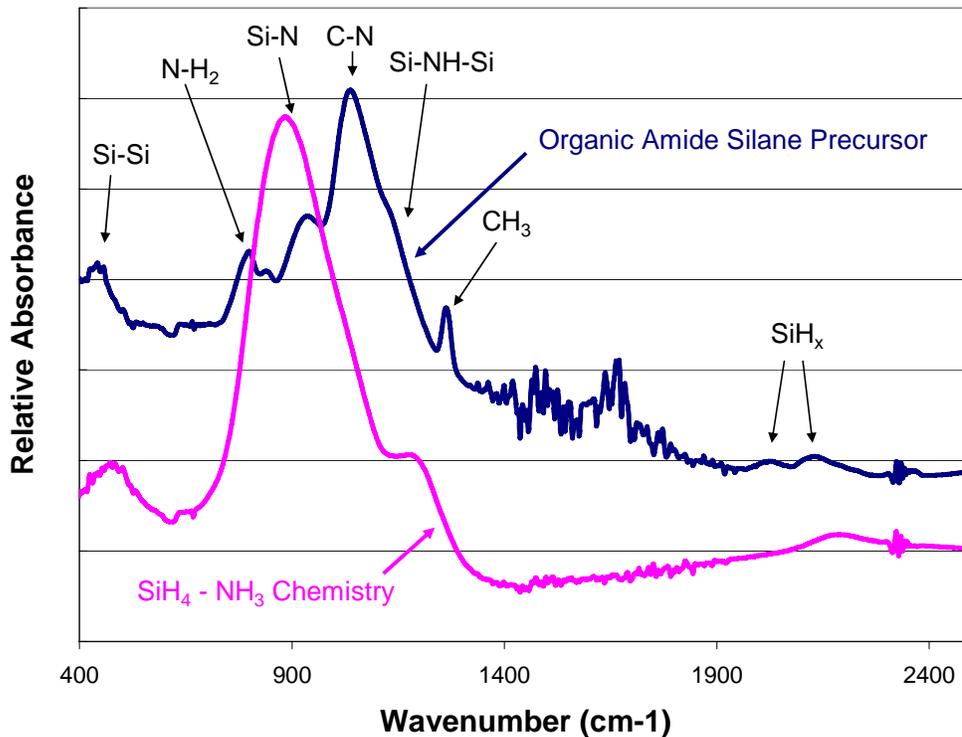
Figure 6. FTIR spectra from SiN thin films deposited from SiH_4-NH_3 and an organic amide silane precursor. (Blue line) thin films deposited from organic amide silane. (Purple line) thin films deposited from $SiH_4 – NH_3$ chemistry.

Uniformity

The development of these thin film coatings has progressed from the laboratory bench scale to a pilot line. Here, the processes have been transferred to a larger 400 mm wide system. This larger width demonstrates the scalability of this PECVD technology to substrate widths that are applicable to large area coatings.

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Figure 7 shows the measured relative uniformity over a 300 width for the films discussed above.

SiO2 ± 1.1%
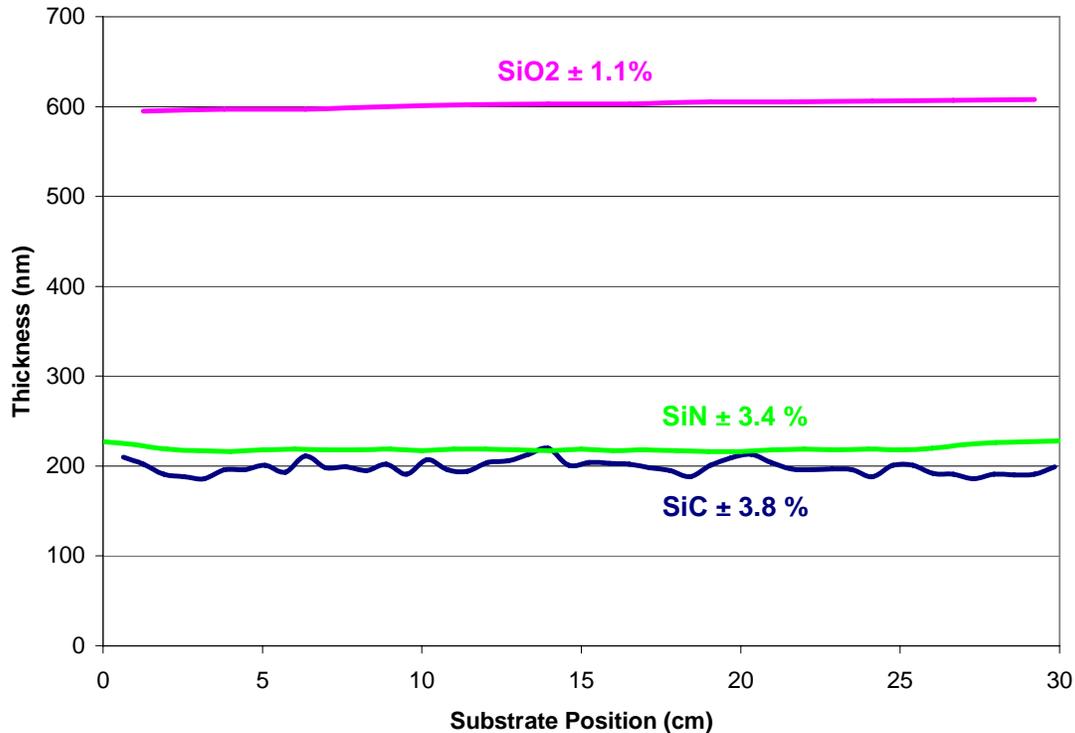
SiN ± 3.4 %

SiC ± 3.8 %

Figure 7. Uniformity over 30 cm for SiO_2, SiN and SiC thin films, which are discussed in this paper.

Comparison of Film Properties

One of the criteria for coatings developed with these processes, as described previously, is optical clarity. Figure 8 provides a comparison of the optical dispersion data for the silicon carbide and silicon nitride thin films. The hydrogenated silicon nitride thin film deposited from SiH_4 and NH_3 chemistry has an index consistent to that of PECVD films deposited from RF sources.   The silicon nitride thin film deposited from the organic amide silane precursor has a lower index and lower absorption. This film is slightly yellow in color, but with an extinction coefficient well below $5x10^{-3}$ over the visual spectrum, the discoloration is barely noticeable for films less than 1 micron thickn which is important for applications requiring optical clarity. The intermediate index of the siicon carbide coating is potentially applicable for protective hard coats on optical reflector surfaces due to its excellent resistance to corrosive ambients.
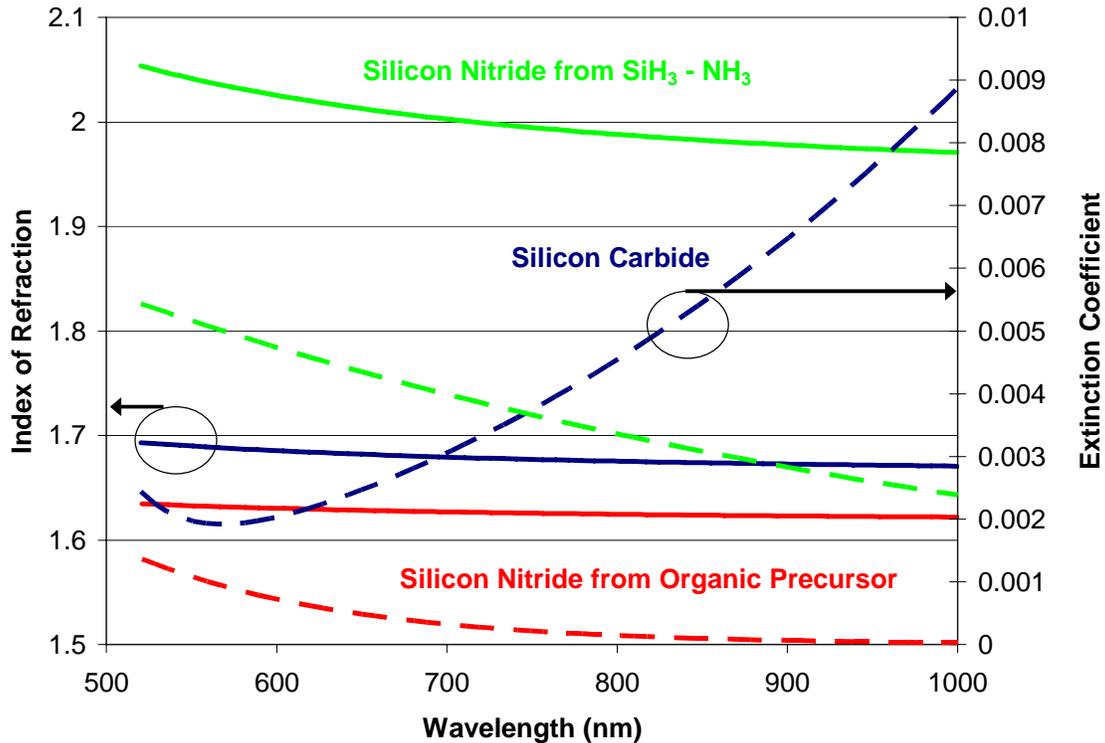
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Figure 8. Dispersion (n & k) data for SiC, hydrogenated: SiN and SiN form an organic amide silane precursor. Solid lines are n data and dashed lines k.

In Table I some of the other relevant thin film properties of the processes developed are presented. We have utilized both an HCl and a KOH etch test to determine the encapsulation and protection potential of the deposited thin films. In these tests, an aluminum reflective substrate is coated with a thin film and we observe the time lapse for the formation of hydrogen bubbles to an aqueous drop of solution applied to the substrate. The film has considered to fail upon the first formation of hydrogen bubbles observable by the unaided eye. In all cases the films typically fail at pinholes and other defects in the films unless they are readily etched, as is the case for SiO_2 by KOH. Our SiO_2 thin films have been measured to etch in aqueaous 10% KOH at a rate of 132 nm/hour, this compares reasonably well with the etch rate for thermal CVD SiO_2 films between 25 and 75 nm/hour[12]. Optimization of these processes and others are on-going in our development laboratory.

Table I. Summary of Process

Thin Film	Dynamic Deposition Rate (μm-m/min)	Pencil Hardness	KOH / HCl Resistance
SiO2	0.3 - 1	3H – 8H	10% KOH < 30 min 3% HCl nil
SiC	0.1	5H – 9H	10% KOH > 24 hours 3% HCl nil
SiN Hydrogenated	0.03	4H	10% KOH nil 3% HCl nil
SiN Organic amide silane	0.2	6H – 8H	10% KOH nil 3% HCl nil

Conclusion

The PBS™ PECVD source offers a unique technology to compete with and complement magnetron sputtering in large area vacuum coating applications. The technology's deposition rate has been demonstrated at 2 to 10 times higher than competing large area sputtering or other in-line PECVD methods without sacrificing film quality. The films coated with this technology are capable of being deposited at low temperatures making them excellent alternatives for temperature sensitive applications like plastics and polymer film. A brief list of possible applications for this new PECVD technology includes: abrasion resistant coatings, barrier and encapsulation films, optical interference coatings, transparent conductive films and photovoltaics.

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