Durable Coatings for IR Windows

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ABSTRACT

Durable coatings of silicon-carbon-oxy-nitride (a.k.a. SiCON) are being developed to protect high-speed missile windows from the environmental loads during flight. Originally developed at Rockwell Scientific Corporation (RSC) these coatings exhibited substantial promise, but were difficult to deposit. Under a DoD DARPA SBIR Phase I program, Surmet Corporation, working closely with RSC, is depositing these coatings using an innovative vacuum vapor deposition process. High rate of coating deposition and the ease of manipulating the process variables, make Surmet's process suitable for the deposition of substantially thick films (up to 30 μm) with precisely controlled chemistry. Initial work has shown encouraging results, and the refinement of the coating and coating process is still underway. Coupons of SiN and SiCON coatings with varying thickness on a variety of substrates such as Si-wafer, ZnS and ALON were fabricated and used for the study. This paper will present and discuss the results of SiN and SiCON coatings deposition and characterization (physical, mechanical and optical properties) as a basis for evaluating their suitability for high speed missile windows application.

Keywords: Silicon-carbon-oxy-nitride (SiCON) Coatings, High speed missile windows, Plasma-enhanced CVD,

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1. INTRODUCTION

Infrared (IR) windows used in high-speed missiles are subject to harsh environments during captive carry and flight. Window materials for these applications should be transparent in the desired IR range, and also be hard, durable and highly resistant to erosion from environmental stresses. In general, the materials with the highest durability, with the exception of diamond **[1]** are those used for short- and mid-wavelength infrared (SWIR, MWIR) applications. Sapphire and aluminum oxynitride (ALON™) have been the more traditionally studied materials **[2]** for these applications. However, these materials do not transmit out to long enough wavelengths for some applications. Furthermore, the materials which are transparent to sufficiently long wavelengths are not particularly durable.

Recently, oxynitride group of materials have demonstrated the potential to be candidate coating materials for high speed windows and domes. Oxynitrides are generally strong, and hard, with good thermal conductivity and IR optical properties. SiCON coatings are extremely durable and are optically transparent from the visible past the mid-wavelength infrared (MWIR) region. The coatings offer:

- Broad band transparency,
- Hardness comparable to DLC coatings, and
- Ability to be deposited in substantial thickness.

Based on their properties, the coatings have the potential to be used for diversified applications such as:

- Durable anti-reflection (AR) coatings (~1 μm thickness),
- Rain erosion protective coatings (~10 μm) thickness), and
- Protective over-coating for conductive coatings/grids

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Under an earlier Air Force funded research program, thin SiCON films deposited by Dr. Alan Harker of Rockwell Scientific Company (RSC) using ion beam sputtering (IBS) process were found to exhibit interesting properties. Selected compositions of SiCON films (with composition approximating C/Si atom ratio = 0.2 and C/N = 0.3) **[3]** were found to be extremely durable, with no apparent midwave infrared (IR) absorptions and an index of refraction ranging between 2 and 2.1. The hardness of such films was measured to be approximately 40 GPa, which is very close to the hardness of diamond-like-carbon (DLC) films. While these coatings demonstrated high hardness, toughness and optical transparency, IBS has certain drawbacks such as low deposition rate and high stress (which limits the feasibility of using the process for thicker films) and the requirement of the fabrication of sputtering targets of the desired material. Thus, there was a need for an alternative deposition process.

1.1. Surmet's Coating Process

Surmet's innovative plasma-enhanced chemical vapor deposition (PE-CVD) has the following advantages over the other conventional coating deposition processes:

- Low deposition temperatures (<150°C)
- Engineered interfaces for strong adhesion
- Very high deposition rates (> 10X), compared to IBS, suitable for depositing thick films
- Unlike IBS, Surmet's PE-CVD process not require costly sputtering target of for each desired composition
- Clean environmentally friendly process, no hazardous chemicals or complicated handling
- Highly reproducible process with easy-to-manipulate process parameters for desired composition and film properties.
- Economically scaleable process.

The PE-CVD coating process is being extensively used for depositing a variety of coatings at Surmet. The ease of manipulating the process parameters and precursor gas ratio makes it very promising for depositing SiCON coatings of desired composition and thickness depending on the application requirements.

2. EXPERIMENTAL RESULTS AND OBSERVATIONS

Working on a DARPA SBIR Phase I, Surmet Corporation demonstrated the applicability of its silicon nitride (Si_xN_y), silicon carbide (SiC) and silicon-carbon-oxy-nitride (a.k.a. SiCON) coatings for IR window application. Using Surmet's proprietary plasma-enhanced chemical vapor deposition (PE-CVD) technique it is possible to deposit these coatings at rapid rate with improved optical transmission, hardness and strength. This program was carried out with the following objectives:

- Growth of SiN, SiC and SiCON films by Surmet's innovative PE-CVD process on various substrates such as silicon, ALON^{TM} optical ceramic.
- Characterize and evaluate the optical, mechanical, and electrical properties of these coatings with varying composition for application as IR transparent anti-reflection (AR) coating.
- Determine the suitable coating composition with potential of being scaled to full size bulk materials for optical windows and domes applications.
- Explore the feasibility of depositing thick films and fabricating free-standing SiCON material at the coupon level.

2.1. Coating deposition at Surmet

Several coupons of SiN, SiC, SiON and SiCON coatings were prepared. These coatings were deposited on 1"x 1" coupons of Si-wafer, ALON and on 1"x3" glass substrates using Surmet's proprietary PE-CVD process. Coating thicknesses varied from 1 to 10 μm. Thicker coatings (8-10 μm) of SiON and SiCON were also deposited on Si-wafer for hardness measurements.

2.2. Testing and characterization of coatings

2.2.1. Coating adhesion

The following qualitative tests were performed on selected coating samples in order to determine the adhesion and integrity of the coating. Si and ALON substrates were used for these tests.

- Tape Testing: Tape testing was performed using 3M 250-scotch tape. The tape was pressed tightly on the film and then was pulled back suddenly. No discoloration or delamination of the film was observed on the tape.
- Exposure to Ultrasonic Agitation: The SiCON coated coupons were then immersed in an ultrasonic bath consisting of isopropyl alcohol for 10 minutes. No loosening of the film was observed. Evidently, the adhesion of the coating is excellent.

2.2.2. Electrical resistivity

The conducting tape method was used to measure the sheet resistivity of these coatings on the glass substrates. These coatings were found to be highly resistive with the values of electrical resistivity ranging between 10^{12} and 10^{13} Ohms/square.

2.2.3. Hardness

Selected test coupons of thicker SiN, SiON and SiCON coatings were tested for their hardness using Tukon^{R} Microhardness Tester. A Knoop indenter was used at 50 gm load to make the indent on the surface of coupons. Indents were measured using attached microscope with scale, followed by hardness calculations based on the standard hardness calculator chart. Five sets of data were collected for each specimen for the sake of consistency and accuracy. Table 1 summarizes various coatings and their selected properties.

Table 1: Test matrix for coating deposition and their properties

#	Sample ID	Thickness	Hardness		Refractive
		(micron)	KPHN;	Gpa	Index
1	SiON-78	10	1960;	19.2	1.84
2	SiCON-79	1.3			
3	SiCON-80	1.4			
4	SiCON-81	1.8			
5	SiCON-82	3	1600;	15.7	
6	SiCON-84	8	1600;	15.7	1.84
7	SiCON-89	1			
8	SiCON-90	1			
9	SiCON-91	1.2			
10	SiCON-92	7	1880;	18.5	1.9
11	SiN (NH3)	2	1900;	18.62	2.08
12	SiN (N2)	2			
13	SiN-101	2.1	1900;	18.62	
14	Si-100	1.8			
15	SiC-102	2.5			
16	SiCON-62	3.7	1500	14.7	2.13
17	SiN-63	2.6	1550;	15.0	1.8
18	SiCON-64	1.4			
19	SiCON-70	3.5	1550;	15.0	
20	SiC-118	3			
21	SiC-128	3.5			

2.2.4. Coating composition

In order to determine the elemental composition of the coating, seven samples from Table 1 were selected for EDAX analysis. Samples were coated with a thin conducting film of metallic Al to avoid charging during EDAX analysis. However, Al peaks of the EDAX spectra were excluded from the calculation of elemental composition. A semi-quantitative elemental analysis of various coating samples were performed based on the quantification of three EDAX

spectra collected from three different locations in the case of each sample. The average compositions in terms of elemental atomic % are presented in Table 2 for various coatings.

Table 2: Elemental composition of various SiON and SiCON Coatings by EDAX

Sample ID	Thickness (μm)	C/Si	C/N	Elemental Composition by EDAX, At.%			
				Si	C	N	O
SiON-78	10	---	---	56.97	0.00	12.78	30.23
SiCON-79	1.3	0.09	0.90	69.47	6.09	6.73	17.70
SiCON-80	1.4	0.09	0.7	65.73	5.76	7.93	20.57
SiCON-81	1.8	0.12	1.06	66.32	8.14	7.63	17.90
SiCON-82	3.0	0.07	0.72	70.75	4.94	6.78	17.51
SiCON-84	8.0	0.10	1.10	69.22	7.38	6.68	16.72
SiCON-90	1.0	0.07	0.62	82.82	6.05	9.65	1.47

2.3. Optical property: comparison between Surmet and RSC coatings

The optical transmission of selected test coupons of SiN, SiC and SiCON coatings were measured using FTIR. The measurements were performed with reference to uncoated Si-wafer for comparison. As a baseline, transmission spectra for some of the SiCON coatings from initial runs were compared with that of one of the SiCON coating sample from Rockwell Scientific Company. This is shown in Figure 1.

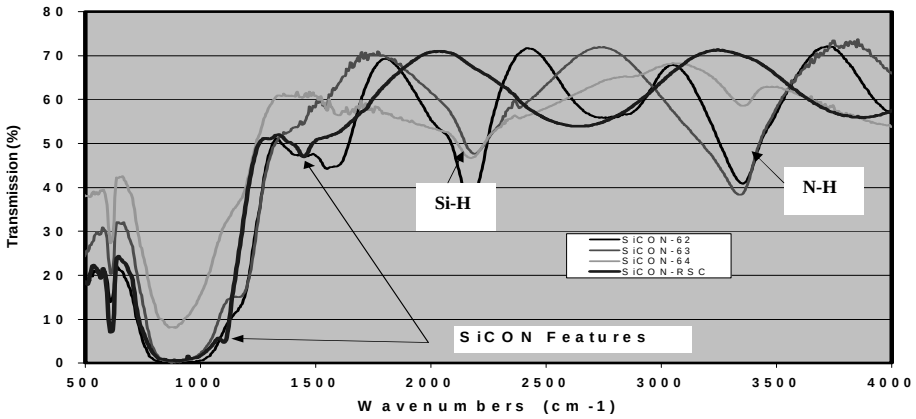

Figure 1: Optical transmission of initial Surmet's initial SiCON coatings in comparison to RSC SiCON coatings. Some additional absorption bands were observed in the case of Surmet's SiCON coatings.

Optical transmission of Surmet's SiCON coatings is comparable to that from RSC. However, a few additional absorption peaks were observed in the case of these coating in contrast to RSC SiCON. There are at least two significant absorption bands at about 3.0 and 4.6 μm corresponding to 3400 cm^{-1} and 2200 cm^{-1} wave numbers, respectively. The one at 3.0 μm is possibly due to stretching vibration of N-H bond and the other at 4.6 μm may be attributed to the stretching vibration of Si-H bands. This is an indication of significant amounts of hydrogen being incorporated in these films as an indirect result of the precursor used in the PE-CVD process.

Figure 2 shows a comparison of two films: SiN-12 and SiCON-92. Both films have the expected phonon band edge in the long-wavelength infrared (LWIR), however both also show strong features at 2200 and 3400 cm^{-1} that appear to be

impurity absorptions in the films. The observation that the features are stronger in the thicker SiCON-92 film leads to the conclusion that the absorbing species is being continuously incorporated into the coatings.

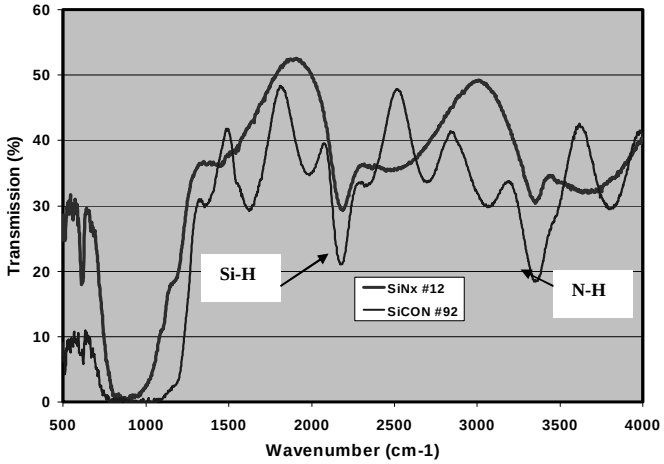

Figure 2: Transmission FTIR spectra from the 2 micron thick SiN-12 and 7 micron thick SiCON-92 films.

2.3.1. Refractive index of Surmet's coatings

Reflection measurements on the films were made to attempt to derive an index of refraction measure using the spacing of the Fresnel fringes in the spectra and the film thickness values. The approximate relationship,

$$\mathbf{n = 1/(2T\Delta cm^{-1})}$$

where T = film thickness, n=index of refraction, Δcm^{-1} = fringe spacing) was used to calculate the index values for the films. The values are listed in Table 3 for the four samples. The values are relatively close together.

Table 3: Index values at 5 microns wavelength for the four samples.

Sample ID	Coating	Thickness (microns)	Calculated Index
SiN-12	SiNx	~2	2.08
SiON-78	SiON	~10	1.84
SiCON-84	SiCON	~8	1.84
SiCON-92	SiCON	~7	1.9

As can be seen in the following Figures (3 and 4), the simple model predictions are a reasonable match to the observed

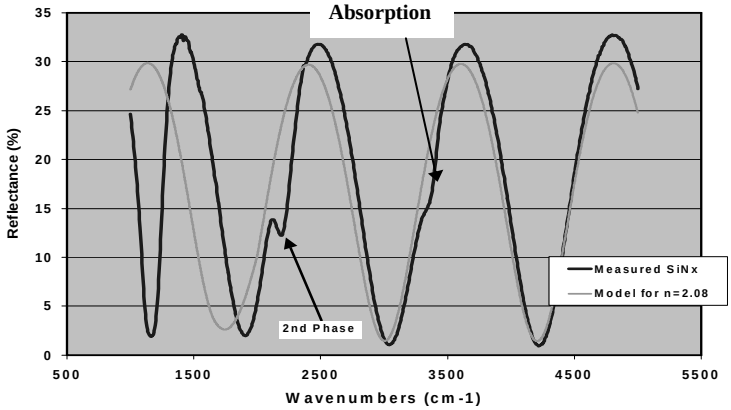

Figure 3: Modeled and measured reflection spectra for the SiN-12 sample. The 2nd phase and phonon edge effects are visible.

fringes in the mid-wavelength (MWIR), but do not match the 2nd phase features or the dispersion effects of the band edge at longer wavelengths.

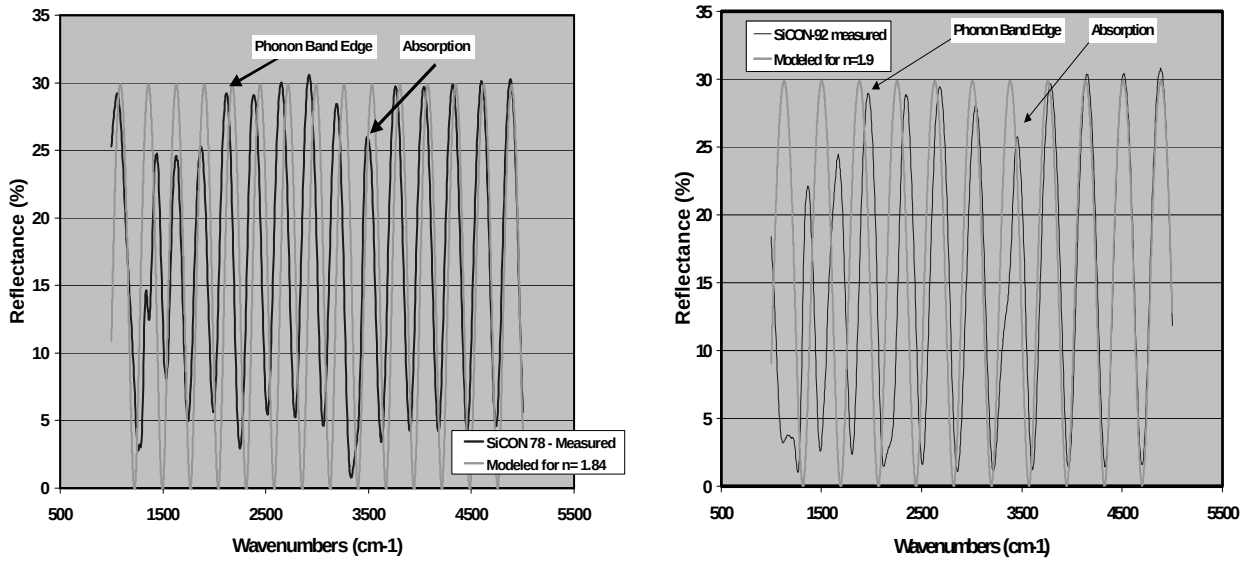

Figure 4: Measured and modeled reflection data for SiCON-78 and SiCON-92

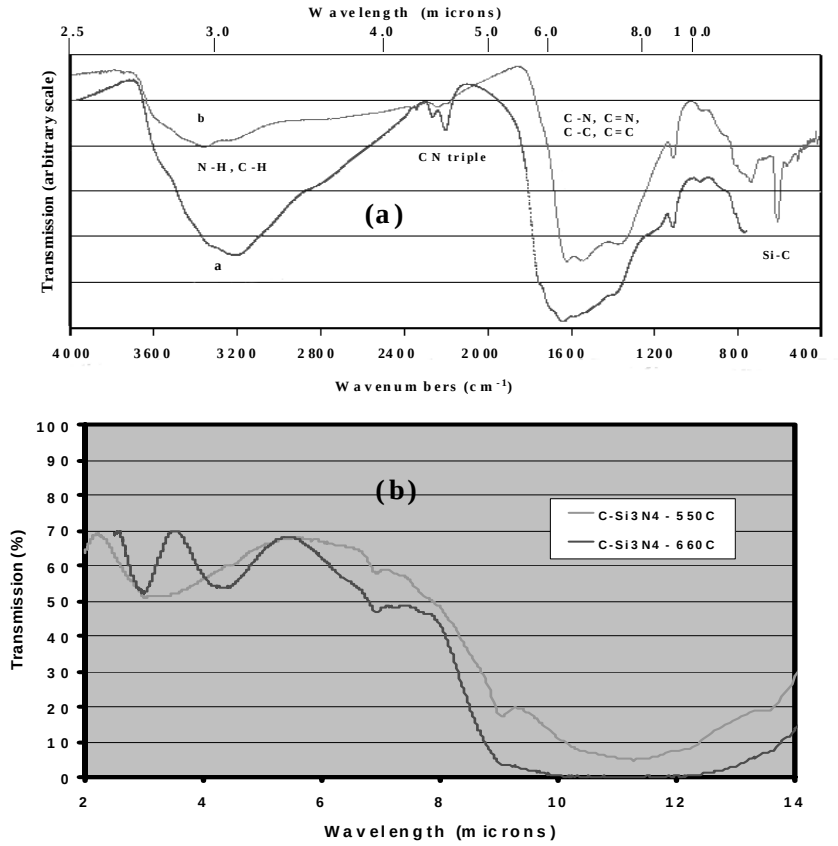

Figure 5: Transmission spectra of (a) PACVD deposited CNx films and (b) reactive ion beam deposited carbon doped silicon nitride.

Early Rockwell Scientific SiCON and CNx films showed a number of impurity and second phase absorptions as shown in Figure 5. However, none of the previously observed bands specifically match with those in the coating samples produced by Surmet's PE-CVD process. Transmission scans for high quality magnetron sputtered SiCON films are shown in Figure 6. The RSC SiCON films matched a modeled index of refraction of 2.1 in the MWIR region.

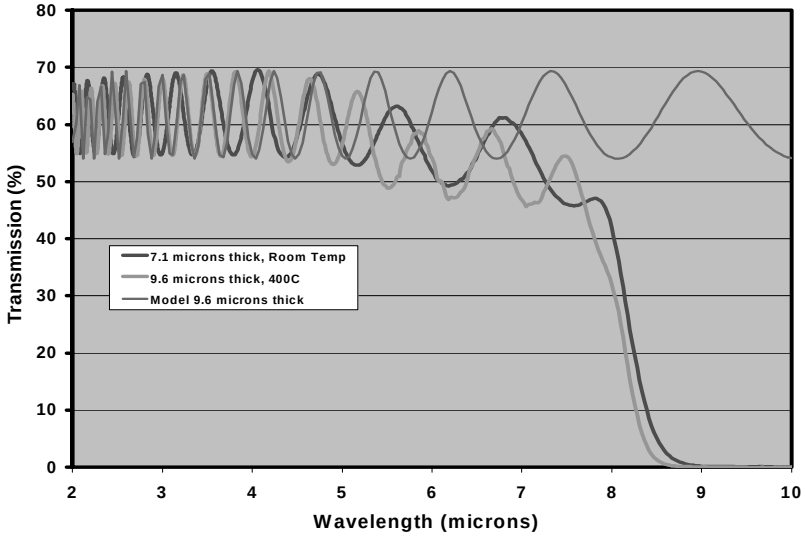

Figure 6: Midwave IR spectra of a 7.1 and a 9.6 micron thick SiCON^{TM} films show no obvious effect of impurities on transmission. The model assumes n=2.1.

The comparison of various coatings deposited by PE-CVD at Surmet to the coatings obtained from RSC, provided important information about properties of these coatings in relation to deposition parameters and precursor gas compositions. In an earlier study **[3]** the SiCON films with composition around the C/Si atom ratio = 0.2 and C/N = 0.3) were found to be extremely durable, with no apparent midwave infrared (IR) absorptions and an index of refraction which varied between 2 and 2.1. Subsequent coating runs were performed with the goal of optimizing the composition of precursor gas ratio and other deposition parameters to be able to deposit SiCON coatings with compositions approximating to $C_2Si_9N_7O_x$ (x ≈2-3).

2.4. Optical properties of Surmet's coatings: effect of precursor gas and coating composition

2.4.1. Comparison between Si, SiN and SiC coatings

Figure 7 compares the optical transmission of Si, SiN and SiC coatings deposited on both side polished Si-wafer. The coating thickness varied in the range of 1.8 to 2.5 microns as shown in Table 4.

Table 4: Thickness of Si, SiN and SiC coatings

Coating	Thickness (micron)
Si-100	1.8
SiN-101	2.1
SiC-102	2.5

Observations:

- As, expected, the simple silicon coating has little effect on the transmission of the silicon substrate. Since these spectra are normalized to that of the uncoated substrate, the spectra of the uncoated substrate would be a straight line at 100%
    - There is a slight difference in index of refraction which causes discernible interference fringes. Since the spectra lies entirely below that of the silicon substrate, the index of refraction of the coating is slightly higher than that of the substrate.

- There is also a small long wave absorption band which is introduced. Presumably this is associated with an impurity.

- The addition of carbon to make SiC, has the following effects:
  - Decreases the index of refraction, creating obvious interference fringes. Since these fringes lay entirely above 100%, the index of the coating is less than that of the substrate.
  - Introduces a long wave absorption

- The addition of nitrogen to make SiN, has the following effects:
  - Creates interference fringes of even greater amplitude than the SiC coating. This shows that the index of refraction is even lower than that of the SiC coating.
  - Introduces a long wave absorption which cuts in at shorter wavelengths than SiC.

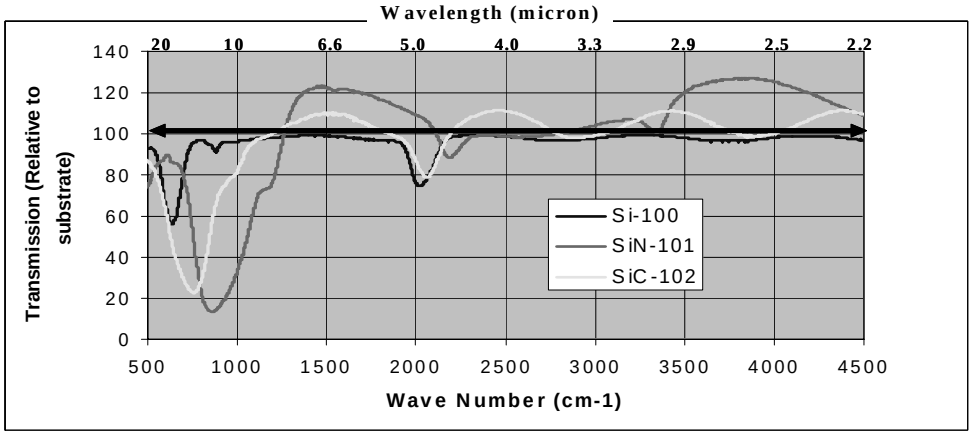

Figure 7: Comparison of optical transmission between Si, SiN and SiC coated Si-coatings.

2.4.2. SiC coatings with varying level of carbon

A comparison of two different SiC coatings deposited using varying amount of carbon as listed in Table 5 is shown in Figure 8. It is evident that increasing carbon level in the coating decreases refractive index and in turn increases long-wavelength infra red (LWIR) absorption.

Table 5: Precursor gas ratio and thickness of two SiC coatings

Coating	Thickness (micron)
SiC-118 (Si:C2H2=2.5:1.25)	3.0
SiC-128 (Si:C2H2=2.5:0.7)	3.5

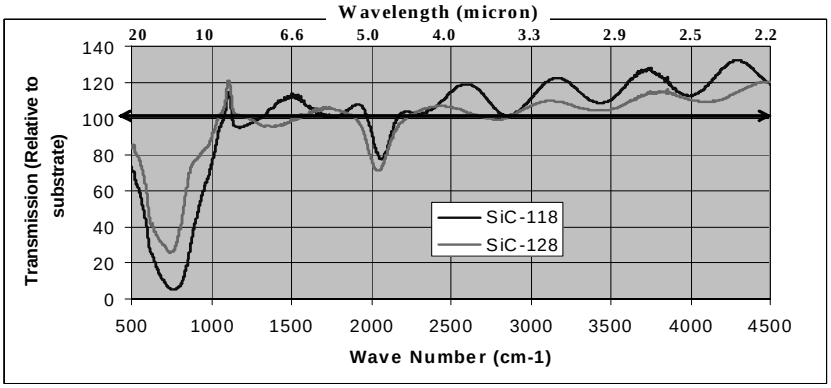

Figure 8: Optical transmission of two SiC coatings with varying levels of carbon. SiC with lower carbon level exhibited less absorption in LWIR range.

Observations:

- The index of refraction of the SiC coating decreases with increasing carbon content.
- The strength of the long wave absorption increase with increasing carbon content

2.4.3. SiCON coatings with different nitrogen precursor

Source of nitrogen may be an important factor affecting the optical properties of resulting SiCON coatings. To determine this, a comparison was made between three different SiCON coatings deposited using three different gases as nitrogen source (Table 6). This is shown in Figure 9.

Table 6: SiCON coatings with different precursor gas as nitrogen source

Coating ID	Thickness (micron)
SiCON-89	1.0
SiCON-90	1.0
SiCON-80	1.4

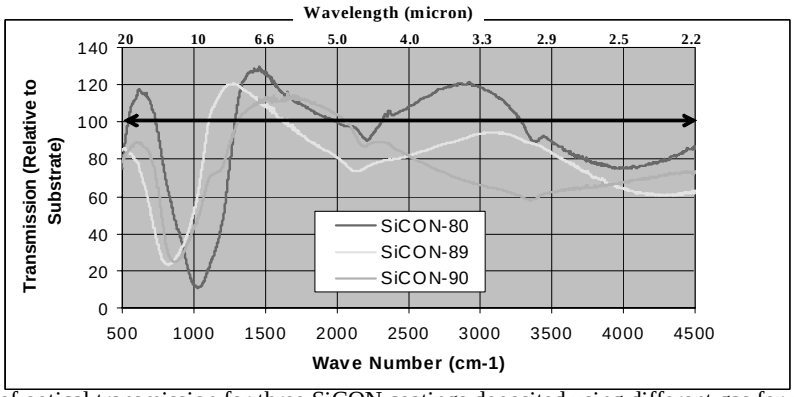

Figure 9: Comparison of optical transmission for three SiCON coatings deposited using different gas for nitrogen source.

Observations:

- Coatings were deposited on silicon substrates which were polished on only one side. This results in transmission which decreases with decreasing wavelength and varies from substrate to substrate depending on the roughness of the unpolished side. For this reason it is difficult to make observations based on absolute transmission.
- The longwave absorption edge is shortest for SiCON-80, then SiCON-90 then SiCON-89.
    - Comparing with the data for SiN and SiC coatings, this suggests that SiCON-80 has the highest nitrogen content and SiCON-89 the lowest nitrogen content
    - This is consistent with the fact that N_2O is the easiest to dissociate, N_2 is the hardest to dissociate and NH_3 is somewhere in between.

SiCON coating deposited using N_2 precursor gas as source of nitrogen (SiCON-70; 3.5 μm thick) is shown in Figure 10.

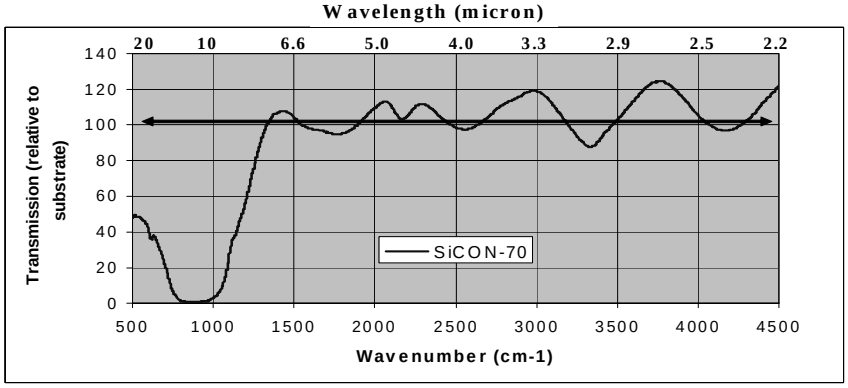

Figure 10: SiCON coatings deposited using N_2 precursor as source for nitrogen (SiCON-70; 3.5 micron thick).

2.5. Erosion resistance of Surmet's coatings

In order to evaluate the abrasion resistance of Surmet's coatings, the selected coating samples were subjected to Falling Sand Abrasion Test (as per ASTM D 968). The test conditions used were as below:

- Abrader: Quack Sand (99% Silica, 25 mesh)
- Impact Angle: 45°
- Sand Quantity: ~2 lbs

In each case the test coupons were impacted by about 2 lbs of free-falling sand at an impact angle of 45°. For comparison purpose, bare Si-wafer was used as reference sample. After the test, the coupons were examined visually as well as with the aid of optical microscope to determine the extent of damage. This is summarized in Table 7.

Table 7: Observation summary of test samples after Falling Sand Abrasion test

Test Sample	**Observation**
Both Side polished Si-wafer	Severely damaged surface. Least resistance.
SiN-15 (4 micron) Coated Si-wafer	No visible damage, OM revealed a few small pits. Good abrasion resistance.
SiCON-92B (9.4 micron) Coated Si-wafer	No visible damage. OM also did not show any damage. Excellent abrasion resistance
SiCON-70 (3.5 micron) Coated Si-wafer	No visible damage, OM revealed some pits. Good abrasion resistance.
SiC-102 (2.5 micron) Coated Si-wafer	No visible damage, OM revealed some pits. Good abrasion resistance.

*OM: optical microscope

Macro-photographs of the test coupons after falling-sand abrasion test are shown in Figure 11. Evidently, the surfaces of the test coupons coated with SiN and SiCON were intact (with no damage) after the test, while in the case of bare Si-wafer the surface was severely damaged.

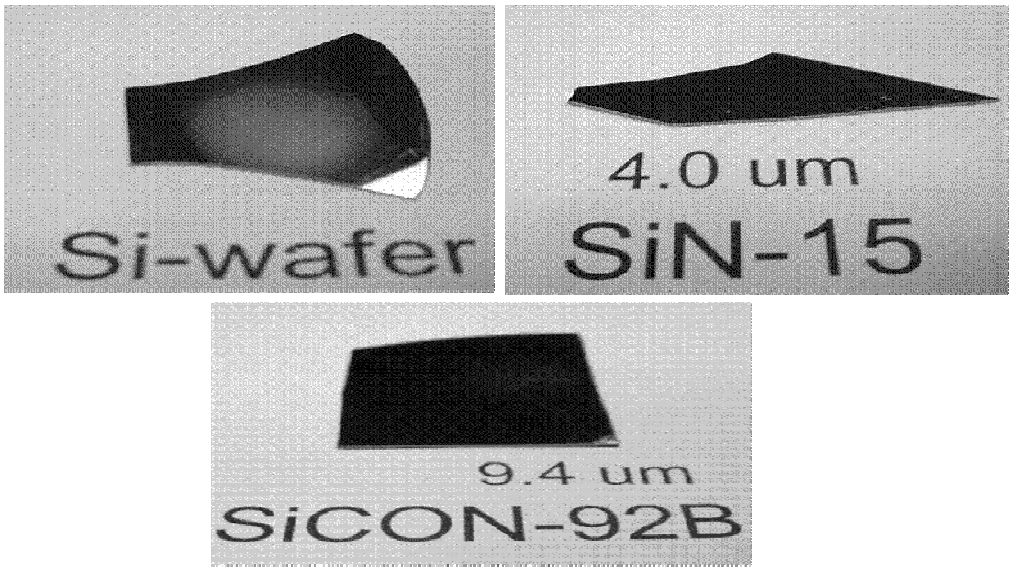

Figure 11: Macro-photographs of test coupons after falling sand abrasion test. SiN and SiCON coated coupons were unaffected indicating excellent abrasive-erosion resistance of Surmet's coating.

This is further confirmed by the optical micrographs of the surface of uncoated and SiCON coated test coupons after falling-sand abrasion test as shown in Figure 12.

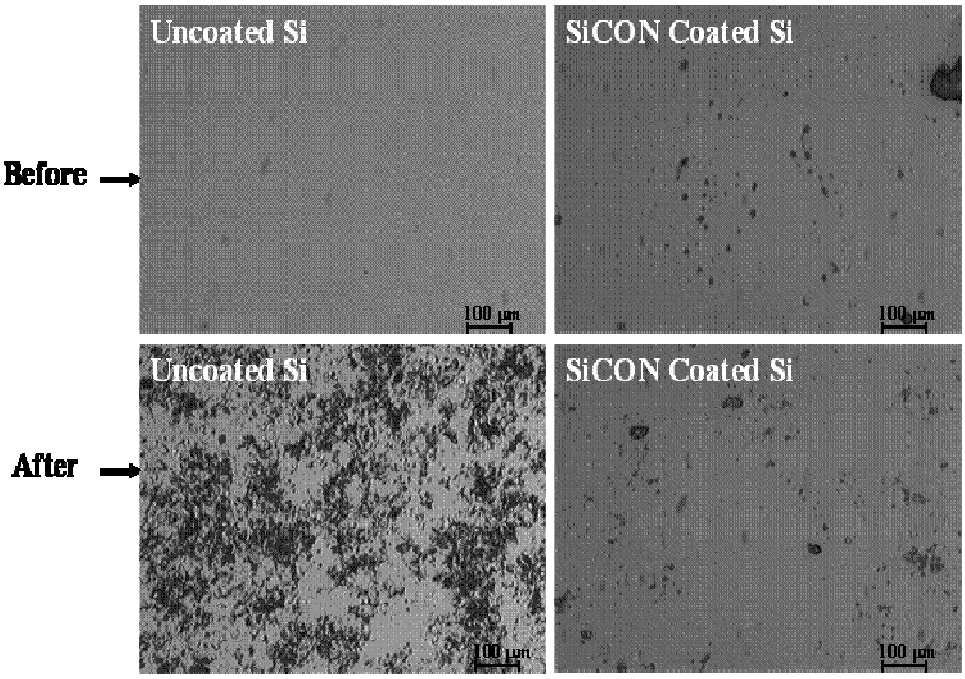

Figure 12: Optical micrograph of the bare and SiCON coated Si-wafer showing the change in surface morphology as a result of falling sand abrasion test. Evidently, the coating has exhibited excellent resistance to erosion.

To further evaluate the performance of these coatings, optical transmission of some of the coated test coupons were compared before and after the sand abrasion test. The results are shown in Figures 13, and 14, for bare Si-wafer and SiCON coated sample, respectively. It is clear that in the case of the uncoated Si-wafer there was a significant loss of optical transmission due erosion of the surface (Figure 13). In contrast, the transmission of the SiCON coated samples, Figure 14, was not degraded at all by the testing.

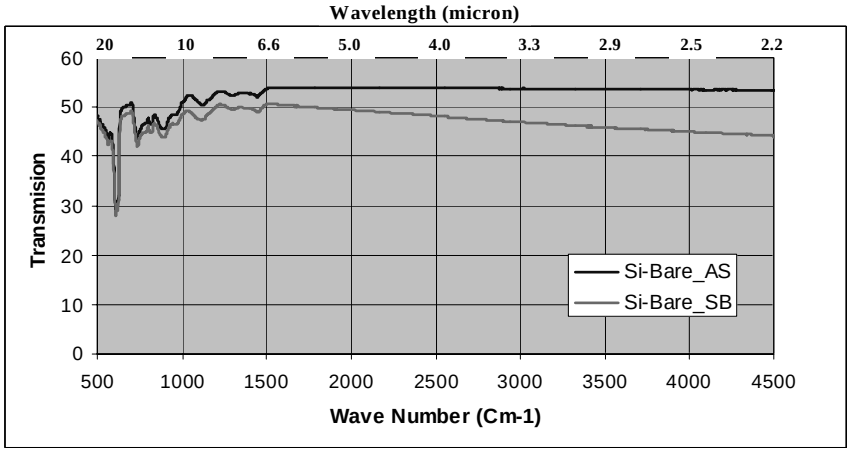

Figure 13: Optical transmission uncoated Si-wafer (blue line) before and the same after the falling sand test (pink line). The erosion damage has resulted in significant loss of transmission.

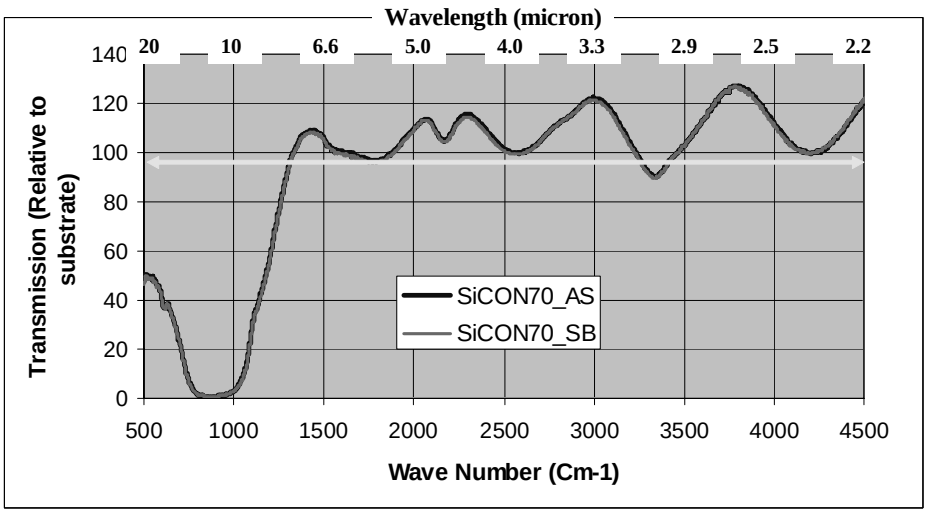

Figure 14: Optical transmission of SiCON coated Si-wafer before and after the falling sand test. The transmission of the coated sample was not affected by the test, demonstrating its erosion resistance.

3. CONCLUSIONS

In the light of experimental results and observations above, the following conclusions are drawn:

- Surmet has been able to deposit durable coatings of Si, SiN, SiC and SiCON with a range of compositions.
- Surmet's PE-CVD process deposits coatings at much higher rates than ion-beam sputtering.
- Process variables were manipulated to control coating composition and coating properties.
    - Independent control of Si, C and N content was demonstrated.
    - The ability to use various precursor gases as nitrogen sources has been demonstrated.
- Surmet's SiCON coatings demonstrated excellent abrasion resistance.

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