FINAL REPORT

NASA Research Grant No. NAG3-1828

for the period

April 8, 1996 to September 30, 1996

Ultra-Low-Cost
Room Temperature SiC Thin Films

Submitted to

NASA Lewis Research Center

by

Cleveland State University

Electrical Engineering Department, Space Photovoltaic Research Center

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Report prepared by the Principal Investigator
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1. Introduction

Under a NASA-Lewis Research Center grant (No. NAG3-1828), for a period covering April 8, 1996 through September 30, 1996, the research group at CSU has conducted theoretical and experimental research on "Ultra-Low-Cost Room Temperature SiC Thin Films."

2. Background

The fast-growing interest in the development of large bandgap materials such as SiC for fabrication of optoelectronics, high temperature electronics, high-power/high-frequency and radiation hard devices is based on their unique advantages as compared to either Si or GaAs such as: chemical, mechanical and thermal stability, a wide bandgap, much higher thermal conductivity, breakdown field, saturated electron drift velocity, and radiation resistance. Therefore, it comes as no surprise to the extent of which R&D efforts are made to fabricate a large variety of such devices.

A large variety of devices with promising characteristics have been demonstrated in SiC. Major applications include SiC devices for high-temperature controls, fast recovery high-voltage diodes, high-efficiency microwave devices, high-voltage power devices, blue-light emitting diodes (LED), and deep UV photodetectors. At present time, however, due to technological difficulties and cost constraints, most of them are single junction devices developed for use as blue LEDs, UV photodiodes and high temperature rectifiers. Most of these devices are fabricated using rather expensive SiC substrates and p-n junctions are preferably formed by epitaxy, because dopant diffusion requires excessive temperatures (> 1800 $^{\circ}$C). Ion implantation diodes were reported, but they exhibited high leakage partially caused by material defects. Thin film 3C-SiC layers can be cost effective grown on large area Si substrates by Low Pressure Chemical Vapor Deposition (LPCVD). However, the growth temperature, in excess of 800 $^{\circ}$C, is still too high for growth of SiC window or passivating layers on heterostructures based on III-V compound semiconductors.

3.   Phase I Results.

Within FY96 Phase I NASA LeRC's Director Discretionary Fund Proposal entitled, "Ultra-Low-Cost Room Temperature SiC Thin Films," we investigated the effectiveness of a ultra-low-cost room temperature thin film SiC growth technique on Silicon, and Germanium substrates and structures with applications to space solar cells, TermoPhotoVoltaic (TPV) cells and microelectronic and optoelectronic devices. The main results of this effort are summarized below.

3.1   Near Room Temperature Growth Processes of SiC Thin Films

Using liquid phase Si and C precursors available to us we were able to grow SiC-rich thin films on intrinsic and n- and p-type Si substrates. Our approach involved two near-room temperature wet chemical growth processes of SiC thin films on large area Si and Ge substrates, The two (i) direct and (ii) indirect growth processes are described below.

3.1.1 Direct growth

The direct deposition process we attempted for the near-room temperature chemical growth of SiC-rich thin film layers on silicon substrates is based on known direct synthesis reactions of methylchlorosylanes, and organochorosilanes containing Si-C-Si bonds (see Appendix 1).

The composition of products grown on the Si surface and reaction rate depend on a number of factors such as the type of the Si substrate (crystalline orientation, and doping type), the nature of the Si and C precursors, the catalyst, the reaction temperature, and illumination.

For this study we used semiinsulating, p-type and n-type LEC grown Si substrates of (100) and (111) orientations, as well as (100) Ge substrates. As C and Si precursors we used methyl chloride, methylene chloride, and chloromethyl-containing organosilanes. As host liquid phase we used ethyl alcohol, methanol and carbon tetrachloride. To enhance the growth reaction we used homogeneous catalysts such as palladium trifluoroacetate. During the growth the temperature of the solution was

kept between 25ºC and 50ºC. A halogen lamp was used for the n-type substrates.

The absorption of Si and C species on the Si surfaces were initially monitored using relative EDAX spectra and, on selected samples, the chemical composition of the deposited SiC layers was extracted from ESCA and XPS data.
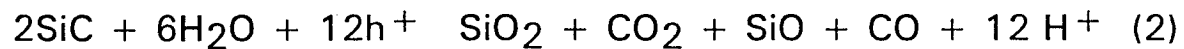
Initial, C-rich thin film layers were deposited on (100) n-type Si using 0.2 M dihydrogen hexafluorosilicate solution as a Si precursor, and 0.1 M methyl chloride in methanol as a C source. In Figure 1 are given some early XPS data of this layer. Fig. 1a shows a surface survey and Fig. 1b and Fig.1c the C1s and Si2p spectra, respectively. As seen from Fig.1a, traces of F could be detected on the surface. The C1s spectrum in Fig.1b reveals the existence of a main C-H bond and the two shoulders, suggest traces of C-O and Si-C bonds. The Si2p spectra in Fig.1c, reveals two main peaks with binding energies of 99. 4 eV and 103.5 eV. The peak at 99.4 eV we attributed to free silicon with Si-H bonds attached to it. The Si-H bonds containing organochrorosilanes are very important starting materials for silicones, because it undergoes hydrosilylation reaction to the unsaturated organic compounds. After a prolonged solution growth, the free silicon peak develops two visible shoulders which we have attributed to Si-H and Si-C bonds. The peak at 103.5 eV we attribute to the formation of SiO in the growth layer.

An important finding of this work is that as the chemical reaction advances the relative intensity of a Si2p peak shoulder at 100.3 (0.25) eV, which we attribute to SiC, increases while the relative intensity of SiO peak decrease correspondingly. Similar, from the increase of C1s peak with the binding energy of 282.2 (0.5) eV, which we attribute to SiC, the relative C1s peak intensities of CH_n and CO at 285.1 (0.3 eV) and about 287 eV respectively decrease as the reaction progresses. We also found that the rate of Si-C bond formation is dependent on the catalyst being used and, within our experimental work, is maximum when using homogeneous catalysts such as palladium trifluoroacetate. This might suggest that in the presence of a catalyst the Si-O, C-O and C-H bonds are replaced by the Si-C bond.

A possible simplified reaction mechanism for the conversion of SiO, CO and SiH_n into SiC can be described by the reverse partial chemical reactions proposed by Lauremann, who observed the formation of CO and CO_2 (but not O_2) during the anodization of SiC in HF:

$$SiC + 4H_2O + 8h^+ \quad SiO_2 + CO_2 + 8H^+ \quad (1a)$$
$$SiC + 2H_2O + 4h^+ \quad SiO + CO + 4H^+ \quad (1b),$$

given an overall reaction of

$$2SiC + 6H_2O + 12h^+ \quad SiO_2 + CO_2 + SiO + CO + 12H^+ \quad (2)$$

The SiC-rich films grown using the direct growth method have a maximum thickness of 20 nm, which is not enough for most applications.

3.1.2 Two Step Growth

During the direct thin film SiC-rich growth on Si substrates described above we observed the formation of SiO (but not SiO_2) in the early stages of the chemical reaction. Based on this observation and in an attempt to grow thicker SiC layers with higher relative concentration of SiC we are proposing a two step chemical reaction. In step I a SiO rich oxide is grown on the Si surface, and in step II SiO layer is converted into a SiC-rich layer.

In order to understand the mechanism responsible for the formation of SiC-rich layers, ESCA analysis of SiC layers in different stages of the chemical reaction was undertaken.

To verify the validity of the reverse partial reaction (1a) we first tried to grow a SiO_2 layer, using the liquid-phase deposition (LPD) growth method (see Appendix 2). After some preliminary experimentation and following the recipes reported by researchers from Japan and China, the white powdery-like deposited SiO_2 layers were not uniform, and have low adhesion to the Si substrate.

An attempt to grow in step II SiC-rich layers was made, and in the early stages of the chemical reaction traces of SiX_n and, CO and CH_n were detected, but not SiC. A longer exposure into the growth solution revealed, in addition to the aforementioned compounds, a C1s peak at 284.2 eV which we attributed to free carbon formation and only traces of SiC.

Next, we tried to grow a SiC-rich layer on a thermally grown SiO_2 layer. The initial thickness of this layer as determined from Dektak measurements on etched spots as well as from ellipsometric measurements was 102 5 nm. In an early stage of the attempted SiC-rich layer growth, the main C1s peak in Figure 2, with a binding energy of 284.2 eV, we attributed to free carbon. The left and right shoulders of this peak, although unresolved, one might argue to be an indication of traces of CH_n and SiC, respectively. After a prolonged chemical reaction, the right shoulder of the C1s peak increased only slightly which indicates the formation of a slightly increased amount of SiC, while the relative peak hight we attributed to free carbon increased more visible. The C-rich surface layer was very thin since, after etching the treated SiO_2 layer its thickness has not change. However, the etch rate in 1M HF of the treated SiO_2 layer was over 10 times lower than the rate of the initial SiO_2 layer, probably due to an increased chemical stability of the treated front SiO_2 surface layer.

Very recently, a joint effort at SPECMAT, Inc. has shown that it is possible to grow thicker (30 nm to 350 nm) SiOF layers on (111) p-Si surfaces by a simple wet chemical growth method (see Appendix 3). By using various concentrations of the F precursor, the relative atomic concentration of these films was varied from near zero to up to 16%.

We used this new technique to grow on (111) p-type Si substrates, 30 to 200 nm SiOF layers, as step I in our chemical growth of SiC-rich layers. The Si2p spectra of a 115 nm thick chemical oxide showed a main peak at 102.6 eV which we attribute to SiOF and a small shoulder at 99.1 eV which we attribute to free Si. After a prolonged (25 mins.) chemical reaction of a sample cut from the same oxidized wafer and the same chemical solution as the one used in connection with the attempted SiC growth using thermally grown SiO_2, above, the Si2p

spectra in Figure 3 shows two distinct peaks at 100 eV and 104 eV. The peak at 100 eV, we attribute to a SiC-rich layer formation, which is in good agreement with the apparition of a main peak in the C1s spectra with a binding energy of 282.3 eV. No free carbon or CO could be detected in this case but a visible shoulder at 285.5 eV appears, which might indicate traces of C-H bonds. The shift of the higher binding energy Si 2p peak from 102.6 eV to 104 eV, could indicate the formation of SiO-rich compounds and the relative decrease in the SiOF peak height, a conversion reaction from SiOF to SiC-rich compound. This presumption seems to be in good agreement with the large decrease in the relative F1s peak intensity as compared to the oxidized only surface.

In a very preliminary attempt to grow SiC-rich layers we used SiO-rich layers (low relative F concentration) grown by this new technique as step I in an attempted two step wet chemical growth process of thicker SiC layers. As step II of the growth process we used a solution based on methyl chloride in methanol.

In Figure 4 is shown a XPS surface survey of the SiC layer. As seen in Table 1 (see Fig.4), the relative atomic concentration of Si and C are very closed (about 28%), while the oxygen concentration is higher (42.7%). No detailed analysis of the composition of the front SiOC layer was attempted so far. However, the Si2p peak at 104 eV, indicates a SiO-rich as the main components of the SiOC layer. After 100 secs. sputtering time, which corresponds to removal of about 2 nm from the surface, data in Table 2 (see Fig.4) indicate a significant drop in the C relative concentration in favor of an increase in Si relative concentration, and a smaller increase in oxygen relative concentration. After prolonged exposure to methyl chloride in methanol solution, the relative concentration of C increased while the O concentration decreased. This suggests that at the surface of the treated SiO oxide, C has replaced O. The relative severe Ca impurification was due to the fact that in step II of the wet process growth we used low purity chemicals, available to us. After removing about 3 nm from the surface C and Ca relative concentration have dropped to the background level and the relative concentration of Si and oxygen became nearly equal.
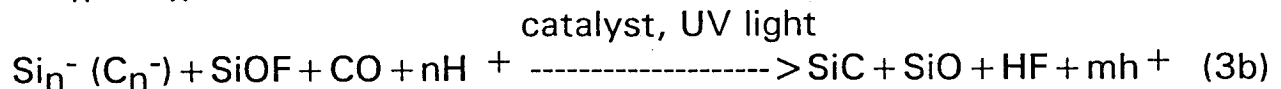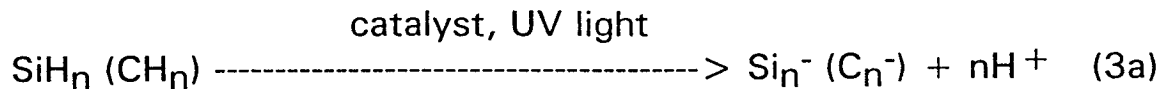
Due to the limited diffusion of C, the sequential two step chemical deposition described above cannot be used for the formation of thick uniform SiC-rich layers. Also, for similar thicknesses, the SiO growth rate should be equal or smaller than the SiO to SiC conversion rate. In the above experiment, the growth of the 115 nm thick SiO-rich layer in step I was done in 6 mins., while the conversion of the first 3 nm into SiC-rich layer in step II took 15 mins. Therefore a chemical solution, which to contain both Si and C precursors has to be developed, and the growth should occur in a two step process, by combining the SiO and the direct SiC growth, rather than in two distinctive steps as in the above experiment if thick uniform SiC-rich layers are to be deposited.

A very preliminary study on the chemical stability of the thin SiC-rich front layer in strong reducing (HF) and oxidizing (HNO_3) acids has shown a dramatic improvement in chemical stability as compared to oxidized only surfaces, cut from the same 2" wafer. (The chemical growth of SiO-rich oxide was done on 2" wafers, which were cut to smaller sizes for the step II reaction, and characterization).

Etching in HF solution and ellipsometry data were used for thickness determination. The thickness of the SiO-rich layer grown during the step I was not changed significantly after the step II growth of the thin front SiOC layer in step II.

Ellipsometry was also used for some preliminary optical characterization of these insulator layers. In Figure 5 is shown the variation as a function of wavelength of the index of refraction (n) and the extinction coefficient (k). Note the very small values of the extinction coefficient, which suggest a very low absorption coefficient for the treated SiO (115 nm thick) layer.

Based on our preliminary experimentation, it appears that the two-step chemical growth of SiC-rich layers on (111) p-type Si surfaces is a better choice than the direct growth discussed above. A simplified possible chemical reaction mechanism for the conversion of SiOF, CO and SiH_n (CH_n) into SiC might be based on the reverse reaction (2) above

$$\text{SiH}_n \text{ (CH}_n\text{)} \xrightarrow{\text{catalyst, UV light}} \text{Si}_n^- \text{ (C}_n^-\text{)} + n\text{H}^+ \quad (3a)$$

$$\text{Si}_n^- \text{ (C}_n^-\text{)} + \text{SiOF} + \text{CO} + n\text{H}^+ \xrightarrow{\text{catalyst, UV light}} \text{SiC} + \text{SiO} + \text{HF} + m\text{h}^+ \quad (3b)$$

The above equations are far from complete and, probably, even not accurate. The chemical reaction mechanism for the formation of thin film SiC-rich layers on Si are certainly more complex since, for instance, the above equations do not take into account a main component of the chemical solutions, namely the chlorine. However, our ESCA study has shown only traces of chlorine in the grown SiC-rich layers, although Cl has a rather large concentration in the growth solution. The lack of a larger Cl concentration on the surfaces is difficult to explain since it is reasonable to assume that the chlorosilanes react with the alcohol producing an alckoxysilane and HCl. Mild warming of the solution (30-40°C) should promote completion of the reaction. Part of the HCl should react with the alcohol to produce small quantities of alkyl halide and water. The water should cause the formation of silanoles from alkoxysilanes and the silanoles are expected to condense on the Si substrate.

3.2 Potential Applications

A room temperature growth of thin film SiC layers on Si and other semiconductor structures, will open up a wide variety of new microelectronic and optoelectronic device design possibilities for a wide variety of space and terrestrial applications such as:

- protective coatings to resist high temperature corrosion;
- transparent thin films with tailorable electrical conductivity for a number of space applications, from solar cell coatings to controlling static buildup on spacecraft surfaces;
- UV emitters and detectors;
- nuclear detectors and medical instrumentation;
- high temperature electronics for automotive and aircraft engine monitoring and control;
- chemical and metallurgical industrial process control;
- indoor and outdoor displays, lighting, and signs.

As an example, in modern integrated circuit (IC) technology the semiconductor structures are subjected to the action of various radiation, only to mention plasma etching or plasma deposition, where apart from electrons and ions also a significant portion of UV light is present. Improving the UV radiation hardness of insulator/semiconductor interfaces could be extremely beneficial to improving the reliability, cost and yield of IC structures, as well as for fabrication of discrete electronic and optoelectronic devices to mention only high efficiency stable UV photodetectors and X-ray or gamma-ray nuclear detectors. For these applications a near-room temperature growth of semiinsulating thin film SiC layers should be extremely beneficial.

Recently we started a very preliminary investigation on the use of chemical growth processes of SiC-rich thin film layers on Si and Ge structures for solar cells, TermoPhotoVoltaic (TPV) cells and microelectronic and optoelectronic device applications. Due to the time constraints, except for some basic experimentation for chemical porous silicon and germanium oxide formation, in our experimentation we used only already fabricated Si solar cells and Ge cells.

3.2.1 Silicon Solar Cells

Light-induced effects in the Si/insulator interface are known to adversely affect the solar cell performances. Although these light-induced effects affect especially surface sensitive devices such as the silicon inversion layer solar cells, these effects have also been reported for high efficiency silicon point-contact solar cells after extended exposure to concentrated sunlight. The light-induced degradation is due to the generation of fast surface states at the silicon/insulator interface. For terrestrial solar cell applications this effect can be minimized, since cover glass and suitable encapsulants act as a filter cutting off the energetic wavelengths ($\lambda < 335$ nm) which are mainly responsible for light induced degradation of solar cell performances. For concentrator solar cells in general and point-contact and VMJ Si solar cells in particular, however, these effects cannot be neglected.

The only high efficiency concentrator solar cells available to us for this experiment were Vertical MultiJunction (VMJ) Si solar cells,

provided by PhotoVolt, Inc. The biggest contributor to efficiency loss in the Si VMJ cell structure is the fact that its illuminated and back surfaces are high recombination surfaces with exposed junctions which are difficult to passivate by means of thermal oxidation. This is because thermal oxidation needs a temperature that is higher than the temperature at which the stack is alloyed together. Additionally, as known, for these cells degradation by nonionizing (subbandgap) radiation (as far as the insulators tantalum pentoxide and silicon oxide are concerned) make the cell performance parameters to decrease significantly, especially if UV or near UV radiation are not completely absorbed by the cover glass and/or encapsulant.

On some Si VMJ cells with Ta_2O_5 as an antireflective (AR) coating, after 1 hour exposure to high intensity (about 50 mW/cm^2) near UV light, the drop in the performance parameters was as high as 20%. After the exposure, the cell performances completely recovered after only about 30 mins. which might suggests that fast surface states at the Ta_2O_5/Si interface were responsible for the performances drop. After removing the Ta_2O_5 layer, passivating the surfaces using a chemically grown thin film SiO layer, and growing a thin SiC-rich layer, the cell performances increased by as much as 50%. Additionally, no UV degradation was observed even after exposure to the aforementioned halogen light for as long as 5 hours. In fact, for some cells, with similar surface treatments, measurements performed in the PV branch at NASA LeRC under AM0, 25°C conditions, showed even a small increase in performances after prolonged light exposure.

3.2.2 Chemical Stabilization of the Porous Silicon Surfaces

Porous silicon (PS) is currently receiving wide-spread interest because of its potential application in electroluminescent devices compatible with Si very large scale integration (VLSI). (see Appendix 4). Chemical stabilization of the PS material and conservation (or enhancement) of the luminescence efficiency are two current challenges faced in the development of porous-silicon-based light emitters.

As is known, good chemical stability is obtained upon oxidizing the PS surface, either thermally or by anodic oxidation. But this does not

appear as a promising route for device application, because this impedes electrical carrier injection. On a single-crystal planar silicon surface, the hydride passivated surface is known to exhibit a fair stability against oxidation and contamination, at least on a time scale of a few hours. In contrast, the PS surface is much more prone to oxidation and contamination, and, especially for high porosity samples, the infrared spectra exhibit traces of contaminated native oxides formation, after a few tens of minutes in air. On the other hand, on flat silicon crystals, methloxylation of the surface has been reported as a key factor in order to account for the long-term stability and the low interfacial recombination characteristics in methanol-based photoelectrochemical cells. Similar modifications of the porous silicon surface then appears highly attractive since it might provide a much more stable surface which could be used as a processing step for device applications. In a recent study after formation of PS in concentrated HF electrolyte, methoxy groups were formed trough partial anodic dissolution of the hydrogenated PS surface in anhydrous methanol. The methoxylated surface exhibits improved optical characteristics (increased photoluminescence efficiency and blue shift of the emission), similar to PS anodically oxidized in a nonfluoride aqueous electrolyte. Its stability against aging was also improved as compared to that of the hydrogenated surface, but without reaching the stability of anodically oxidized PS. The relative instability is ascribed to the amount of SiH species which remain on the methoxylated surface upon the modification process.

Recently we started a very preliminary study on the possibility of increasing the stability of PS material against aging using chemically grown SiC-rich thin film coatings. The PS was formed chemically on (111) p-type Si, using a solution based on HF and HNO_3. Then, a direct chemical growth of a SiC-rich layer was attempted. In Figure 5 are shown three photoluminescence intensity (PLI) spectra of (a) RCA cleaned p-type substrate, and of the (b) p-type substrate, and (c) PS coated p-type substrate, after the attempted coating the surfaces with a thin film SiC-rich layer. One can see that after the surface treatment the position of the peak in curve (b) did not change, while the relative PLI significantly decreased. This means that no SiC-rich surface layer could be grown in this case, probably due to an oxide free surface after the

RCA surface preparation. The two distinctive orange and red luminescent peaks in curve (c) indicate the formation of a good quality PS layer and the smaller intensity peaks and shoulders might be an indication of traces of SiC, SiO and SiH_n compounds on the surface. However, no attempt was made so far to either analyze the composition of the treated PS layer or to interpret the PLI spectra. We tried to grow PS layers on already fabricated Si solar cells so as to be able to globally asses the quality of the chemically treated PS layer and its stability from the variations in the performance parameters of these cells. However, this could not be done due to the fact that the Ag-based cell contacts lifted-off during the chemical formation of PS layers in strong acidic solutions.

3.2.3 Germanium Cells

In a previous work we fabricated planar n^+pp^+ and p^+nn^+ Ge cells. Although due to their very good performance parameters these cells appeared to be good potential candidates for high efficiency, low cost TPV applications, a major drawback we noticed was their instability. We have tried native oxides grown both by chemical and electrochemical (anodic) oxidation of finished planar cell surfaces for surface passivation. Although we have not yet performed a systematic spectroscopy related characterization of these oxide layers, from the instability of these oxides, determined both chemically and from the decrease of solar cell performance parameters with time, we concluded that these oxides might have been a mixture of hydrous GeO and hexagonal GeO_2. Using these oxides, the cells were very unstable, even at room temperature in the dark, except when kept in nitrogen atmosphere. Using a chemical etch based on HNO_3, H_2O_2, and CH_3COOH, however, the cells became much more stable, as a result of the native oxide formed by this etch. From the color (dark brown) and an increased stability in various acidic solutions we believe this native oxide was rich in tetragonal GeO_2. As opposed to cells using native oxides supposedly rich in hydrous GeO and hexagonal GeO_2, the cells on which the chemical oxide was grown using the above mentioned etch, are stable at room temperature in air. Furthermore, as long as the cell is not exposed to atomic oxygen or UV radiation, the tetragonal GeO_2-rich native oxide drastically reduces the surface recombination velocity (SRV) as revealed by the sharp increase in the blue response. However, the

assumed tetragonal GeO_2-rich oxide is not stable under strong illumination, or atomic oxygen, as revealed by the decrease in the performance parameters (I_{SC} and V_{OC}) of cells exposed to such environments. Using a UV filter, the rate of decrease of cell electrical performance parameters is very small as compared to the rate of decrease when no UV filter is used; this means that UV radiation is mainly responsible for the observed instability.

We used the direct chemical growth process and methylene chloride, and tetramethoxysilane as C and Si precursors, respectively, on the chemically oxidized n^+pp^+ Ge cell front surface. No investigation on the composition of the resulted layers were attempted, but after the chemical treatment the chemical oxide layers became more chemically stable. The chemical reaction proved to be compatible with the Au-based front and back cell contacts. After the surface treatment, the relative I_{SC} and V_{OC} of these cells, increased by as much as 25% for I_{SC} and as much as 11% for V_{OC}, which suggest a significant relative decrease in the surface recombination velocity of cell surfaces coated with a treated chemically grown oxide. The relative drop in performances after exposure to high intensity UV light was also noticeably reduced. This suggest that, if further developed, treated chemical oxides can be used not only for surface passivation, but as first layer AR coating as well.

3.3 Conclusions

Within phase I of this work, we investigated two growth processes: (1) direct growth and (2) a two-step growth. The direct growth process involves a chemical reaction of a chemical solution containing liquid Si and C precursors with the Si surfaces in presence of a catalyst. In the two-step growth process, first a thin film SiOF layer is grown chemically on the semiconductor surface, and then using chemical solutions as those used in the direct growth process, SiC-rich layers are formed.

Using liquid phase Si and C precursors and catalysts we were able to grow SiC-rich thin films on intrinsic and n- and p-type Si substrates. These proof-of-concept semi-insulating thin films grown at near-room temperature ($< 50^{\circ}C$) are (i) rich in SiC, (ii) uniform and chemically inert in reducing (e.g. HF) and oxidizing (e.g. HNO_3) agents; (iii) stable in air at temperatures of up to 1000 $^{\circ}C$; and (iv) passivate and stabilize the Si and Ge surfaces, as suggested by the increase in performance parameters and UV stability of high intensity VMJ Si solar cells and Ge cells.

The chemical growth mechanism of these layers is not entirely understood. Using the two step growth process is possible to grow thicker and better quality thin film SiC-rich layers and also to better control the thickness of these layers. A chemical solution, which to contain both Si and C precursors has to be developed, and the growth should occur in a two step process, by combining the SiO chemical growth and the direct SiC growth, rather than in two distinctive steps such as in the above experiment if thick uniform SiC-rich layers are to be deposited.

Acknowledgments

k
C
P
S

Binding Energy (eV)

O

F

O

Ca

C

Si

Si

Figure 1a

C
P
S

C-O

CH₂

SiC

C1s region

Binding Energy (eV)

Figure 1b

XPS
ANALYSER
SOURCE
LABEL

Si2p   C:\EXP95.COL\0519950Z.COL\SI2P
CAE = 20eV   STEP = 100 meV   SCANS = 4   TIME = 6m 42.00s
0   Depth Profile - 0 s etching
survey of Au film plus course gr

Si

SiO

Binding Energy (eV)

C
P
S

Figure 1c

284.2

C_{1s}

$3600 \ ^c/_s$

$3600 \ ^c/_s - 1722 \ ^c/_s = 1878 \ ^c/_s$

$11.1 \ C/m$

284
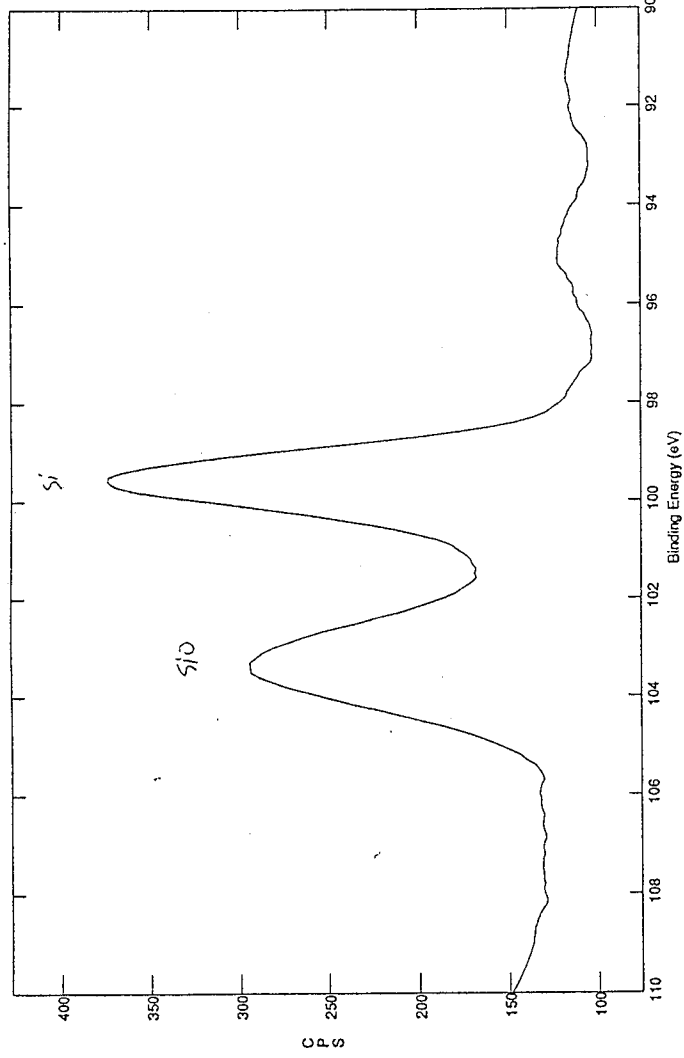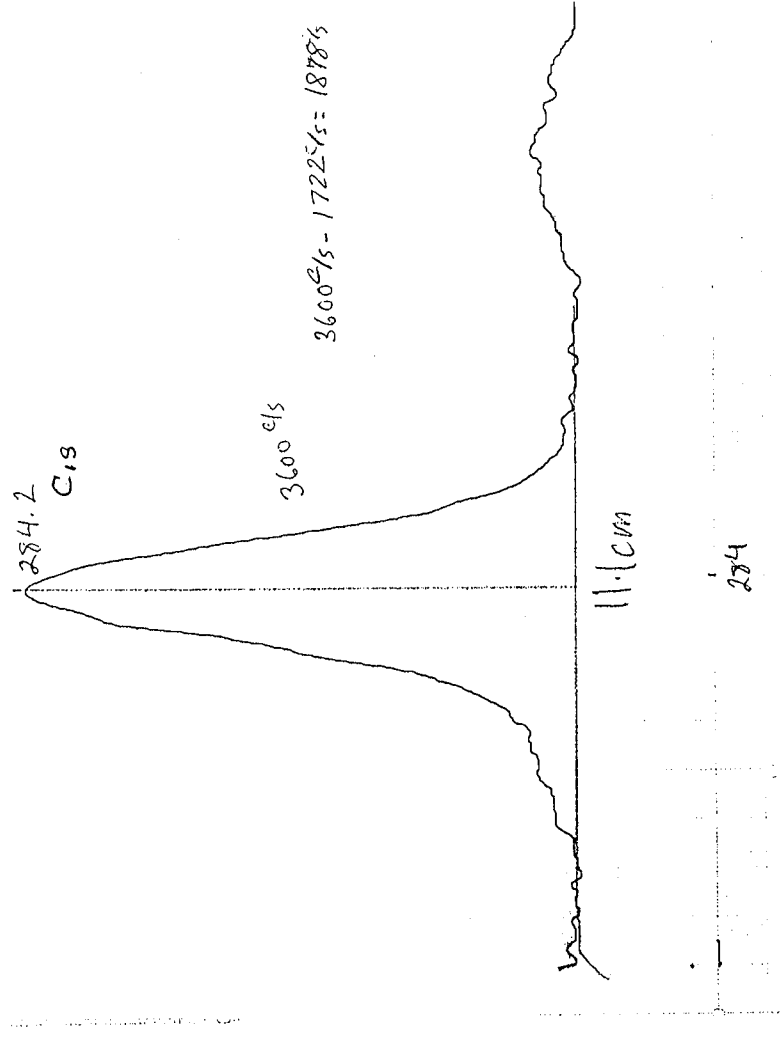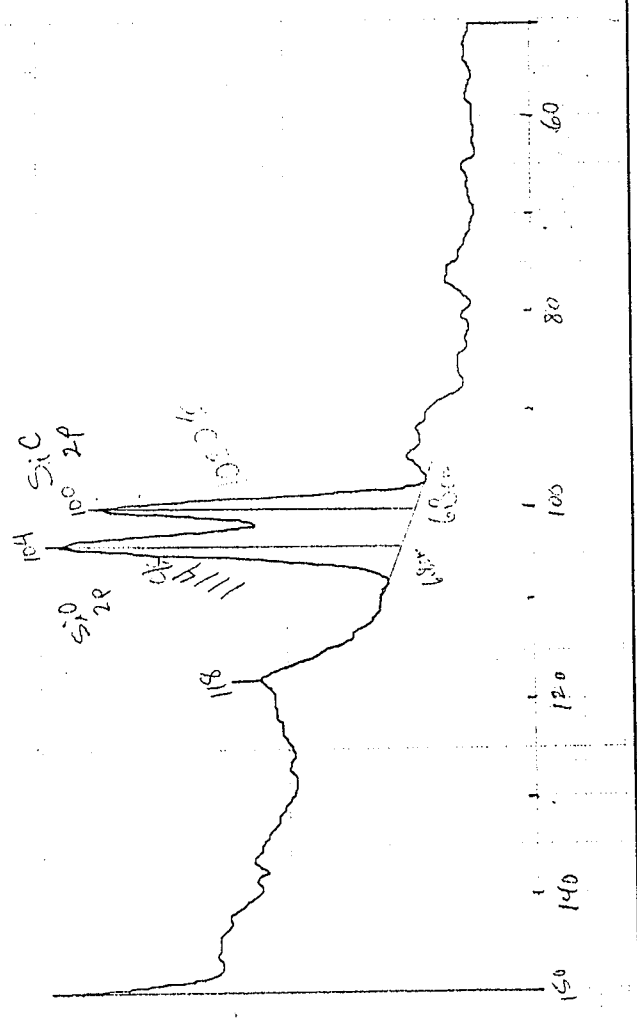
Figure 2

Figure 3

SI5.SPT   p-Si (MF), 10mW, 4.2K, 1mm
SiC_SI5.SPT   SiC/p-Si (MF), 10mW, 4.2K, 1mm
SiCO_SI2.SPT   SiCO/p-Si (MF), 10mW, 4.2K, 1mm

Figure 5

TABLE 1 - Quantification Table for Experiment C:\FAUR\08159604\SURVEYAL.DTS. As Received

Peak	Center	SF	Pk Area	Norm. Area	[AT]%
0 1s	533.00	0.66	403527.188	1979.91125	42.698
Ca 2p	346.00	1.58	33540.363	62.85560	1.356
C 1s	286.00	0.25	113928.898	1315.20886	28.364
Si 2p	104.00	0.27	128404.758	1278.99561	27.583

TABLE 2 - Sputtered 2 nm.

Peak	Center	SF	Pk Area	Norm. Area	[AT]%
0 1s	532.00	0.66	8891.347	43.60265	46.904
Ca 2p	342.00	1.58	1542.824	2.88624	3.105
C 1s	284.00	0.25	611.570	7.05416	7.588
Si 2p	100.00	0.27	3963.183	39.41893	42.403

C:\FAUR\08159604\SURVEYAL.DTS

Figure 4

Chemical Oxide Sample 6

Sample 6
 Chemically Oxidized #6
 Filename: Chemical6-75b
  Cauchy Fit
   MSE = 44.1
   Thickness = 2083±6.5

Figure 6a

Chemical Oxide Sample 7, SiO+voids fit.

Sample 7
 Chemically Oxidized #7
 Filename: Chemical7-75b
 Material Fit
   MSE = 35.8
   Thickness = 539±6
   % voids = 35.0±1.4   The rest is SiO.
 Cauchy Fit
   MSE = 2.54
   Thickness = 596.5±3.9

Figure 6b

Thermal SiO2.

Thermal oxide (after removal of white tape)
Filename: Photovolt\Thermal
Material Fit
MSE = 6.5561
Thickness = 1028±0.8
% SiO_2 = 99.56±0.1   The rest is Si_3N_4.

Index of refraction 'n'

Extinction Coefficient 'k'

Wavelength in Å

Figure 7

Evaporated SiO.

Sample 2
Evaporated
Filename: Photovolt\Evaporated
Material Fit
MSE = 21.73
Thickness = 696±1.8
% SiO = 89.8±0.3   The rest is voids.

Index of refraction 'n'

Extinction Coefficient 'k'

Wavelength in Å
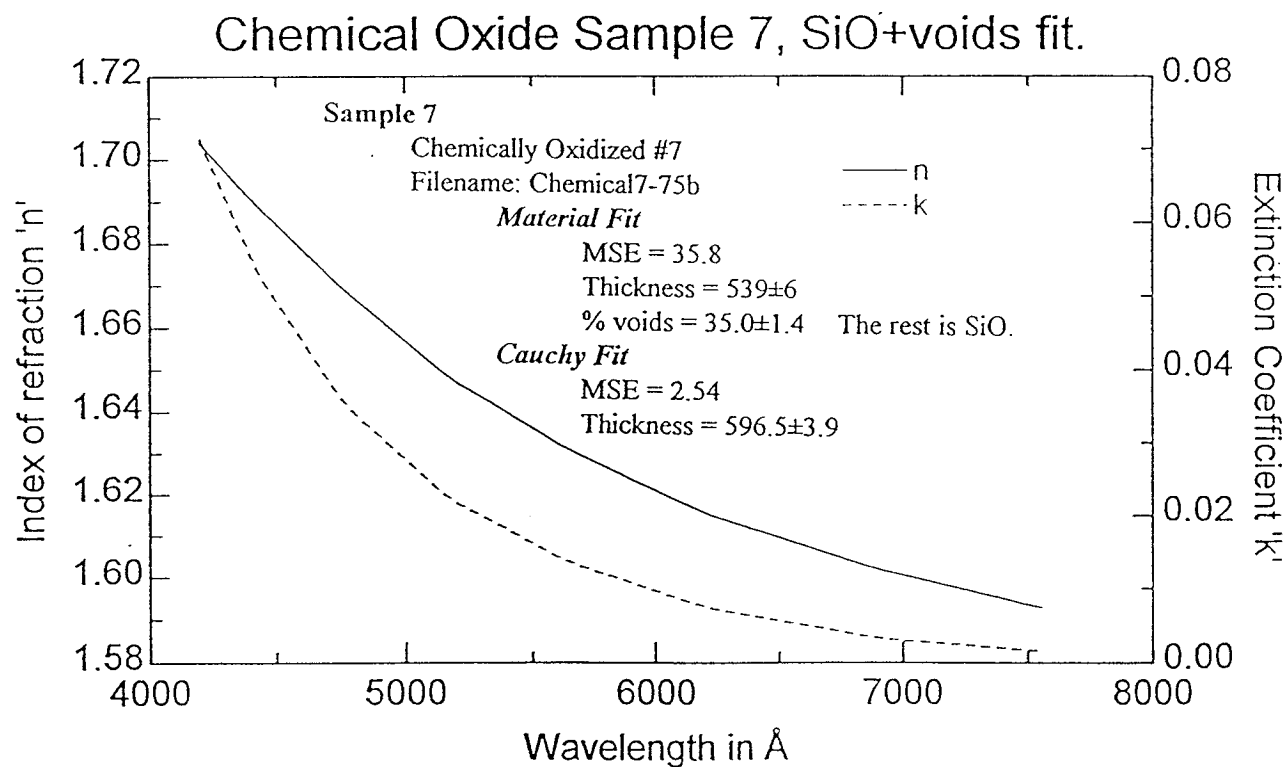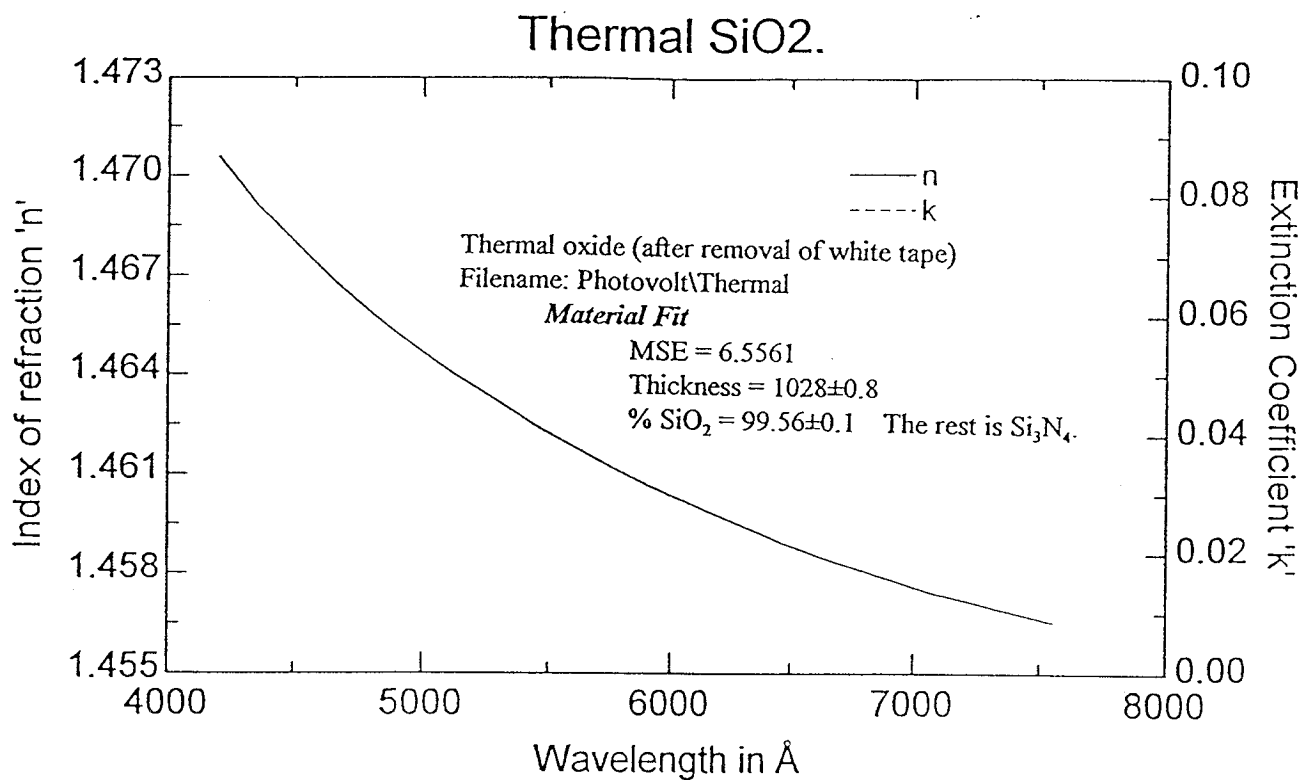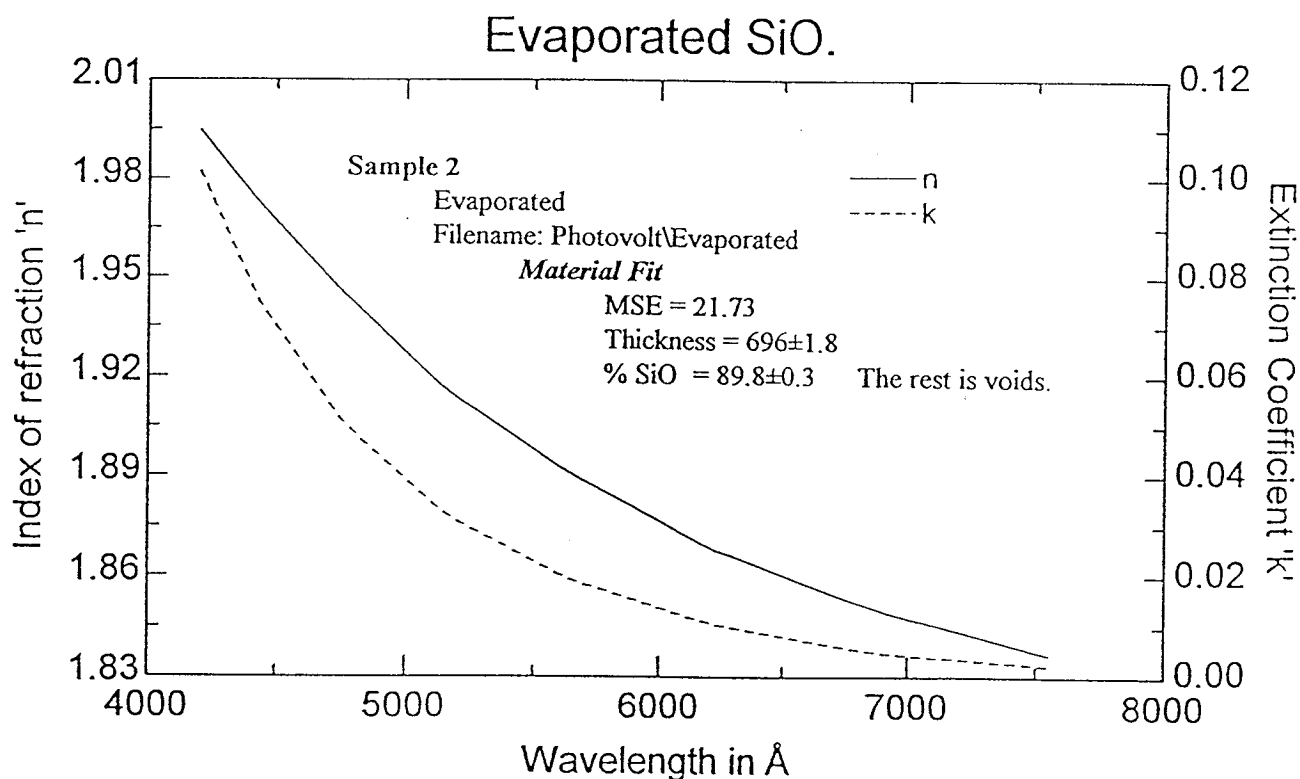
Figure 8

Appendix 1 - Direct Chemical Synthesis of Silicones and Carbosilanes

Organosilicon polymers known as silicones are compounds in which the elements silicon and oxygen alternate in the molecular skeleton. Organosiloxanes containing Si-O-Si bonds can be considered to be structurally derived from silica.

Polycarbosilanes are compounds in which the element silicon and carbon alternate in the molecular skeleton. They are similar to silicones except that the oxygen bridges of silicones are replaced by methylene units. Polycarbosilanes have been reported to be useful as precursors for the silicon carbide continuous fiber. The synthesis of organochlorosilanes containing Si-C-Si bonds from elemental silicon and organic polychloride or chloromethyl group containing silicon compounds are relatively well documented. Some of these direct synthesis chemical reactions are briefly discussed below.

(a) Direct Synthesis of Methylchlorosilanes

The direct synthesis of methylchlorosilanes, known as Rochow reaction is the reaction of methyl chloride with elemental silicon in the presence of a cooper catalyst. The direct process is one of the most widely used technique in the silicone industry. The reaction gives dimethyldichlorosilane, methyltrichlorosilane, tetrachlorosylane and small quantities of a large number of high boiling temperature compounds.

	Si/Cu composition (%)		bp (°C)
CH_3Cl ---------------------->		$(CH_3)_2SiCl_2$	70
75			
		$(CH_3)_3SiCl$	66
10			
		CH_3SiCl_3	58
4			
		CH_3HSiCl_2	41
6			
		Others	>50
5			

The composition of products and reaction rate depend on a large number of factors such as the nature of the starting material, the catalyst, the reaction temperature, the reaction pressure, illumination, the type of reactor used, and the degree of conversion of silicon and methyl chloride. The industry catalyst for the direct process is usually copper, and in some cases co-catalysts such as zinc, aluminum, cadmium etc. are added. The co-catalysts enhance the reactivity of elemental silicon and shorten the induction period and increase the selectivity of dimethyldichlorosilane production. With the above catalysts the reaction is carried out at 250-350°C, and the yield of dimethyldichlorosilane decreases at temperatures above 300°C. In the absence of a catalyst, the reaction is sluggish and gives irreproducible results.

(b) Direct Reactions with Chloromethyl-Containing Organosilanes

The reaction of -chloromethlsilanes with elemental silicon is very similar to that of methyl chloride. -Chloromethlsilanes are readily prepared by the chrorination of corresponding methylsilanes under UV irradiation in refluxing carbon tetrachloride. In the presence of copper catalyst using a stirred reactor at temperatures between 250 and 350°C, trisilaalkenes are obtained as a major product (up to 88%) and bis(Silys)methanes as the minor products.

(c) Direct Reactions with Polychrorinated Alkenes.

The direct reactions of elemental silicon with polychrorinated alkenes, such as methylene (methyl) chloride and chloroform produce linear compounds of formula $Cl_3Si(SiCl_2CH_2)_nSi_2Y$ (Y = H or Cl, n = 1-4) as well as cyclic organosilicon compounds of formula $(SiCl_2CH_2)_3$. In general, methylene chloride reacts with silicon at lower temperatures than methyl chloride.

Appendix 2 - Liquid-Phase Deposited SiO$_2$ Growth

Recently, in a series of publications researchers from Japan, China and Taiwan, claim to have successfully grown SiO$_2$ layers on Si by using a low temperature (30 to 50°C) solution growth. The growth of liquid-phase deposited (LPD) SiO$_2$ initially proposed by Nagayama et al. is presumably based on the chemical reaction of H$_2$SiF$_6$ with water to form hydrofluoric acid and solid SiO$_2$. The initial H$_2$SiF$_6$ solution is saturated with SiO$_2$ powder (usually in a sol-gel from). One of the major disadvantages of LPD is the low deposition rate which limits its use. By the addition of boric acid (H$_3$BO$_3$), or aluminum to the solution the deposition rate is claimed to have been increased to up to 20 nm/hour. This is still too low and the additions contaminate the surfaces which limits the LPD SiO$_2$ applications.

Our own experimentation using the LPD method seem to indicate that (i) a true chemical reaction with the underlying Si substrate does not take place; instead the SiO$_2$ might be chemosorbed from the solution on the Si surfaces, which might explain the poor adhesion of the white powdery-like deposits we obtained; (ii) the growth rate is much smaller than the reported values (less than 5 nm/hour); (iii) the Si surfaces are seriously contaminated, especially with boron, and (iv) the thin "oxide" layer is a mixture of Si, SiO$_2$, adsorbed on the Si surfaces and some unidentified compounds based on boron (most probably a mixture of H$_3$BO$_3$, BF^{4-} and SiF$_6{}^{2-}$).

Appendix 3 - Chemical Oxidation of Silicon. Proof-of-Concept

Background

Silicon dioxide (SiO_2) forms the basis of the planar technology. In industrial practice SiO_2 layers are most frequently formed by thermal oxidation of Silicon (Si) in the temperature range 900 to 1200 C. SiO_2 is also deposited by chemical vapor deposition (CVD) techniques at lower temperatures (200 to 900 C) on various substrates. Room temperature oxidation is possible using anodic oxidation.

Thermal and CVD-grown SiO_2 layers are used as diffusion masks, to passivate device junctions, as electric insulation, as dielectric material in Si technology, and as capping layers for implantation-activation annealing in III-V compound semiconductor technology, to name a few.

The thermal oxidation process is one of the key steps in the fabrication of Si semiconductor devices and integrated circuits. There are two commonly used chemical reactions in thermal oxidation:

1) one is due to oxidation of pure dry oxygen (dry oxidation) or chlorine (e.g. chlorine gas, anhydrous HCl or an organic molecule such as trichloroethylene) is added to a dry oxygen carrier in small amounts to enhance the oxidation rate, and

2) the other is due to oxidation with water vapor added to the oxygen carrier (wet oxidation).

SiO_2 has more than one crystalline form. The SiO_2 layers grown either by thermal oxidation, or CVD techniques, however, have no long-range crystalline order; they are amorphous in structure and tend to return to the crystalline form at temperatures bellow 1700 C. The rate of transformation is, however, negligibly small at about 1000 C or lower.

The density of thermal SiO_2 (2.15 to 2.27 g/cm^3) is less than that of crystalline SiO_2 (2.65 g/cm^3). The density of CVD (APCVD, LPCVD and PECVD) grown SiO_2 layers is usually even smaller than that of thermal oxides. Because of its low density and amorphous structure and therefore more open structure, a number of impurities may diffuse

through SiO_2 interstitially. Due to their high diffusivities, some of these impurities (such as Na, O and Ga) in fact, can diffuse rather rapidly through the amorphous SiO_2 layers. This is a big concern for most of the applications mentioned above.

In the last two decades or so, there has been a continuous search for an alternate gate dielectric to SiO_2 grown by thermal oxidation, needed for a series of applications such as the high performance ULSI. The SiO_2 has already been replaced by slightly modified SiO_2, i.e. oxynitrides. Most recently, for fast speed logic devices a new low dielectric constant material, SiOF, has been proposed. The search continues for alternate to SiO_2 layers for many microelectronic device applications.

Main Disadvantages of Thermal and CVD-Grown SiO_2 Oxides:

- High temperature (thermal, LPCVD)
- High investment cost
- Low deposition rate
- Chemical and Particle contamination (thermal and PECVD)
- Poor step coverage (APCVD)

Wet Processes for Growth of SiO_2 Based Layers

The growth of SiO_2 films at low temperature is very attractive for most device applications due to reduced capital cost, and high throughput.

A simple chemical oxidation of Si at room temperature is a very desirable technique for many device applications. Good passivating SiO_2 based layers can easily be grown on Si (i.e. by using HNO_3 based solutions). However, to the best of our knowledge, no thicker than a few monolayers of SiO_2 have been reported as yet.

Thicker SiO_2 layers can be grown by anodic oxidation of the underlying Si substrates. However, even if these layers are of good enough quality for certain optoelectronic applications such as discrete electronic devices, they are reported not to be very stable for

microelectronic device applications. Additionally, since the anodic oxidation process is not compatible with most of the metallization schemes, their applications are going to be limited even if the stability problem could (and most probably can) be solved.

Recently, in a series of publications researchers from Japan, China and Taiwan, claim to have successfully grown SiO_2 layers on Si by using a low temperature (30 to 50°C) solution growth (see Appendix 2). From a chemical reaction kinetics point of view, and based on our own experimentation, we question the validity of their claimed results.

Wet Chemical Growth of SiOF Layers

Using an acidic solution, proof-of-concept SiOF layers have been grown by SPECMAT, Inc. at room temperature in the dark on 2" p-Si (111) substrates. The layers have:

- A thickness from about 0.07 to 0.35 m (as determined from the color code and ellipsometry)
- Good uniformity
- An etch rate in 10% HF and buffered HF much lower than that of SiO_2 thermal oxides.

The exact composition of these oxides, derived from ESCA data, and some other determinations, such as ellipsometry-related parameters are in progress. In Fig. 6a and Fig. 6b are given two examples of ellipsometric data of two chemical oxides with different concentrations of fluorine. For comparison, in Fig. 7 and Fig.8 are given the same ellipsometric data for a thermally oxidized SiO2 and resistive evaporated SiO, respectively.

Note that the extinction coefficient (k) of sample #6 has a very small variation as a function of wavelength. Since we could not find any data on SiOF, material fit (MSE) assumes that the sample contains 2 or 3 of the following 5 materials: SiO, SiO_2, voids (i.e. material is less dense than the reference material in literature), amorphous Si and crystalline Si. This explains why the MSE of sample 6 has such large values (a fit is considered good when the value of MSE is lower than around 25).

Appendix 4 - Porous Silicon

Following the discovery of its room temperature light emission, porous silicon (PS) is currently receiving wide-spread interest because of its potential application in electroluminiscent devices compatible with Si very large scale integration (VLSI). It has been suggested that structures with PS exhibit quantum size effects leading to an increase in the effective bandgap and show an efficient radiative recombination. Photoluminiscence (PL) from PS films with energies greater than the bulk silicon bandgap was first reported in 1984. Since its significance first became obvious in 1990 when efficient PL in the visible range was obtained at room temperature, external PL efficiencies of up to 10% have recently already been achieved.

Nanometer-size network of PS structures is usually formed in a concentrated HF-based electrolyte, by anodic dissolution of a silicon crystal. However, even a simple chemical (stain) etching under controlled conditions can produce the porous luminescent material.

For electrochemically formed PS structures, it has been known for several years that during the dissolution reaction in a concentrated HF electrolyte, the PS surface is covered by SiH bonds. The role of the surface has been invoked either as a part of the luminescence recombination scheme in PS, or as a key factor for surface passivation in order to prevent nonradiative recombination and thus reach a good luminescence efficiency. The hydride-passivated surface obtained after PS formation, and also on a planar silicon crystal after an HF dip, results in good electrical properties (e.g., low surface recombination velocity).

Chemical stabilization of the PS material and conservation (or enhancement) of the luminescence efficiency are two current challenges faced in the development of porous-silicon-based light emitters and other optoelectronic applications.