

NOVEL PASSIVATING/ANTIREFLECTIVE COATINGS FOR SPACE SOLAR CELLS.

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ABSTRACT

We are developing a novel process to grow passivating/antireflective (AR) coatings for terrestrial and space solar cells. Our approach involves a Room Temperature Wet Chemical Growth (RTWCG) process, which was pioneered, and is under development at SPECMAT, Inc., under a Reimbursable Space Act Agreement with NASA Glenn Research Center.

The RTWCG passivating/AR coatings with graded index of refraction are applied in one easy step on finished (bare) cells. The RTWCG coatings grown on planar, textured and porous Si, as well as on poly-Si, CuInSe₂, and III-V substrates, show excellent uniformity irrespective of surface topography, crystal orientation, size and shape.

In this paper we present some preliminary results of the RTWCG coatings on Si and III-V substrates that show very good potential for use as a passivation/AR coating for space solar cell applications. Compared to coatings grown using conventional techniques, the RTWCG coatings have the potential to reduce reflection losses and improve current collection near the illuminated surface of space solar cells, while reducing the fabrication costs.

1. INTRODUCTION

The main reasons for low current collection efficiency near the illuminated surface for many conventional planar and textured terrestrial and space solar cells are: increased reflection, and damaged AR coating/emitter interface.

The anti-reflection (AR) coating is one of the most important part of a solar cell design. It allows a substantial reduction in the amount of reflected light [e.g. 1,2]. A proper single layer AR coating (e.g. MgF₂, SiO₂, SiO, TiO₂ and Ta₂O₅) can reduce reflection to about 10%, averaged over the 0.4 μm to 1.1 μm wavelength range. A double layer AR coating can reduce reflection to 3 - 5% on the average. For uncoated Si cells, a textured front surface, e.g. regularly spaced pyramids or porous silicon (PS), can lower the reflection coefficient to 12 - 18%. For textured surfaces with well designed single or double layer AR coatings, such as ZnS/MgF₂, TiO₂/MgF₂, and TiO₂/Al₂O₃ [3, 4] the reflection is on average down to 2 - 5%. Due to the difficulty of depositing uniform AR coatings on textured surfaces, especially on fine pyramid-coated surfaces, some cell manufacturers are choosing not to use any AR coating. The penalty they pay is up to 10% loss in efficiency along with surface stability problems.

Depositing/growing uniform AR coatings on PS is even more difficult using conventional techniques due to the nanometer-sized features of the PS structure: uniform, stable coatings have yet to be produced.

For simple cell structures, conventional AR coating layers are deposited directly onto the emitter surface usually by physical vapor deposition and spin-on techniques. This approach destroys the stoichiometry at the cell's front surface which by increasing the scattering at the grain boundaries, decreases the AR coating/semiconductor interface transparency and introduces additional defects at the emitter/AR coating interface. For Si cells the above problems can be partially addressed by using a combination of a thin passivating oxide (e.g. SiO_2 , SiN_x) and a single or double layer AR coating. Using this approach contributed, for example, to the improvement of the PERL one sun terrestrial Si solar cells efficiency, at the University of South Wales [5] and at SunPower [6], to about 24% (AM 1.5, 25°C), and 20.3% (AM0), respectively.

This approach has been proposed for III-V solar cells as well. For instance, for InP solar cells we suggested a three layer AR coating structure, namely $\text{In}(\text{PO}_3)_3/\text{ZnS}/\text{MgF}_2$ [7]. In this case the thin $\text{In}(\text{PO}_3)_3$ layer (about 10 nm thick) is grown by chemical oxidation of the emitter surface. Its role is to passivate the surface, and to prevent damage to the emitter surface during the evaporation of the second layer. Technological difficulties due to insufficient development and probable cost constraints, have prevented the use of the three layer AR coating structures for both commercial terrestrial and space solar cells.

We are proposing a novel RTWCG technique to grow a passivation/AR coating with graded index of refraction on terrestrial and space solar cells. The RTWCG process of SiO-based coatings was pioneered [8], and is under development at SPECMAT, Inc., under a Reimbursable Space Act Agreement with NASA GRC.

At the 2nd World PVSEC Conference we demonstrated the effectiveness of using the RTWCG technique to grow stable passivating oxide layers on planar silicon cell surfaces [9]. In this paper, we demonstrate the potential of using this simple-to-apply RTWCG process to grow cost effective passivating/AR coatings for space solar cell applications. The next sections will provide some preliminary results on the use of RTWCG coatings for Si and GaAs solar cells.

2. RESULTS AND DISCUSSION

2.1 RTWCG Process

SPECMAT's approach involves a Room Temperature Wet Chemical Growth (RTWCG) process of SiOX thin films on large area silicon (Si) substrates. The composition of the RTWCG oxide layers is $\text{Si}_x\text{O}_y\text{X}_z$, (SiOX) where x is from 0.9 to 1.1, y is from 0.9 to 1.9 and z is from 0.01 to 0.2. X is usually carbon (C), and nitrogen (N) of various concentrations depending on the redox system being used [8].

To date, most of the work has been concentrated on the growth and characterization of SiOX coatings on Si. However, the RTWCG process has also been tried in order to grow dielectric coatings on other than Si substrates such as GaAs, GaP, AlGaAs, and CuInSe_2 thin films. These latter coatings aren't however fully characterized yet.

The SPECMAT proprietary, patent pending process comprises soaking the substrates into the growth solution. The process utilizes a mixture of inexpensive liquid precursors along with homogeneous

catalysts that increase the growth rate. Non-invasive acidic or alkaline solutions are added to the growth system in order to adjust the pH.

The composition of the RTWCG coatings and their growth rate is dependent on a number of factors such as the nature of the precursors and additives, pH, the catalyst, and to a lesser extent on the type of the substrate (crystalline orientation, and doping type). The RTWCG rate of SiOX coatings on single crystal Si surfaces is from 2 nm/minute to up to 64 nm/minute, depending on the composition of the liquid-phase growth system.

2.2 Surface Passivation

2.2.1 Si Surfaces

Without any need for post-growth annealing, the RTWCG process produces SiOX coatings that are chemically stable and passivate well the Si surfaces. However, both the chemical stability and passivating properties of these SiOX coatings depend on their chemical composition which is in turn dependent on the chemical system being used.

Within our work, the best candidate for surface passivation is the Si-O-C-N coating grown in the BS:B19 chemical system. An example of an XPS profile of a RTWCG Si-O-C-N coating is shown in Fig.1. The relatively large surface C concentration and the relatively large N interface concentration explain the excellent chemical stability, and good surface passivation capability of this oxide.

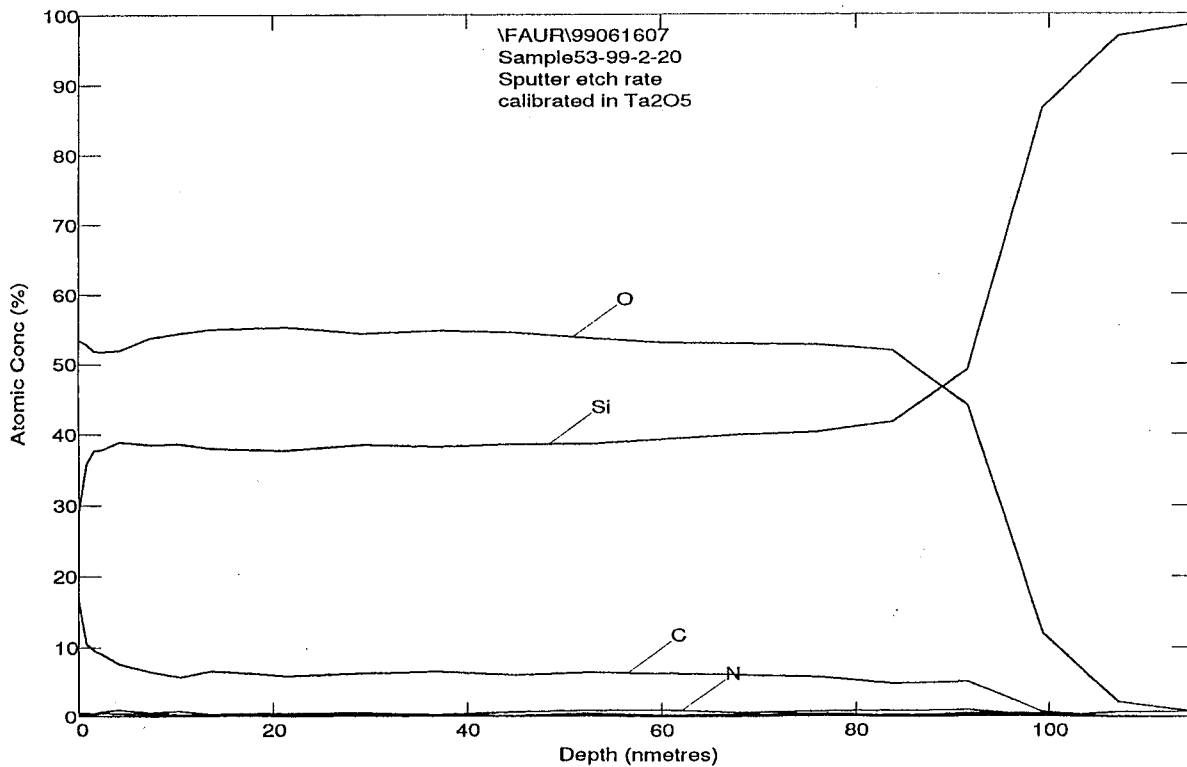


Fig. 1 XPS depth profile of a RTWCG Si-O-C-N coating (about 110 nm thick), grown on p-type Si in the BS:B19 chemical system. Growth time:3 minutes.

No in-depth investigation of the RTWCG SiOX/Si interface has been performed thus far. However, the good passivating properties of the RTWCG Si-O-C-N coatings on Si substrates are suggested by an analysis of coated devices, e.g. the improvements in the performance parameters of VMJ Si cells, as can be seen in paragraph 2.4.2.

2.2.2 GaAs Surfaces

Very uniform RTWCG coatings have been grown on both n- and p-type GaAs substrates in several chemical systems. These coatings haven't been fully characterized yet. In order to show the potential of these as-grown coatings for surface passivation of GaAs, we present some recent room temperature photoluminescence (PL) data acquired on 5 n-GaAs samples, prior to and after the growth of RTWCG coatings. The peak intensity of the PL spectra are compared in Fig.2. The coatings were grown in five different chemical systems. For consistency, the growth time (2 to 10 minutes) has been adjusted such that the oxide thickness has about the same thickness, as estimated from our calibrated color code (e.g. about 100 nm - dark blue). The data for two of the coatings, 115-99-2, and 116-99-5, show that the PLI increases noticeably compared to the uncoated surfaces. This data show that the room temperature oxide can be grown without damaging the GaAs surface and may provide some electronic surface passivation of the GaAs surface.

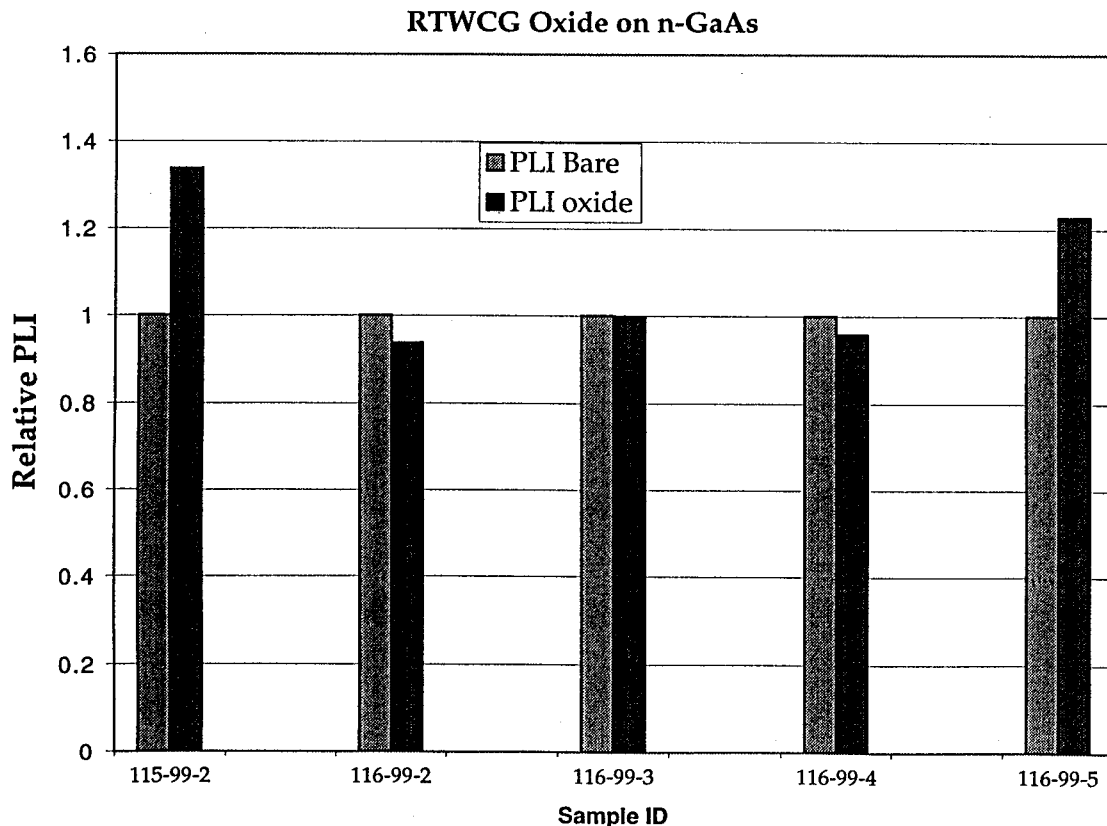


Fig. 2. Relative PLI of RTWCG coated vs. bare surfaces for coatings grown on n-GaAs substrates in five chemical systems.

2.3 Optical Properties of RTWCG Coatings

2.3.1 Reflectance

Low reflectivity coatings require a multi-layered structure that has an increasing index of refraction relative to the depth of the coating layer to the underlying Si surface. We have previously demonstrated that on Si substrates, by varying the chemistry of the chemical system it is possible to grow Si-O-X AR coatings with graded “n” [9]. Ellipsometric analysis of various RTWCG SiO-based coatings have shown that the index of refraction for the C-rich top layer is smaller than that of SiO₂; it is between that of SiO₂ and SiO for the mid-layer, and between that of SiO and that of the underlying Si substrate for the Si-rich interfacial layer.

2.3.1.1 Si substrates

For bare Si, the loss of incident light amounts to about 42% at long wavelengths (1.1 μm), has a minimum of 37% at 1 μm and rises to about 54% at short wavelengths (0.4 μm) (see Fig. 3-a). A proper single layer AR coating can reduce the reflection to about 10%, averaged over this wavelength range, and a double layer AR coating can reduce it to around 3% on the average. The RTWCG Si-O-C-N coating in Fig.3-b, grown in similar conditions as the coating in Fig.2, has a reflectivity of below 1.8% from 600 nm to 950 nm and below 3.3% on the average from 400 nm to 1100 nm.

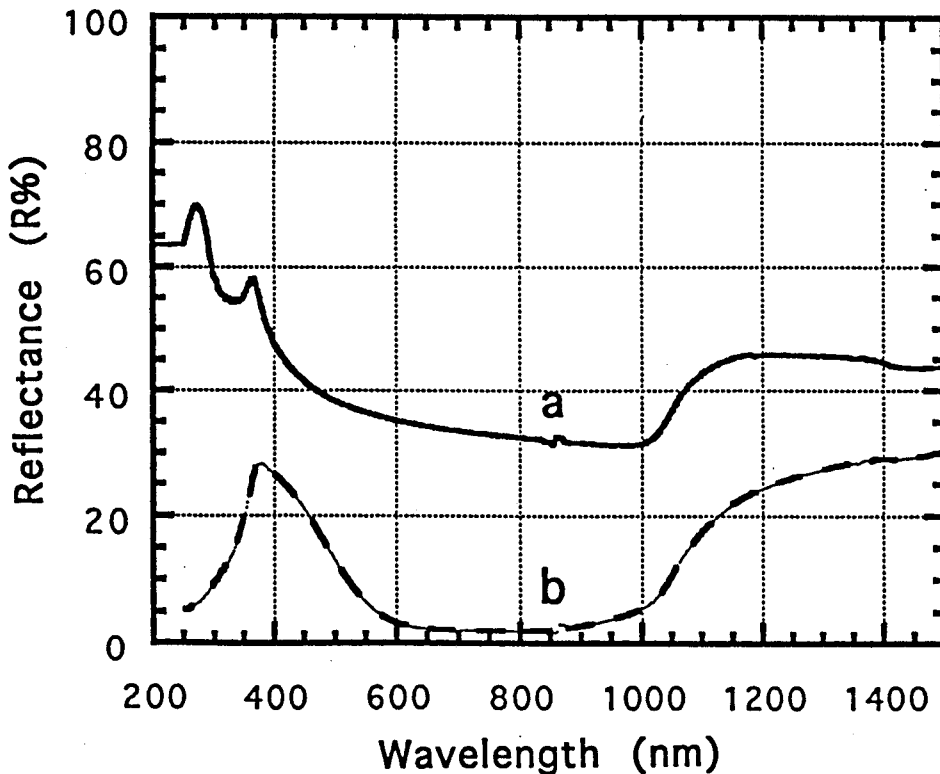


Fig. 3 Reflectivity of: (a) bare and (b) RTWCG Si-O-C-N (about 0.1 μm thick) coated p-Si wafer.

Recent work was directed toward increasing the reflectivity of the unusable red part of the solar spectrum, while maintaining the low reflectivity in the visible. The first good results, such as shown in Fig. 4, show an increase in red reflectivity to over 60%. However, an increase in the red reflectivity also increases the blue reflectivity. More work is still necessary to find a way of increasing the red reflectivity while maintaining the visible reflectivity and lowering the blue reflectivity.

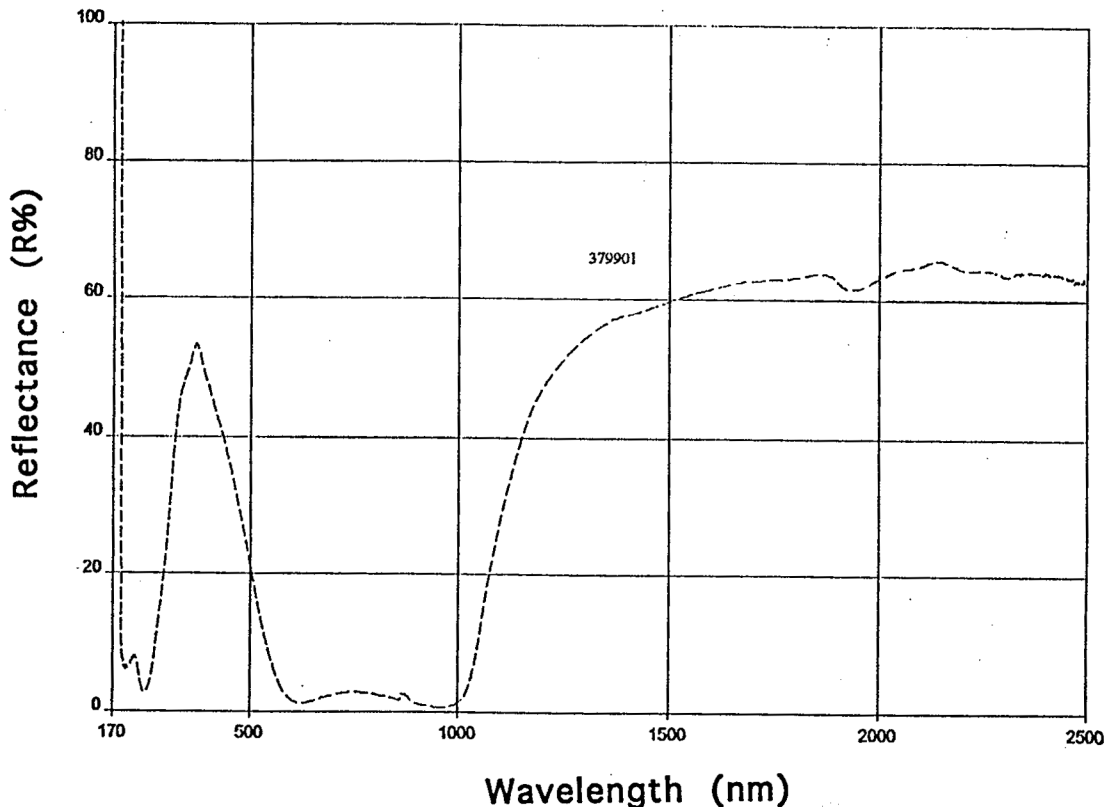


Fig. 4 Reflectivity of a RTWCG Si-O-C-N (about 120 nm thick) coated p-Si wafer.

2.3.1.2 GaAs Substrates

As mentioned above, the work on RTWCG dielectric coatings on GaAs has only recently been started. The chemical system hasn't yet been optimized either for the passivating nor for the optical properties of the oxide. The reflectivity plots of the five n-GaAs RTWCG coated substrates as compared to the reflectivity of a bare substrate in Fig. 2 are shown in Fig 5. As seen, the 115-99-2 and 116-99-5 coatings might qualify the RTWCG oxide for the dual use as a passivation/AR coating for GaAs. Still more work is necessary to further decrease the reflectivity of the RTWCG coated GaAs, while increasing its passivation capabilities.

2.3.2 Transmittance

Qualitative Transmittance studies of the RTWCG coatings have thus far been conducted only on Si-O-C-N coatings grown on Si substrates. The transparency of these coatings was qualitatively evaluated from the values of the extinction coefficient (k) derived from ellipsometric measurements in

the 400 nm to 800 nm wavelengths range. Si-O-C-N coatings similar to those in Fig.3 have "k" values that are at least 3 times lower than that of a thermal SiO₂ of a similar thickness (about 100 nm) grown in dry oxygen at 1000°C on a similar Si substrate.

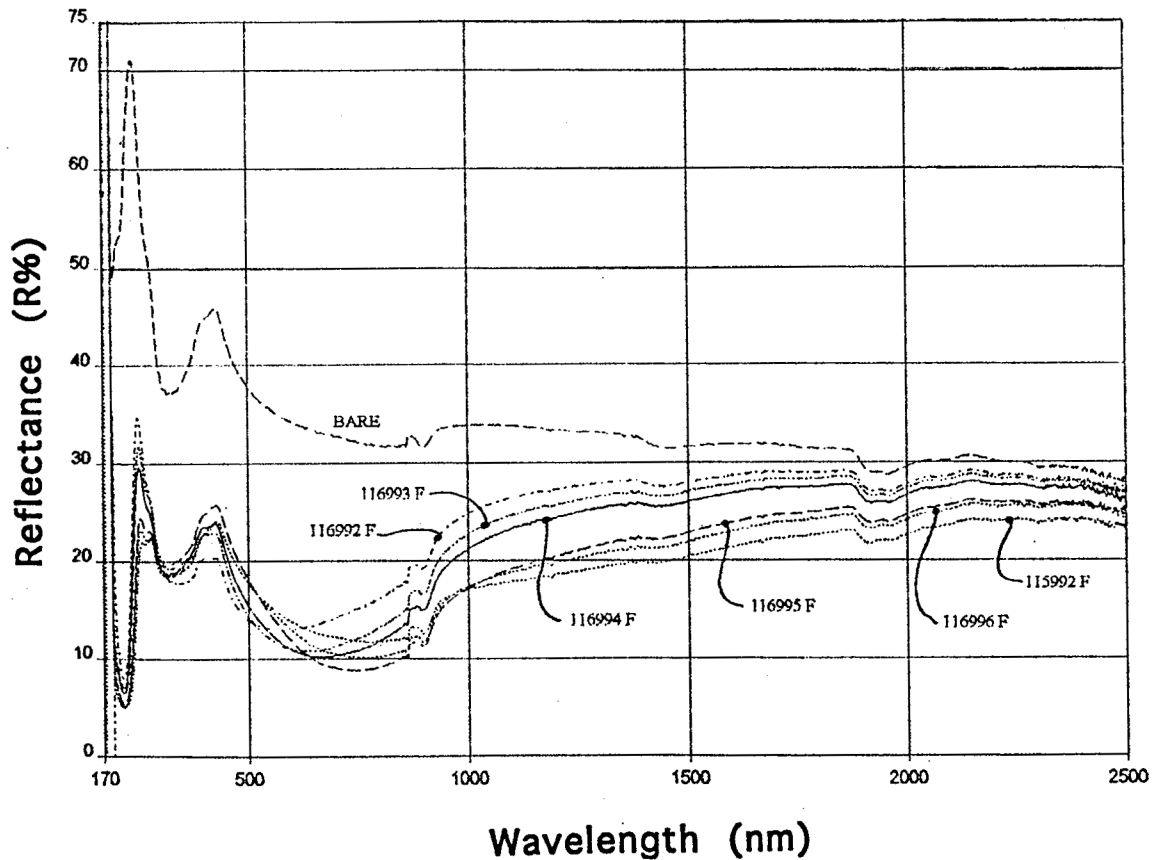


Fig. 5 Reflectivity plots of RTWCG coated and bare n-GaAs samples in Fig. 2.

2.4 Si Solar Cells

2.4.1 Planar n/p Si Solar Cells

For our preliminary study we used several dozen readily available planar 2x2 cm² n/p Si solar cells with an AM0, 25°C efficiency of about 7% (bare cells). RTWCG Si-O-C-N coatings were grown in 3 to 5 minutes using several chemical systems. The performance parameters were measured under AM0, 25°C conditions at NASA GRC prior to and after the coatings. A selection of the performance parameters can be found in Table 1. After the RTWCG SiOX coating, the only treatment the cells received prior to the AM0 measurements was a DI water rinse and followed by N₂ drying.

The increase of AM0 efficiency of coated relative to bare cells was from 32% to up to 37.3%. For these cells the gain in efficiency was mostly due to corresponding gains in I_{SC}, with little or no change in V_{OC} or FF values. The explanation might have to do with the fact that the surfaces of the 15 year old planar cells could not be properly cleaned prior to growing the Si-O-C-N coating, without removing some or all front grid fingers. For instance, a one minute dip in 5% HF solution started to remove some of the front grid fingers. To avoid this, prior to the AM0 measurements, the front surfaces

of the bare cells were only cleaned with organics, followed by a few seconds dip into a 2% HF bath. This surface treatment may have left some contaminated native oxide on the surface. This might explain the apparent lack of surface passivation provided by the Si-O-C-N coating. The same coating applied to the surfaces of a Si VMJ cell which was properly cleaned prior to the oxide growth, clearly passivated well the Si surfaces. In any event, although the passivating quality of this room temperature Si-O-C-N coating is certainly not yet as good as those of CVD grown Si₃N₄ or thermal SiO₂ thin films, for which sensitive gains in V_{OC} have been reported, the optical properties of this simple to apply coating is as good or better than those of conventional two layer AR coatings.

Table 1. AM0, 25°C performance parameters of selected 2x2 cm² n/p Si cells prior to (bare) and after RTWCG of Si-O-C-N coatings. Growth time: 3 to 5 minutes; Oxide thickness: 95 to 120 nm; No annealing.

Cell	Bare Cell				Coat. Cell				(η _{ox} -η _{bare})/η _{bare} (%)
	I _{sc} (mA)	V _{oc} (mV)	FF (%)	η (%)	I _{sc} (mA)	V _{oc} (mV)	FF (%)	η (%)	
Cox 12	89.2	583.9	75.2	7.16	118.9	579.5	75.0	9.45	32.0
Cox 27	88.0	573.1	70.4	6.49	117.2	572.7	71.8	8.81	35.7
Cox 23	88.3	570.9	68.7	6.33	119.9	571.0	69.5	8.69	37.3
Cox 12	After 16 months in air in a chemistry laboratory environment				121.8	573.7	72.6	9.27	
Cox 23					119.8	566.6	67.2	8.35	

In Table 1 are also shown the AM0 performances of two of the cells, Cox 12 and Cox 23, after being stored in air in a chemistry laboratory for about 16 months. As can be seen, there are no significant differences in the I_{sc}, while the small drop in V_{oc} and FF are to be expected due to humidity and contaminants adsorbed on the surfaces.

2.4.2 VMJ Si Solar Cells.

For this preliminary experiment some early Vertical MultiJunction (VMJ) Si solar cells [10] were provided to us by PhotoVOLT, Inc. The biggest contributor to efficiency loss in the Si VMJ cell structure is the fact that its illuminated surfaces, back surfaces, and two edge surfaces uncovered by metallization are high recombination surfaces with exposed junctions that are difficult to passivate. Also, traditional AR coatings are difficult to form on these cells because of temperature constraints and because of their configuration with the four exposed surfaces.

The RTWCG process grows SiOX coatings simultaneously on the four exposed surfaces. The performances on both sides of a Si VMJ cell were measured by PhotoVOLT, Inc. after cleaning and etching the bare "PV4-14-x" cell. The performances were measured after growing a RTWCG Si-O-C-N coating for three minutes, and subsequently for additional 0.5 minutes each, during the second and third growth.

After the initial 3 minutes growth the thickness of the Si-O-C-N oxide was evaluated from the color code at about 100 nm. The second and third growth each successively added about 15 nm to the thickness. After each growth, the only treatment the cell received was a rinsing in DI water and nitrogen drying.

After the measurements, following the second growth, the cell was measured again after two minutes under light. This slightly increased the cell performance parameters is due to a partial removal of humidity from the cell surfaces. The drop in performances after the third growth is consistent with reflectivity plots, such as in Figs. 2 and 3, which were acquired on Si-O-C-N coated Si surfaces with an oxide of about 110 nm thick. After the third growth, annealing the cell for 10 minutes in air increased all performance parameters noticeably. However, after a subsequent overnight annealing under similar conditions as above, no further change in the cell parameters was noticed. The short time illumination and the annealing experiments, might indicate the fact that the Si-O-C-N oxide is only hydrated at the surface. The approximately 15 hour annealing in air at 100°C gives a qualitative indication of the good stability of this room temperature oxide.

Table 2. Performance parameters of a bare and RTWCG Si-O-C-N coated VMJ Si concentrator cell (PV4 -14 -x). PhotoVolt, Inc. performed the initial etching and surface cleaning of the bare cell surfaces, as well as the performance parameter measurements.

		Etched and Cleaned	1 st Growth 3 min	2 nd Growth		3 rd Growth	
				Additional ½ min Growth	After 2 min Under Light	Additional ½ min Growth	10 min Annealing In Air At 100* C
Side 1	V _{oc} (V)	8.786	9.883	9.641	9.659	9.239	9.272
	I _{sc} (mA)	0.17	0.34	0.30	0.31	0.26	0.33
	FF	.5365	0.6073	0.579	0.579	0.5575	0.5570
	P _p (mW)	0.779	2.022	1.66	1.712	1.321	1.699
Side 2	V _{oc} (V)	8.699	9.672	9.951	9.909	9.363	9.575
	I _{sc} (mA)	0.15	0.30	0.33	0.35	0.28	0.35
	FF	.5139	0.5934	0.6005	0.6029	0.5660	0.5775
	P _p (mW)	0.672	1.741	1.989	2.095	1.494	1.919

Note that the V_{oc} and FF values for the VMJ cells increase significantly after the coating. These values, and the large increase in I_{sc}, after coating, cannot be explained simply by a reduction of optical-type losses. They offer a clear indication that surface passivation plays an essential role in increasing the maximum power (P_p) as much as three fold compared to that recorded for the bare cell.

3. CONCLUSIONS

In summary, our results show that using the novel RTWCG process of SiOX coatings, has the potential of improving the efficiency and stability of space Si solar cells. The process can lower the cost of conventional passivating/AR coating structures, and simplify the Si or GaAs solar cell structures. The

RTWCG process is very attractive for a one-step growth of surface passivation/AR coatings on Si and III-V solar cells because these coatings:

- ◆ passivate the surfaces;
- ◆ their reflectivity is equal to or lower than that of well designed double layers AR coatings;
- ◆ are transparent in the spectrum of interest;
- ◆ are physically hard, and non-straining on the substrate;
- ◆ should have good stability with respect to factors such as heat, humidity, prolonged exposure to UV light, and resistant to high fluences of energetic electrons and protons.

The RTWCG process for growing SiO-based coatings, once fully developed, should be an attractive alternative to conventional passivation/AR coating techniques for the Si, GaAs and other space solar cell manufacturers because the novel process:

- ◆ eliminates several concomitant photoresist, etching and surface passivation steps, thus reducing cell fabrication costs;
- ◆ after the RTWCG process, the contacts are readily solderable since the coating is not covering the metallization;
- ◆ the growth process should be applicable to any surface, irrespective of surface topography, crystal orientation, size and shape;
- ◆ has high output due to large growth rates;
- ◆ has reduced capital and materials costs;

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