

# POSS<sup>®</sup> COATINGS AS REPLACEMENTS FOR SOLAR CELL COVER GLASSES

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## ABSTRACT

Presently, solar cells are covered with Ce-doped microsheet cover glasses that are attached with Dow Corning DC 93-500 silicone adhesive. This general approach has been used from the beginning of space exploration, however, it is expensive and time consuming. Furthermore, as the voltage of solar arrays increases, significant arcing has occurred in solar arrays, leading to loss of satellite power. This problem could be ameliorated if the cover glass extended over the edges of the cell, but this would impact packing density. An alternative idea that might solve these issues and be less expensive and more protective is to develop a coating that could be applied over the entire array. Such a coating must be resistant to atomic oxygen for low earth orbits below about 700 km, it must be resistant to ultraviolet radiation for all earth and near-sun orbits and it must withstand the damaging effects of space radiation. Coating flexibility would be an additional advantage.

We have been exploring the use of newly discovered PolyOligomericSilSesquioxane (POSS<sup>®</sup>) materials with metallic additives for these applications. This technology has several significant advantages: the glass-like composition of POSS<sup>®</sup> provides excellent resistance to radiation and VUV and the POSS nano-building blocks can be incorporated into all known plastics using conventional polymerization or compounding techniques that can lead to tailored optically transparent materials with entirely new performance levels. We will report on the results of POSS coatings containing various additives (e.g. organic and metallic). Thick samples (150  $\mu\text{m}$ ) are being applied to various substrates and have been exposed to 2 MeV protons up to  $10^{15}$   $\text{p}^+/\text{cm}^2$  and UV/VUV irradiation up to 1000 hrs. The 2 MeV protons are absorbed within about 85  $\mu\text{m}$  depth with  $\sim 2\mu\text{m}$  straggle so the damage is contained entirely within the layer. Results of these tests with several POSS<sup>®</sup> matrices will be presented.

## INTRODUCTION

Current practice, for protecting solar cells from the space environment involves attaching 150  $\mu\text{m}$  thick cover glass to the top surface of the individual cells with Dow Corning 93-500 silicone adhesive. To protect the adhesive from UV degradation the glass is doped with cerium. Antireflective coatings are applied to the finished assembly to enhance performance. This fabrication process is expensive and time consuming.

Although this arrangement has been successful for solar arrays with standard voltage configurations, when arrays have been designed for higher voltages, significant arcing has occurred resulting in the total loss of satellites. The cause of this arcing has been traced to differential voltages between strings and the close spacing between them with no insulation covering the edges of the solar cells. The problem could be ameliorated if spacing were increased and the cover glass extended over the edges of the cell. But higher voltage would come at a cost of decreased packing density and subsequent decrease in system's specific power.

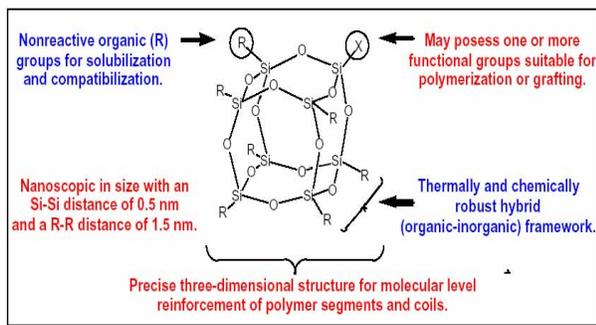
Another solution would be to coat the entire array with a curable insulating material that would cover the cell surface and conform to the edges. The challenge of this approach is to develop a material that maintains a high level of transparency across the full range of the solar cell's conversion spectra during long periods of exposure to space radiation, VUV and atomic oxygen.

Development of a suitable material and implementation of high voltage arrays would enable new classes of high power satellites, open up new orbits for use, including regions of high radiation flux such as within the Van Allen belts, and new propulsion systems such as direct drive solar electric propulsion for promoting satellites from low earth orbit into geosynchronous earth orbit (GEO) or beyond.

## POLYHEDRAL OLIGOMERIC SILSESQUIOXANE

A new class of materials has recently been developed by the Air Force Research Laboratories at Edwards Air Force Base and exclusively manufactured by Hybrid Plastics Inc. (Hattiesburg, MS) called POSS<sup>®</sup>; polyhedral oligomeric silsesquioxane. POSS<sup>®</sup> is a nanostructured polymer/ceramic hybrid, which incorporates the mechanical and processing attributes of a polymer while incorporating the stability and durability of a ceramic material. POSS<sup>®</sup> building blocks are comprised primarily of an inorganic silicon-oxygen cage structures 0.5 to 3 nm diameter, shown in figure 1. The exterior of the nanostructure is covered with sites that can be populated with a variety of functional groups (-R). The substitution of polymer monomers onto these sites allows the siloxane cage be bonded within the polymer structure and dispersed within the material on a molecular level. Additionally, other species can be substituted onto the cage to enhance the inherent optical,

radical trapping and/or radiation tolerance characteristics. The POSS's polymer characteristics allow the material to be applied using a variety techniques including, spin coating,



**Figure 1:** Anatomy of a POSS<sup>®</sup> nanostructured<sup>®</sup> chemical

doctor blade and spray coat using standard methods. The material is cured using catalysts, elevated temperature or UV light depending upon the nature of the base polymer bound to the silica cages. The surface layer can then be glassified by exposure to an oxidizing environment.

Gilman [1] and Gonzalez [2] have reported that when exposed to atomic oxygen POSS forms a silica passivating layer, which protects the underlying material from further degradation. The formation of a protective layer in response to exposure to an oxidizing environment gives the material benefits that cannot be achieved with standard protective coating methods which tend to fail once the coating is compromised by either coating defects or orbital impacts.

## EXPERIMENTAL DESCRIPTION

Various POSS enhanced materials have been evaluated. The focus of this paper is PM1287, a nano-cage structure substituted with vinyl groups and various concentrations of phenyl groups to provide additional radical trapping. The PM1287 is cured using a combination of thermal and catalysis initiators. The samples were coated onto standard 3.5 cm by 2.5 cm Thales CMG200 Ce-doped microsheet glass slides. The coatings were applied ~150 $\mu$ m thick by brush method. Optical transmission of the samples was measured between 200 and 1200 nm with a Shimadzu UV3600 UV-VIS-NIR Spectrophotometer using an uncoated Ce-doped slide as the background reference. Because an uncoated slide was used as the reference, the data do not take into account transmittance differences due to reflection at the interfaces. After initial characterization samples were sent for irradiation.

### Proton Irradiation Facility:

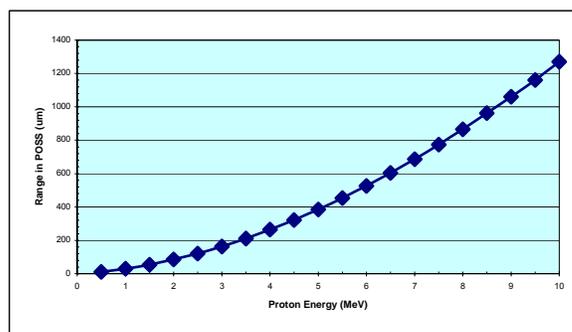
Proton irradiations were performed in a NEC Pellatron 2 MV Dual Source Tandem Accelerator shown in figure 2. This accelerator can provide a beam of protons from a SNICS ion source with energies from 100 keV to 4 MeV.

All samples were irradiated with 2 MeV protons. The initial irradiation was a dose of  $10^{12}$  protons/cm<sup>2</sup> (p+/cm<sup>2</sup>). After each irradiation the samples were visually inspected,



**Figure 2:** NEC Pellatron 2 MV Dual Source Tandem Accelerator

photographed and transmission spectrum characterized before continuing irradiation. The following irradiation total dose schedule was used, second irradiation  $10^{13}$  p+/cm<sup>2</sup>, third irradiation  $10^{14}$  p+/cm<sup>2</sup> and finally a fourth irradiation  $10^{15}$  p+/cm<sup>2</sup>. Beam currents ranged from 55 nA for the lower doses to 190 nA at the final dose ( $10^{15}$  p+/cm<sup>2</sup>). The proton beam was scanned over a 5 cm diameter area with the samples at room temperature. Scan rate was 517 Hz in the x-direction and 64 Hz in the y-direction. All irradiations were done in vacuum,  $5 \times 10^{-7}$  to  $1 \times 10^{-6}$  torr at room temperature. Two samples were irradiated at a time.



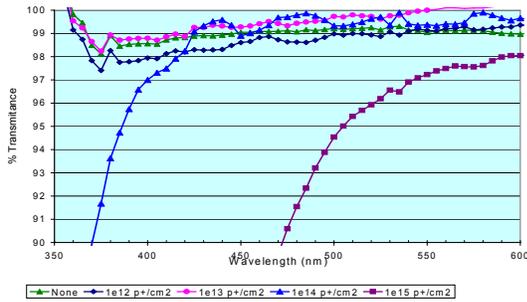
**Figure 3:** Proton range-energy curve in POSS with 1.2 g/cm<sup>3</sup> density

To ensure complete blocking of the proton beam in the 150 $\mu$ m thick film the penetration distance was calculated using SRIM [4]. The range-energy calculation for the POSS materials is shown in figure 3. At 2 MeV, the range of the protons in POSS is 85  $\mu$ m with a straggle of ~2  $\mu$ m. Thus the entire proton beam is expected to be absorbed within the 150  $\mu$ m thick POSS layer.

## EXPERIMENTAL RESULTS

The PM1287 resin was tailored to have different concentrations of substituted phenyl group on the siloxane cage. The percentages indicated in this paper indicate the mole percentage of the phenyl groups. A total of 4 samples were made: 10% phenyl, 15% phenyl, 20% phenyl and 50% phenyl. The 50% phenyl PM1287, shown in figure 4, demonstrated the best proton radiation tolerance. The region of interest is limited to between 300 and 600 nm. Below 300

nm the CMG200 slide has limited transparency and above 600 nm the film transmittance does not vary with wavelength. For the 50% phenyl sample, the transmittance did not decrease until the  $10^{14}$  p<sup>+</sup>/cm<sup>2</sup> dose and substantial darkening and cracking did not occur until the  $10^{15}$  p<sup>+</sup>/cm<sup>2</sup>

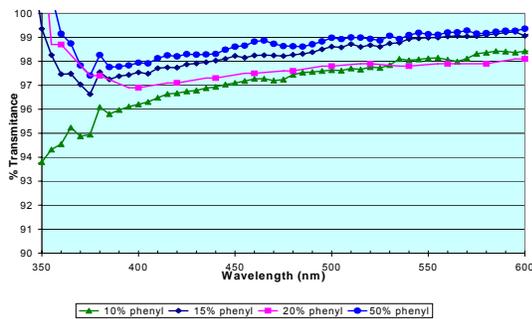


**Figure 4:** Spectral transmission curves of PM1287 with 50% phenyl



**Figure 5:** Images of PM1287 with 50% phenyl dose as shown in figure 5.

For the  $10^{12}$  p<sup>+</sup>/cm<sup>2</sup> dose, the highest phenyl formulation (50%) provided the best radiation tolerance while the lowest concentration (10%) provided the least tolerance as seen in figure 6. Because the intermediate samples 15% and 20% do not follow this trend there may be additional factors (i.e.



**Figure 6:** Spectral transmission curves of PM1287 with 10 to 50% phenyl additions at  $10^{12}$  p<sup>+</sup>/cm<sup>2</sup>

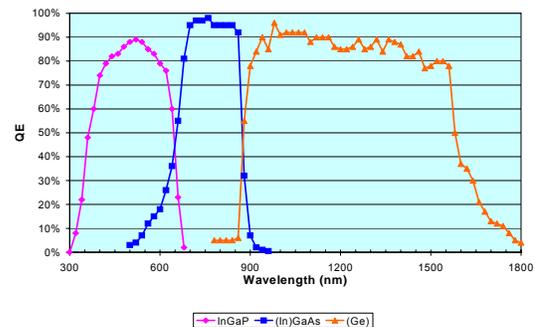
catalyst loading) that affect the radiation tolerance.

In addition to darkening, the sample films showed evidence of structural stress at large total dosages. The damage typically started as micro-fractures on the surface which then developed into long cracks, followed by delamination and separation from the cover glass substrate. The 10% and 15% phenyl films cracked during the  $10^{13}$  p<sup>+</sup>/cm<sup>2</sup> irradiation,

the 20% cracked 72 hrs after the  $10^{13}$  p<sup>+</sup>/cm<sup>2</sup> test, and the 50% phenyl film developed one long crack after  $10^{15}$  p<sup>+</sup>/cm<sup>2</sup>. The mechanism for this internal stress is currently under investigation.

### RELATIONSHIP TO SOLAR CELL PERFORMANCE

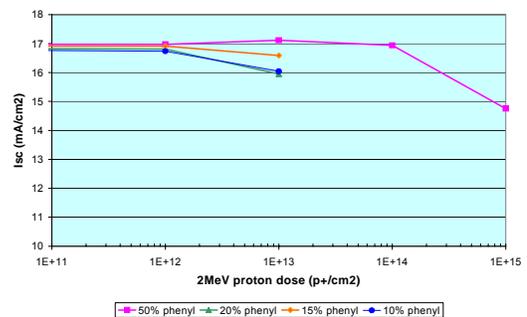
The effect of changes in the spectral transmittance upon the performance of the underlying solar cell is dependent upon the region of the spectrum in which the degradation is occurring. In order to evaluate the effect radiation induced transmission losses the transmission spectrum was multiplied by the quantum efficiency, shown in figure 7, of a triple junction solar cell [5] (Emcore ATJ) to determine the short circuit current, I<sub>SC</sub>. Because the second (InGaAs) and



**Figure 7:** External quantum efficiency of an Emcore ATJ cell

third junction (Ge) have a current excess and most of the transmission loss for the POSS material is in the spectral region of the first junction (InGaP) the I<sub>SC</sub> analysis was limited to the first junction spectral response region.

For ATJ cell the I<sub>SC</sub> was calculated to be 17.1mA/cm<sup>2</sup>, which agreed with data provided on Emcore's product datasheet.



**Figure 8:** Calculated I<sub>SC</sub> variation with 2 MeV proton dose for PM1287-coated samples

Because the transmittance measurements were made using an uncoated cover glass reference, the data do not incorporate effects due to reflective losses at the interfaces. A final solar cell design tailored for the POSS coating would include optimization of the antireflective coating between the cell and the cover material.

As can be seen in figure 8, the PM1287 with 50% phenyl showed no decrease in  $I_{SC}$  for dosages up to  $10^{14}$  p<sup>+</sup>/cm<sup>2</sup>. Even at lower phenyl substitutions, the  $I_{SC}$  decrease was less than 5% for the sample containing 10% phenyl with a dose of  $10^{13}$  p<sup>+</sup>/cm<sup>2</sup>. It is important to note that no cell degradation has been taken into account. A dose of  $10^{14}$  p<sup>+</sup>/cm<sup>2</sup> is roughly equivalent to a 2000-year mission in GEO. Therefore the stability of this POSS coating is quite acceptable for this type of mission.

## DISCUSSION

The results presented show that the material compositions studied here show a regular progression in resistance to damage by 2 MeV protons as the phenyl content increases in the PM1287 resin. It is important to note, that with the calculated  $I_{SC}$  of an ATJ cell with these coatings, the PM1287 with 50% phenyl substitutions decreased only about 13% at  $10^{15}$  p<sup>+</sup>/cm<sup>2</sup>. This is exceptional durability. The mechanisms behind the role of the POSS additives are under study and may lead to even greater resistance. However, we can speculate that the chemical stability of the phenyl group may play a key role in limiting proton damage in these tests. Substitution of atoms with high cross sectional area and known radiation shielding properties to the POSS functional sites may also further increase the durability of these coatings. The inclusion of metallic elements can lead to additional stopping power as has been shown for Gd-POMS and neutrons [6].

While these results are very encouraging, many other space durability tests must proceed before any final conclusions can be drawn. Preliminary UV/VUV exposure has indicated that the film is stable for exposures up to 1024 equivalent sun hours. At this level, the film had a calculated decrease in  $I_{SC}$  for the Emcore ATJ cell of ~3% for the PM1287 50% phenyl composition. Ongoing efforts to increase the radical trapping of the POSS functional groups are working to minimize this UV degradation. The cracking seen in the coatings will also be explored but may well be due to the

proton dose rate or other conditions of the irradiation.

These coatings must be applied to current production cells to confirm that no inherent damage occurs to the cells; however, preliminary work with thin film solar cells uncovered no problems with performance [7]. As expected,

those tests did confirm that the antireflection coating on the cell will have to be adjusted to match the refractive index of the POSS material. POSS coatings have been applied to

current multijunction solar cells as shown in figure 9. As can be seen, the coating conformally coats the cell. Conformal coating of the cells in a space array can serve to prevent arc discharges that have crippled many satellites.

Deposition parameters continue to evolve in order to produce uniform coatings with controlled thickness. Coatings can be applied by many techniques such as brushing, spraying, spin coating. Coating thickness can similarly be varied from micrometers to 6 or more mils thus providing adaptability to different mission needs.

## CONCLUSIONS

These tests represent preliminary screening of the concept of an easy-to-apply, space durable, conformal encapsulant for solar arrays. The results demonstrate that these coatings are exceptionally resistant to damage by 2 MeV protons. More materials combinations and modifications will be tested over a range of conditions, not just proton exposure. Furthermore, direct application of these coatings onto production solar cells is an essential next step. However, despite positive results from diligent ground testing, the ultimate verification will only come through successful demonstration in space.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. J.W. Gilman, D.S. Schlitzer and J.D. Lichtenhan, "Low Earth Orbit Resistant Siloxane Copolymers", J. Appl. Polymer Sci. **60**, 591-596 (1996)
2. R.I. Gonzalez S.H. Phillips and G.B. Holland, "In Situ Oxygen-Atom Erosion Study of Polyhedral Oligomeric Silsesquioxane-Siloxane Copolymer", J. Spacecraft and Rockets, **37**, #4, 463-467, (2000)
3. J. D. Lichtenhan, J. J. Schwab, W. A. Reinert, "Nanostructured Chemicals: A New Era in Chemical Technology," Chemical Innovation January 2001 pp 3-5. (<http://pubs.acs.org/subscribe/journals/ci/31/special/0101lead.html>)
4. J.F. Zeigler and J.P. Biersack, "SRIM 2003.26" Srim.org, 1201 Dixona Dr, Edgewater, MD 21037, 2002.
5. Private communication: N. S. Fatemi, P. R. Sharps, M. A. Stan, D. J. Aiken, J. S. Hills, M. B. Clevenger and M. Sherwin, "Production of Very High Efficiency Advanced Triple-Junction (ATJ) Space Solar Cells at Emcore Photovoltaics", Space Power Workshop 2003, April, 2003
6. J. Spratt, et. al., "A Conformal Coating for Shielding Against Naturally Occurring Thermal Neutrons", to be published in Transactions of Nuclear Science, December 2005
7. H. W. Brandhorst, J. D. Lichtenhan and B. X. Fu, "A POSS Coating for Thin Film Solar Cells", pp. 778-781, Proceedings of the 31<sup>st</sup> IEEE Photovoltaic Specialists Conference, January, 2005

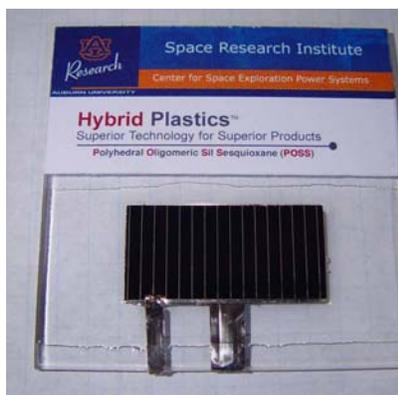


Figure 9: Solar cell with POSS conformal coating