Graded Index Sol-Gel Antireflection Coatings

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***Abstract* — We explore graded index antireflection coatings that can reduce reflection of light at the ambient/cell or ambient/module boundary at all wavelengths and incidence angles. Simulations show that graded index coatings individually enhance absorption in solar cells across nearly the entire wavelength range. Silica sol-gel coatings with varying refractive indices deposited onto glass and silicon substrates are used to form graded index coatings, and the sol-gel layer processes have been adjusted so that the refractive indices are tunable from n=1.1 to n=1.5. Reflectance measurements also show that reflectivity decreases across the entire spectrum with added sol-gel multilayers.**

***Index Terms* — Solgel, antireflection coating, photovoltaic cells, silicon.**

I. Introduction

In order to enhance light absorption in solar cells and modules, antireflection coatings (ARC) are used to reduce Fresnel reflection. Reflection occurs when light travels between media with different refractive indices. A single-layer ARC can significantly reduce reflection and multiple-layer graded index coatings can act as effective ARCs over a larger spectral range. Typical ARC processes require fabrication of layers of optically transparent material with refractive indices intermediate between ambient and semiconductor values on the solar cell. Most solids have refractive indices of at least 1.5 (~ refractive index of glass) preventing graded index ARCs from beginning with refractive index values near unity. [1]

Sol-gel chemistry enables creation of porous gels with tunable indices that can approach n=1. The most common gels made are composed of silica from various precursors including metal alkoxides, water, acid/base catalyst, and a solvent medium. Sol-gel chemistry uses hydrolysis and condensation reactions to transform a colloidal solution into a solid network (gel) (Figure 1). Gel formation processes use various acidic and/or basic precursors; the main factors affecting processability are whether the gel is more colloidal or polymeric and the time needed to gel. The gel refractive index can be tuned based on the composition of the sol as well as the drying process. [2]

After the gel forms, there is still solvent in the pores of the network. If the gels are allowed to air dry at ambient temperatures, the liquid in the pores will evaporate. However, due to capillary stress, when the liquid evaporates, some of the pores will collapse, leading to densification of the gel and a higher refractive index. Gels dried by this method are called xerogels. Xerogels, though still porous, are unable to reach refractive indices near unity. To obtain ultralow density gels, a supercritical drying process can be used. Under supercritical drying methods, the capillary stresses are avoided and the pores remain largely intact forming extremely porous gels with lower densities and refractive indices. [3] We investigate here the range in thickness and refractive index over which stable coatings are attainable by dip coating and spin coating.

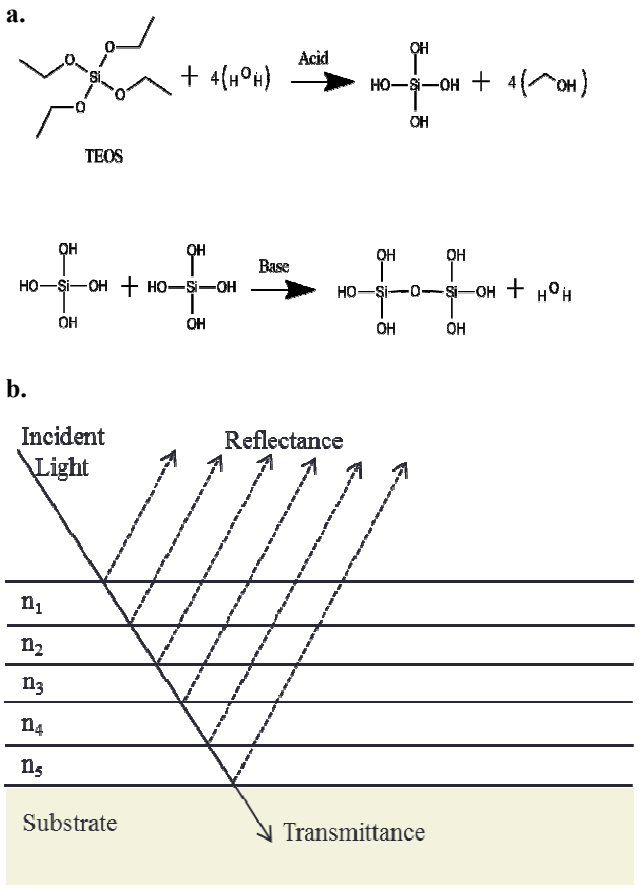

Fig. 1. a. Sol-gel hydrolysis and condensation reactions b. Diagram of graded index ARC showing reflectances from multiple layers.

II. Materials and Methods

Multiple processes were tested to determine the most suitable sol-gel reaction. One-step processes were investigated using various catalysts. Tetraethyl orthosilicate (TEOS), pure ethanol, and purified water mixed at a molar ratio of 3:3:4 (TEOS:Ethanol:Water). Then 0.03 M of six different catalysts were added. Later formulations for sol-gels used varying molarities of hydrofluoric acid and varying molar ratios of TEOS, water, and ethanol. In these one-step processes, gelation is extremely slow during formation of ultralow density aerogels because of the excess solvent. At the same time, large pore sizes can result in loss of transparency. An optimized sol-gel process that uses a two-step approach incorporating both an acid catalyst (hydrochloric acid) for hydrolysis to create a "sol" solution of condensed silica and a base catalyst (ammonium hydroxide) for polycondensation forms the final gel. [4] This two-step process allows for much faster turnover of ultralow density gels as well as transparent gel coatings. For dip coating, sol-gel coats were made using an automated dipping mechanism (KSV NIMA LB instrument) because the down and upstroke speeds could be finely controlled. After the solutions were made, they were either left at room temperature or stored at -20 °C before dipping because the solution viscosity increased exponentially as it gelled. It was also found that storing the solution at -20 °C could keep the viscosity constant for a longer period of time to make more consistent films. [5] The substrates were dipped in the time between mixing and gelation of the solution at room temperature. Both glass and boron doped p type silicon were used as substrates for coatings. Before dipping, the glass and silicon were rinsed with acetone and isopropanol to clean the surfaces. Dipping speeds of 100 mm/min down and 25 mm/min up were used for both the glass and silicon substrates. Spin coating was also used to obtain uniform coats. After the sol-gel solutions were made, 200 µL were dropped onto each sample to cover the entire surface. Then spin cycles of 2000, 3000, 6000, and 8000 rpm were tested, and all ran for 30 seconds. Coatings fabricated as xerogels were dried at room temperature and usually hardened after about two hours. For aerogel coatings, the substrates are immersed in acetonitrile during deposition, and then undergo a supercritical heating process. [4] Sol-gel thickness measurements were taken using surface profilometry after the gel coats were dried. For spin coating at all spin speeds, the first complete coating was consistently 700 nm thick and, subsequent coats would continue to increase overall thickness. Atomic force microscopy (AFM) was used for surface roughness and thickness measurements (Figure 2). An ellipsometer was used to determine the refractive index (using a Sellmeier or Cauchy model). Finally, an integrating sphere was used for reflectance measurements at multiple wavelengths (Figure 3).

III. Results

Characterization of one-step sol-gel processs using hydrofluoric acid as the catalyst revealed that gelation times varied inversely with acid molarity and with the water/TEOS ratio. Though the gels created were usually clear, when the gels formed on the glass substrates, they were cloudy either due to the roughness or to the large pore sizes. As a result, a two-step process was used for subsequent sol-gel layers. The gelation times of the new sol-gel process also depended on the sol/water ratio as well as the amount of catalyst added. The thickness was found to change depending on the time of substrate was dipped, even at constant dipping speed. [5] The thicknesses ranged from ~ 50 nm to ~ 600 nm. The abrupt changes in viscosity complicated fine control of thicknesses from sample to sample. Storage at -20 °C significantly lengthened the gelation time to several hours. However, it is so far unclear if this freezing period can slow the change in viscosity after the sol-gel is again placed in room temperature.

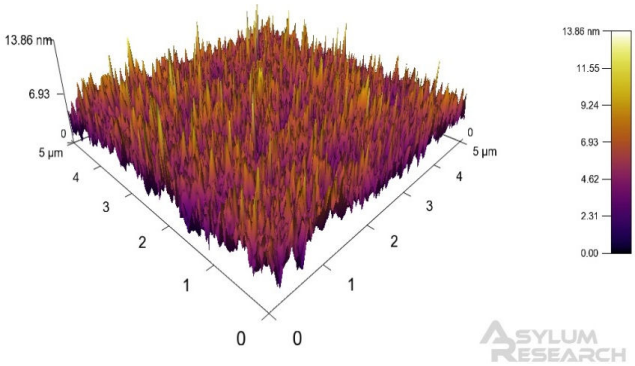

Fig. 2. AFM scan shows that the sol-gel surface is very smooth.

Single coats on silicon were used to determine the refractive indices as a function of "sol" concentration. As the "sol" concentration increased, the refractive indices also increased. Only one batch of aerogels coats has been produced and the refractive (n~1.1) is significantly lower than those of the xerogels (n ≥ 1.4). AFM data showed that the surface was extremely smooth with a RMS roughness ~1.317 nm (Figure 2). A few multilayers were also made with .35/.15, .35/.15/.09, and .35/.15/.09/.15 (aerogel) sol concentrations. Integrating sphere measurements revealed that reflectance decreased with the added ARC layers compared to a bare silicon wafer from 400-1000 nm wavelengths. MATLAB reflectance simulation results closely followed the experimental data for the bare silicon wafer. Modeled multilayer ARCs did not exactly agree with the measured reflectances from the integrating sphere, which is attributed to uncertainty in layer widths and individual layer refractive indices (Figure 2).

IV. Conclusion

Sol-gels as ARCs have the advantage that, under certain drying processes, they can reach refractive indices of near unity which is extremely rare in solids. Graded index coatings can utilize this by forming a multilayer coat ranging from n=1

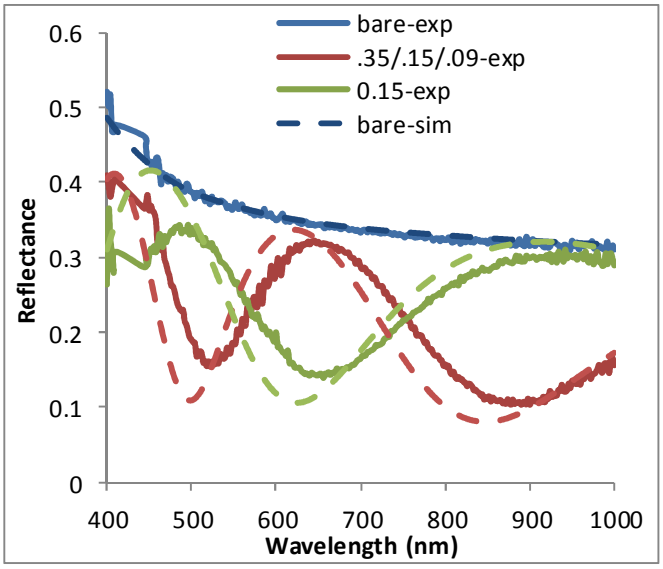

Fig. 3. Overlay of the simulated and real reflectances for a few chips show a good fit between expected and experimental values.

to $n=n_{substrate}$ thereby reducing the reflection across a wide spectrum and incidence angles. It is possible to make tens of coating layers going from xerogels to aerogels in a nearly continuous index range, causing minimal reflectance as the light travels through air and into the substrate. The AFM data show that sol-gel coatings are both flat and uniform in thickness. The main advantage of the dip coating method is that the process can create scalable smooth films much more efficiently than thermal/spin coat processes. Ellipsometry data indicate that sol-gel films can have tunable indices from n=1.1 to n=1.5. While more measurements need to be done to better characterize the sol-gel process, initial reflectance results are promising in that they show a marked reflectance decrease relative to bare silicon is possible.

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