

## Liquid Phase Deposition of Anti-Reflective Coatings (ARC) in Solar Applications Using an Intelligent Process Station™

Liquid Phase Deposition (LPD) is a method for the “non-electro-chemical production of polycrystalline ceramic films at low temperatures.” LPD, along with other aqueous solution methods has evolved as a potential substitute for vapor-phase and chemical-precursor systems. Aqueous solution methods are not dependent on vacuum systems or glove boxes, and the use of easily acquired reagents reduces reliance on expensive or sensitive organometallic precursors. Therefore, LPD holds potential for reduced production costs and environmental impact. Films may be deposited on substrates that might not be chemically or mechanically stable at higher temperatures. Also, the use of liquid as a deposition medium allows coating of non-planar substrates, expanding the range of substrates that can be coated. Aqueous deposition techniques have not reached the level of maturity that vapor-phase techniques have in respect to a high level of control over composition, microstructure and growth rates of the films, but that gap has been narrowing in recent years.

In 1950 RCA was granted the first patent using liquid phase deposition (LPD) of silicon dioxide via fluorosilicic acid solutions ( $H_2SiF_6$ ). Initially, RCA used LPD as a method for coating anti-reflective films on glass, but the patent had promise for future applications. Since this initial patent there have been many further patents and papers utilizing this method to coat substrates, usually silicon, with silicon dioxide. The motivation behind this work is to create an alternative to the growth of coatings by thermal oxidation or chemical vapor deposition (CVD) for planar silicon integrated circuit technology. Thermal oxidation and CVD are performed at elevated temperatures, requiring a higher output of energy and more complicated instrumentation than that of LPD. The most simple and elegant of the LPD methods uses only water to catalyze silica thin film growth on silicon from a solution of fluorosilicic acid supersaturated with silicon dioxide.

Recently, and because of the push to reduce production costs in solar cell applications, LPD has been in process development work to deposit films, predominately anti-reflective coatings (ARC). Anti-reflection coatings on solar cells are similar to those used on other optical equipment such as camera lenses. They consist of a thin layer of dielectric material, with a specially chosen thickness so that interference effects in the coating cause the wave reflected from the anti-reflection coating top surface to be out of phase with the wave reflected from the semiconductor surfaces. These out-of-phase reflected waves destructively interfere with one another, resulting in zero net reflected energy. Therefore, the solar cell becomes more efficient.

MicroTech of Fremont, CA, and Natcore Technology of Red Bank, NJ, have recently teamed together in a developmental project to use LPD for solar cell anti-reflective coatings.

### Intelligent Process Station™

MicroTech is a wet process systems supplier with over 20 years experience, initially in semiconductor technology, but they also supply production equipment to the solar, MEMS, and LED markets. As many suppliers to the semiconductor industry have been pushed to evolve over the past decade or so, MicroTech began supplying not only equipment but also process development capability with each delivered system. Strongly urged by suppliers to control the process, MicroTech has developed systems to control agitation, chemical mixing and blending, chemical concentration monitoring, metrology and drying of the substrates processed in their equipment. This system has become known as their Intelligent Process Station™, a technology that integrates a toolbox of process control solutions into the tool.

Natcore Technology has a suite of technologies aimed at migrating current technology of dry processing to wet. They are the exclusive licensee, from Rice University, of a new thin-film growth technology. Although the implications of this discovery for semiconductors and fiber optics are significant and wide-ranging, the technology has an immediate and compelling application in the solar sector: using LPD to grow anti-reflective coatings on silicon wafers, the central component of solar cells.

### System Description

Figure 1 below shows a block diagram of a generic Intelligent Process Station. Most systems will be customized to some degree from this generic diagram for individual process requirements. All control elements of temperature, flow rate, ph, film thickness and turbidity are under central process control.

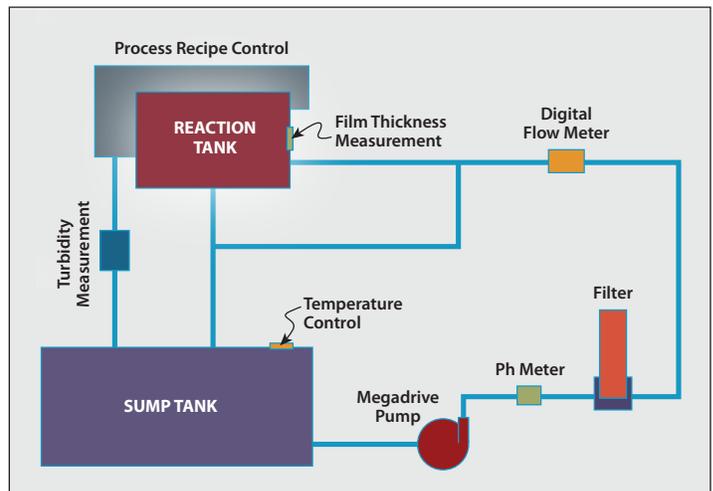


Figure 1. LPD Intelligent Process Station.

**Film Description/Photos**

Anti-reflective properties of a thin film single layer AR coating are determined by the thickness of the film and its refractive index. The optimal reflection suppression is achieved when the thickness of the film  $T = \lambda / (4 * N)$ , where  $\lambda$  is the wavelength, and  $N$  is the refractive index. Therefore, uniformity and consistency of the film thickness and its refractive index is very important for the anti-reflective coating.

Wafers with different SiO<sub>2</sub> film thicknesses have different colors, and different reflectance spectra (reflectance vs. wavelength) as shown in Figure 2 below. Both properties remain uniform and consistent within samples with the same film thicknesses (same deposition times). Films are completely conformal and uniform with excellent adherence to the silicon wafer. The LPD process station provides process control satisfactory to consistently end-point with the appropriate film.

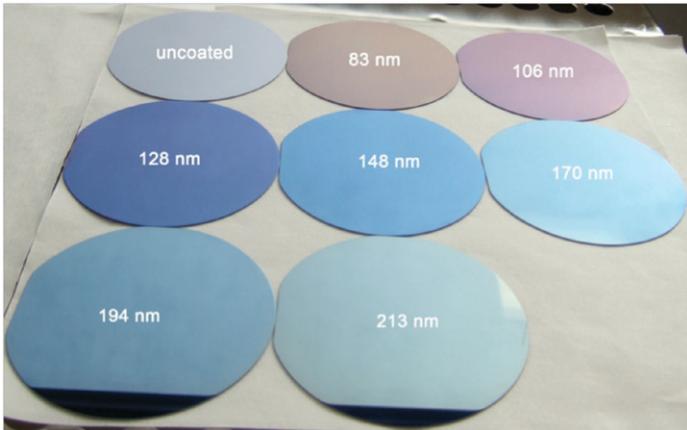


Figure 2. Different colors and reflectance spectra occurring on wafers with different SiO<sub>2</sub> film thicknesses.

**Process Monitoring and Control**

Automated techniques have been in use for a number of years for control of semiconductor processes. These have allowed tighter control of process parameters and enabled the production of ever improving films. Solar applications are adopting some of these methodologies.

The liquid phase antireflective coatings required careful control of liquid process parameters in order to assure consistent, optically appropriate, and conformal coatings. Without these controls, particles begin to form and migrate onto the substrate, resulting in deposition that was no longer homogeneous.

MicroTech has implemented a full suite of process measurement and control subsystems to assure tight process control. These include pH control, temperature control, flow rate control, turbidity control to minimize particle formation, and film thickness control

to provide a process endpoint and thickness determination while still in the process bath. The combination of these metrology subsystems provide the measurement and control capabilities to assure film formation which is now being demonstrated to be superior than those deposited using conventional high temperature deposition systems.

Figures 3 and 4 below detail both turbidity and film thickness control during the demonstration of AR coatings using the MicroTech Intelligent Process Station™.

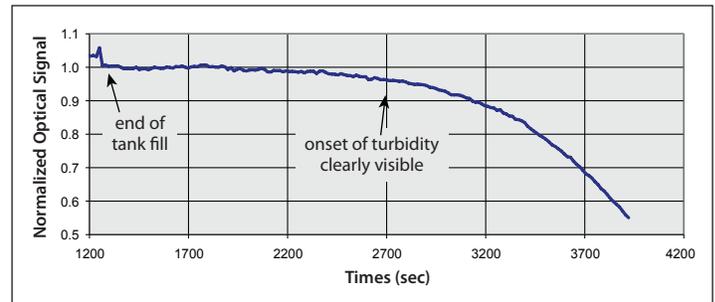


Figure 3. Optical detection of process fluid turbidity.

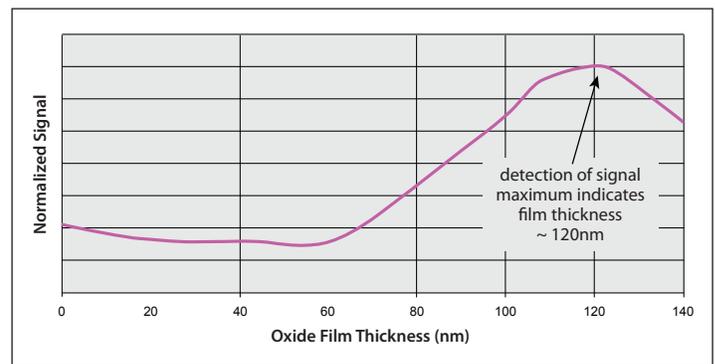


Figure 4. Film thickness end point detection.

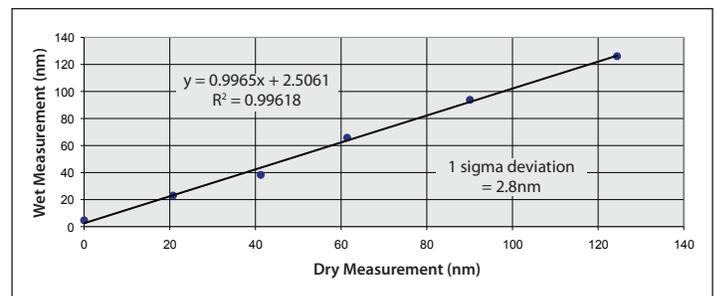


Figure 5. Accuracy of in situ wet measurements (LPD oxide / Si).

In Figure 5 above, dry measurements were correlated with wet measurements at a standard deviation of 2.8nm.

**Reflectivity**

To gauge the effectiveness of LPD on solar cell wafers, an experiment was set up to test total reflectivity on textured and non-textured (bare) silicon wafers. The apparatus used for this experiment was compact integrating sphere with a tungsten-halogen light sources and a wide-range optical fiber-coupled CCD spectrometer. An Intelligent Process Station™ LPD development tool provided by MicroTech processed Natcore wafers.

**Methodology**

For each wafer, a full range optical spectra (~360-930nm) were recorded for background (in other words, no wafer), standard surface, and wafer under test. A percent reflectance vs. the standard was calculated at each wavelength. The standard reflectance surface was a low reflectance (~3%) diffuse reflector, which itself was calibrated against a high reflectance (~99%) diffuse reflectance surface. The results are shown in Figure 6:

The LPD development tool and the methodology produced the following conclusions:

- 1. Reflectance spectra shows good signal-to-noise ratio, even for very low reflectance samples.
- 2. Coating reduces reflectance of single crystal silicon ~ 4x.
- 3. ARC Coating reduces reflectance of textured silicon from 8% to better than 2% in the full visible optical range down to 450nm.

**Conclusion**

The Intelligent Process Station™ for Liquid Phase Deposition has proved in preliminary development work to be a viable alternative for depositing thin film growth on silicon without the use of thermal oxidation or chemical vapor deposition. Results in experimentation on actual silicon wafers showed decreased reflectance on single crystal silicon by a measure of four. MicroTech is now building additional Intelligent Process Stations™ for LPD and Natcore Technology is offering a LPD tool for both development and production of solar cell processes.

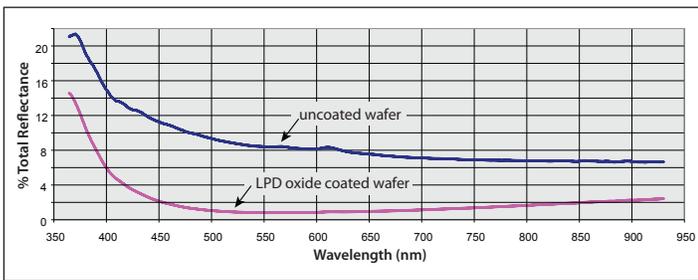


Figure 6. Total reflectance measurements, on textured single crystal silicon. Note that LPD oxide coating reduces visible reflectance to < ~ 1%.



**MICROTECH**

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