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High productivity combinatorial study of wet chemical texture etch of sputter deposited Al-doped ZnO thin films for thin-film Si solar cells

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ABSTRACT

This paper presents a high-productivity combinatorial (HPC) parallel processing method based on multiple site-isolated cells on a single substrate. This method has been applied to the acidic wet chemical texture etch of sputter-deposited Al-doped ZnO (AZO) film on glass substrates for light-trapping enhancement for thin-film Si solar cells. Taking a fraction of the time and resources that would usually be required for such a project, the HPC method allows fast chemical screening of various inorganic and organic acids as potential replacements for the standard hydrochloric acid (HCl) texture etch process currently used in R&D and pilot production. Several candidate acids have shown either similar texture performance at much reduced AZO film etch or superior texture performance at the same etch depth as compared to the standard HCl texture etch. The large amount of data collected using the HPC approach also enabled us to ascertain the crystal orientation-dependent anisotropic etch as the dominant texture etch mechanism for AZO films using a wide selection of acids.

Background

Surface texturing of aluminium-doped zinc oxide films (AZO) is an efficient way of increasing the efficiency of amorphous silicon-based solar cells by trapping light more effectively. Dilute HCl solutions have routinely been used to etch the sputter-deposited (or physical vapour-deposited, PVD) AZO films to generate the necessary surface texture. Up to now, relatively few chemicals have been tested to improve the surface texturing process, and there appears to be a very limited understanding of the relationship between chemical structure, surface topography and light trapping efficacy.

> "Up to now, relatively few chemicals have been tested to improve the surface texturing process."

The combinatorial methodology is demonstrated as a fast, efficient, and accurate mode of improving research and development of solar applications. Using Intermolecular's HPC technology, a large number of potential formulations were tested in a fraction of the time and resources normally required. A new methodology is presented for screening thousands of samples in far less time and with fewer substrates than previously possible. The large amount of experimental data enables the identification of different classes of chemicals that can be used to control the resulting topography, and to formulate an empirical understanding of the relationship between surface topography and light scattering. These empirical and phenomenological models will be further used to find the best texturing formulation to obtain maximum solar cell efficiency.

Experimental

Deposition of AZO films

AZO films were deposited on circular glass substrates with 8" diameter on an Applied Materials Endura PVD tool at Intermolecular's lab in San Jose, California. Process conditions were optimized to obtain good quality AZO films with resistivity in the range of 550-650μΩ/cm and good transparency. As a nominal baseline, films with thickness from 1200 to 1300nm were deposited from a composite ZnO target with 2 weight % Al doping. Substrate temperature during deposition was 300°C; deposition time was 600 seconds. The root-mean-square (RMS) roughness as measured by atomic force microscopy (AFM) was in the range of 4-6nm.

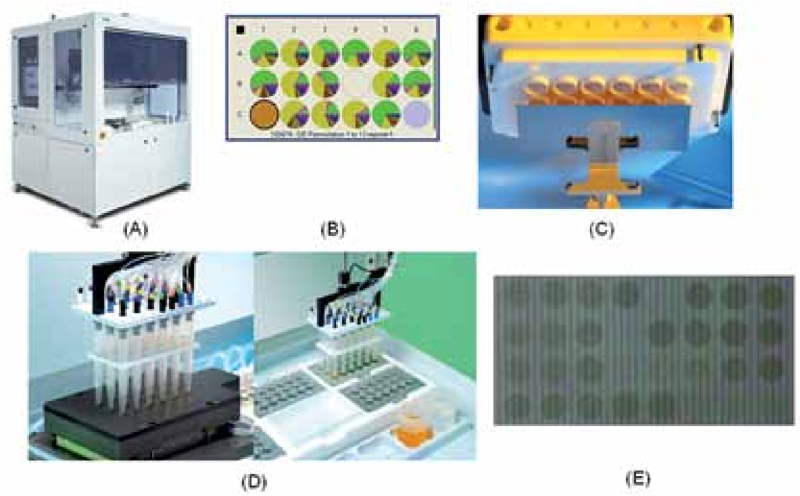

Figure 1. Intermolecular Tempus-F20 tool set. A: Tempus-F20 photo; B: chemical formation library schematics; C: reaction cells; D: chemical solution dispense system; E: example of the 32 reactor cells after texture etch.

Texturing and characterization

The circular substrates with AZO films were cut into rectangular pieces of ~120mm x 60mm in size for performing multiple experiments in parallel on the Intermolecular Tempus F-20 platform as described in the following sections (see Fig. 1). Rectangular substrates with 32 unique experiments were placed in various characterization tools and mapped in an automated manner. Intermolecular's Informatics system automatically acquires process and characterization data from various tools and organizes them in the database by correlating the process and characterization results of each experiment. This structured data is then made available for analysis on the Informatics platform. Automated mapping on characterization tools, data acquisition and data organization are important aspects of the HPC approach, and are made all the more necessary when dealing with hundreds of experiments and characterizations in one day (see Fig. 2).

Film thicknesses of untextured AZO films were measured using spectroscopic ellipsometer (Woollam M2000) and x-ray fluorescence (XRF) techniques (Panalytical PW2830). Sheet resistance and resistivity were measured using a four-point probe (CDE ResMap 273). Thickness loss after texturing was measured by change in sheet resistance and confirmed by XRF measurements, and AFM measurements were obtained using Veeco's Dimension 3000. Diffused light scattering and total transmission measurements were carried out on Shimadzu 3700 tool using a 60mm integrating sphere. X-ray diffraction (XRD) measurements were performed on a Panalytical X'Pert Pro MRD XL DY-2709. Fig. 3 shows the XRD spectra of a representative film.

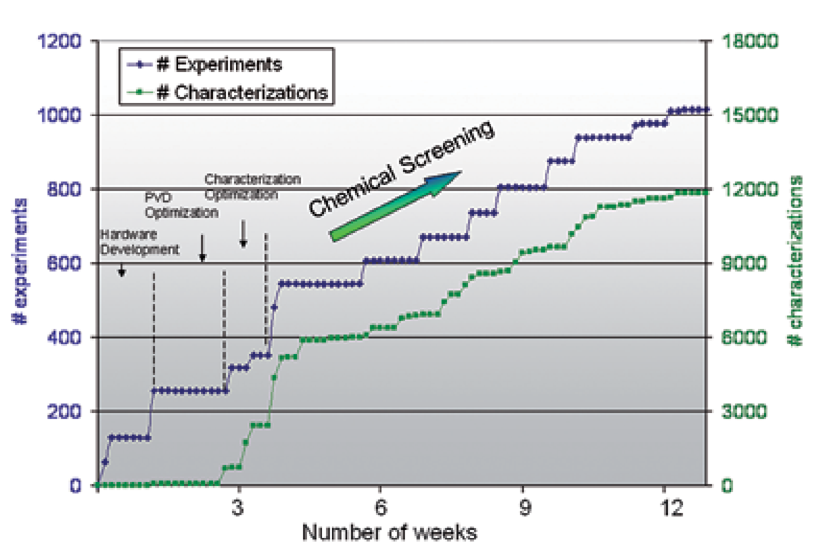

Figure 2. AZO texture etch process progress over three months using the Intermolecular HPC approach including the Tempus-F20 process tool, the Informatics system, and the automated film characterization methods.

Intermolecular Tempus F-20 platform for HPC research

The Tempus F-20 platform was used to make chemical formulations and multiple texturing experiments on a single substrate. The reactor of the Tempus F-20 is shown in Fig. 1. Up to 32 different formulations can be processed in isolated reaction sites on a single wafer coupon. The formulations to be tested can be mixed automatically on the tool or on a Tempus F-10, both of which eliminate human error from the mixing process to yield better repeatability without any loss of precision. After the solutions are prepared, the robotic arm shown in Fig. 1D picks up the solutions and dispenses them into the isolated reactor sites. Process steps and process parameters such as temperature, solution agitation and reaction cell rinse procedures, etc. are all automated while still giving the user full flexibility. All process and formulation information is captured by the Informatics platform and organized along with characterization data to help data analysis.

Results and discussion

Employing the HPC approach enabled the performance of a large number of experiments with varying etching chemicals, compositions and etch rate in a very short time (see Fig. 2). After few days of hardware improvements and development of AZO films, we were able to do a large number of experiments and test four inorganic acids, 11 organic acids and their mixtures in a very short time. In a few weeks, nearly 700 unique experiments were conducted. The massive amount of experimental data generated during these experiments helped the development of formulations that appear to offer performance advantages compared to the standard HCl-based formulation. In addition, this massive data set also enabled us to better understand the fundamental etching mechanism at work in this process.

Properties of AZO films

The same AZO films and deposition conditions were used for all experiments. The crystal orientation of AZO film relative to the substrate is important to obtain the correct texture. The modified structure zone diagram [3] indicates that compact crystallites with c-axes perpendicular to the substrate surface are needed to produce a suitable texture for thin-film solar cells. Fig. 3 shows typical XRD spectrum of AZO films used in this study. The existence of only two major XRD peaks for (0002) and (0004) faces confirmed that the c-axis of the crystallites is indeed perpendicular to the substrate surface. The size of the crystallites calculated using Scherrer equation [1] from XRD analysis is in the range of 20-30nm, consistent with most previous reports [2].

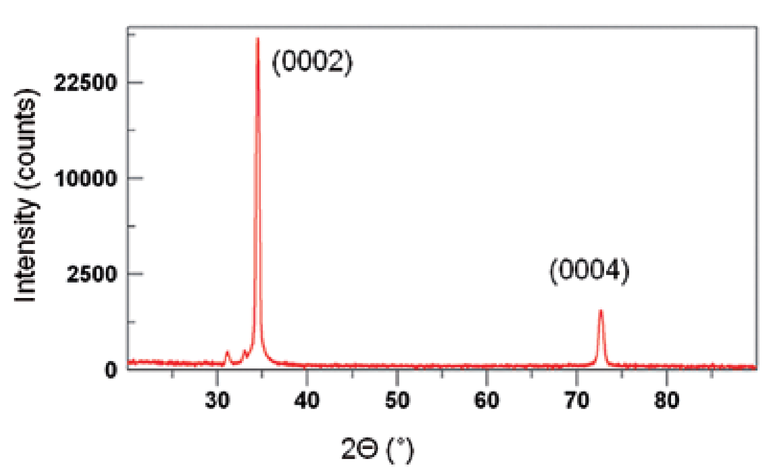

Figure 3. XRD spectrum of typical AZO films used.

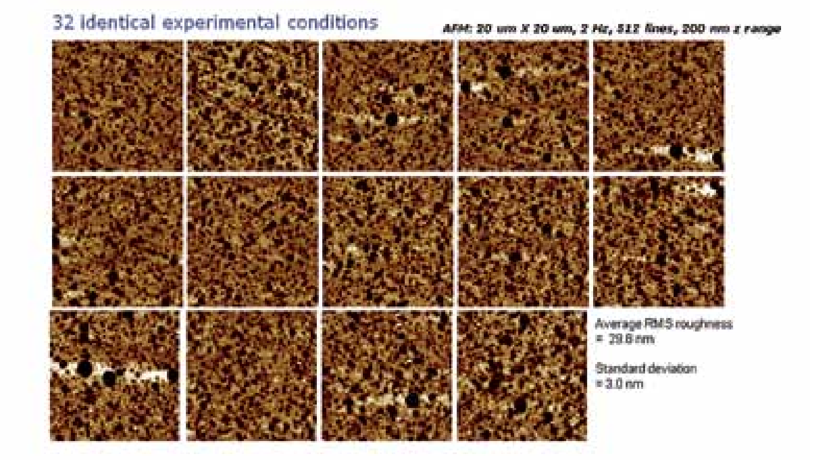

Figure 4. 2D AFM morphology for 14 selected cells from 32 cells on a single AZO substrate processed under identical conditions.

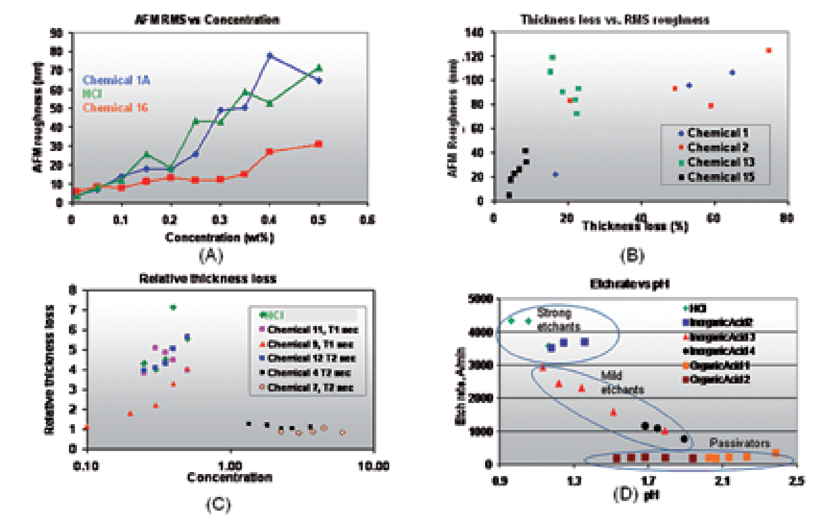

Figure 5. Primary screening results for wet texture etch of AZO films. A: AFM roughness as a function of acid concentration; B: AFM roughness as a function of AZO film thickness loss with different acid etch; C: relative AZO film thickness loss as a function of acid concentration; D: AZO film etch rate as a function of acid solution pH.

Reproducibility for site-isolated parallel processing of wet chemical texture

Fig. 4 shows the AFM morphology of 14 selected cells obtained under the same process condition as an example of the process reproducibility for site-isolated parallel processing. Cell-to-cell variation was confirmed to be small enough to allow for the comparison of various experimental results.

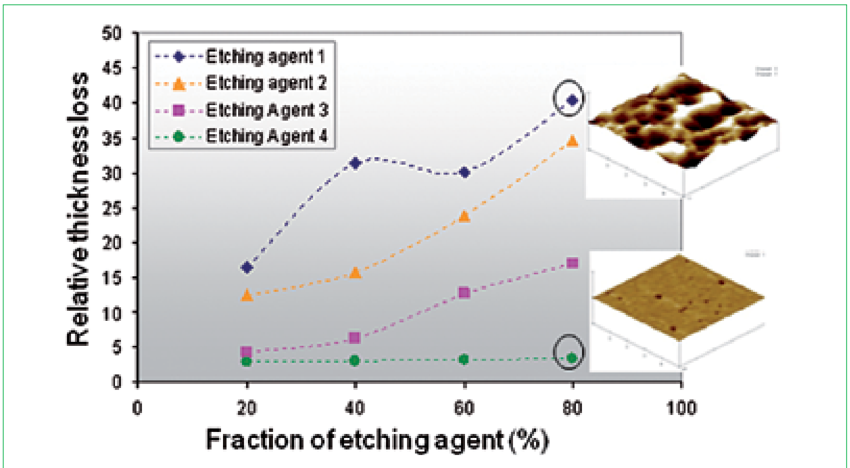

Figure 6. Relative AZO film thickness loss as a function of passivator concentration for mixed acid formulations containing various active etchants and passivator chemicals.

Primary screening

Experiments were performed in screening phases known as primary screening and secondary screening. In primary screening, various chemicals were tested to determine whether or not they produced sufficiently textured surfaces with reasonable loss in thickness at varying concentrations. The texturing performance was characterized by thickness loss and RMS roughness as shown in Fig. 5. The graph in image A shows that almost all chemicals displayed increasing texture with increasing concentration. However, some chemicals were more efficient at producing texture at lower concentrations. Image C in Fig. 5 shows thickness loss by various chemicals at different concentrations, which enables the identification of what chemicals can etch AZO and determine etch rates. The graph in B compares the texturing performance of various chemicals, and through the use of the primary screening process, those chemicals that produce higher RMS roughness with less thickness loss can be identified. The chemicals were also classified into strong etchant, mild etchant and passivators based on the etch rate and pH plots (image D, Fig. 5).

Mixed formulations were also tested for their texturing performance. Fig. 6 shows a plot of few combinations of etchants with one passivator, clearly showing that varying the relative concentration of passivator has different effects with different etchants. For example, the passivator is very effective in reducing the etch rate of etchant 4; however, when combined with etchant 1, its effectiveness in lowering the etch rates is reduced.

Secondary screening

After selecting various potential chemicals and mixtures of chemicals based on etch rate and RMS roughness, secondary screening was performed by measuring the optical spectrum in diffused transmission mode. Illustrative optical spectra of some textured surfaces are shown in Fig. 7A. The optical performance was evaluated by the peak value of percentage transmission in the optical spectrum. Fig. 7B shows the optical performance of various formulations at varying etch times plotted with respect to the thickness loss (only data from some selected formulations are shown here). It is clear from this plot that many chemical formulations perform better than the industry standard HCl formulations. Similar optical performance is obtained at smaller thickness loss, while better optical performance is obtained at the same thickness loss. In this manner, by using a phased screening approach and HPC tools, we were able to obtain many formulations that show better optical performance compared to HCl while also classifying different chemicals based on their texturing performance.

Topography of textured surfaces and optical performance

During the primary and secondary screening, we used RMS roughness as a preliminary quantitative measure of surface topography. RMS roughness is a very rudimentary method of characterizing surface roughness. Fig. 8 shows optical performance of various textured surfaces plotted against the respective RMS roughness. In general, the optical performance increases with the RMS roughness as a first order effect, but it is also evident that the samples with almost the same RMS roughness have very different optical performances. AFM images of respective samples are also shown in Fig. 8, which also illustrates the significant differences in surface topology.

These results show that RMS roughness is not a sufficient parameter to characterize surface topography and the resulting light scattering and optical performance of the textured surface. Optical modelling to predict light scattering from the surface of known topology using fundamental Maxwell equations is very difficult, and to date, such models have only been able to predict the effect of surface roughness on light scattering texture feature sizes $<< \lambda$ [4,5]. Optical models based on the fundamental Maxwell Theory that can predict the effect of higher order surface topographical parameters are not currently available.

Recently, Krasnov [4] presented a semi-empirical model that can correlate light scattering with multiple surface topographical parameters obtained from AFM images. Surface topographical parameters, such as RMS roughness, Skewness, Kurtosis, and 3D FFT spectra were used to precisely predict angle-resolved scattering (ARS) and spectrum-resolved scattering (SRS) from textured surfaces of AZO films. The model was able to explain the difference in peak positions and width of ARS with various surface topographical parameters.

Currently, we are applying Karsnov's model with the vast amount of data obtained using the HPC approach to further refine the model and develop a phenomenological model and library to correlate the chemical structure of texturing molecules and formulation parameters with light scattering performance of the resulting textured surfaces. Furthermore, we are using this data to find the formulation that can be used to generate textured surfaces that produce highest efficiency solar cells.

Mechanism of chemical texturing and relationship with molecular structures

Anisotropic etching on single crystal ZnO by HCl and other acids to produce hexagonal craters is well understood and is described in literature [2]. The differential etch rates of various crystal planes at the sites of surface defects causes the formation of very uniform hexagonal structures. However, formation of such regular hexagonal craters has not been reported in literature for PVD-deposited AZO films. The hexagonal crater geometry is observed on most of our samples etched with many different inorganic and organic acids, and therefore is independent of the type of acids used for texture etch. Fig. 9 shows 3D and 2D AFM images of such samples.

The graph and images in Fig. 10 show RMS roughness and indicates the bottom angle of the crater for some formulations.

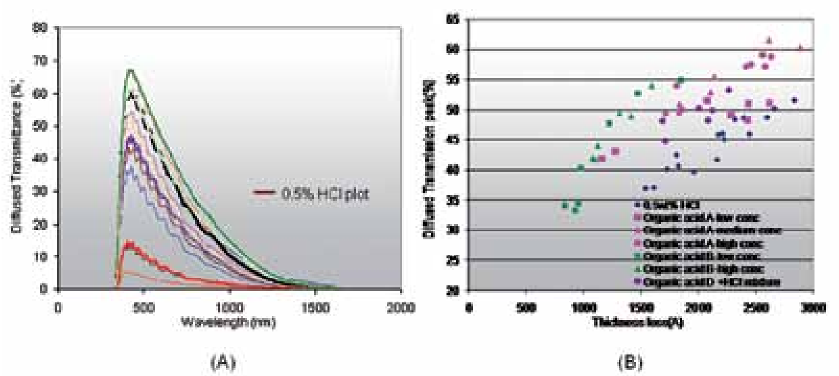

Figure 7. Diffused transmission of textured AZO films from UV-Vis-NIR measurements using a 60mm integrating sphere. A: diffused transmission spectra from AZO films etched in various acid solutions; B: diffused transmission of textured AZO films as function of film thickness loss.

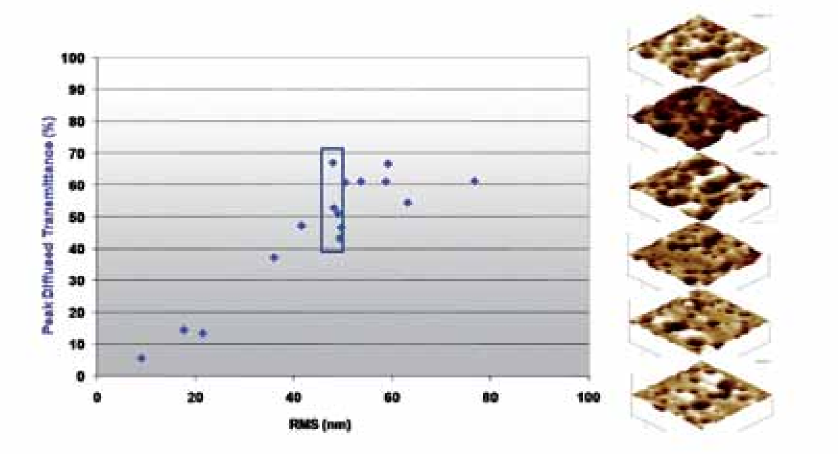

Figure 8. Correlation and lack of correlation between diffused transmission and AFM film roughness for textured AZO films.

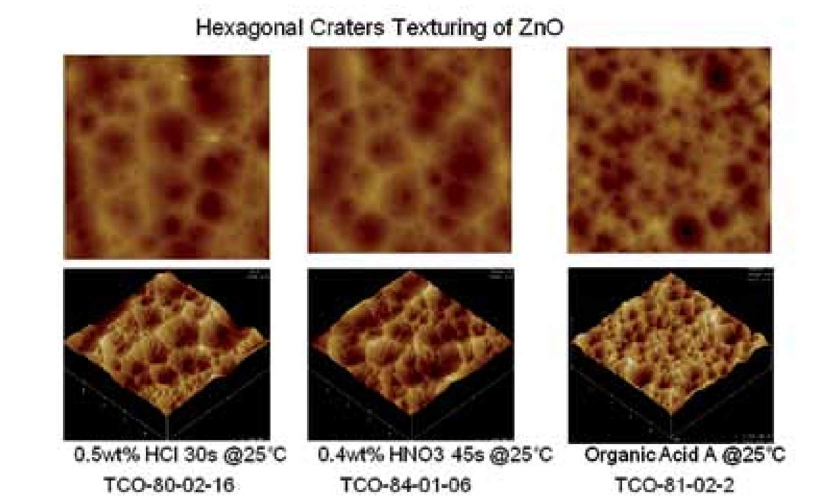

Figure 9. 2D (top row) and 3D (bottom row) AFM morphology of selected textured AZO films showing hexagonal geometry of the craters giving rise to AZO film texture.

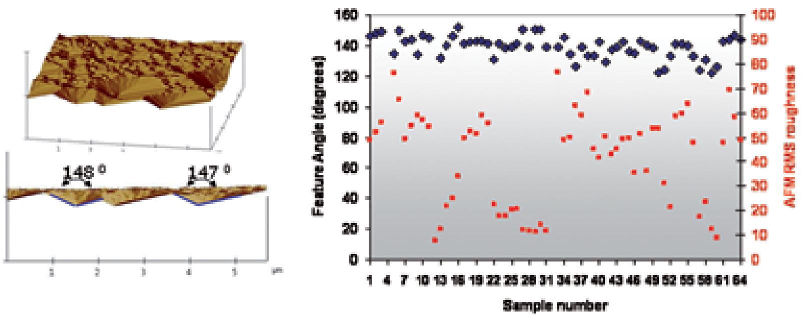

Figure 10. Crater bottom angles measured from AFM for textured AZO films.

Figure 11. Pathway from chemical structure of acid molecules used for texturing AZO film to the resulting solar cell efficiency.

It is clear from this plot that even though the surface roughness varies by an order of magnitude from sample to sample, the crater angle remains relatively invariant between 110° and 150°. The crater angle for a single crystal ZnO surface is ~123° to 130° [2]. We also observed correlation of the bottom angle with molecular structure and composition of various acidic formulations. It has been observed that some classes of acids result in lower angles than others. Furthermore, for some formulations, the crater angle increased or decreased with increasing extent of etching, thereby changing the shape of the craters. This also suggests that relative etch rates of different crystal planes changes with the extent of etching.

"It has been observed that some classes of acids result in lower angles than others."

For other formulations, the crater angle remained the same with increased etching and the crater shape also remained the same while the crater size increased. For these formulations, relative etch rates of different crystal planes did not change with the extent of etching. We have been able to identify various classes of acid etchants that result in different crater shapes, and are currently using this information along with Krasnov's model to find the optimum formulations.

Conclusion: from molecular structure of acids to solar cell efficiency

In most cases, there is no sufficient theoretical, empirical, and phenomenological understanding of each of the steps in the pathway from the chemical structure of AZO-texturing acid molecules to cell efficiency (Fig. 11), and so each step must be investigated separately. As a result, a reasonably good understanding of how the chemical structure of molecules affects solar cell efficiency is not available and the best solution is often never found. The use of Intermolecular's HPC platform enables parallel experiments on a single substrate and allows scientists to perform a great number of experiments to test the many chemicals, process and formulation parameters in a short time. Parallel and automated characterization combined with a phased screening approach allowed us to quickly identify the chemical classes and chemical formulations that result in the best possible surface texture with minimum loss of AZO thickness. Light-scattering measurements enabled us to develop empirical correlations between surface texture, topography and optical performance, the data from which are being used to further test and validate Krasnov's mathematical model. We are in the process of developing technology for making and testing multiple solar cells on a single substrate in a HPC approach, which will allow us to quickly find the best formulations to produce the highest efficiency solar cells. In parallel, selected formulations will be tested using conventional approaches.

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