Effective Cleaning of Glass Substrates

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Abstract

Surface contamination is one of the major causes of yield loss, with a unique set of challenges for large display glass sheets that support the industry. Here, we review the use of different cleaning approaches applied to display glasses during manufacturing, discussing the advantages of some choices over others.

1. Objective and Background

Surface contamination is one of the major causes of semiconductor yield loss, with a unique set of challenges for large glass sheets that support the flat panel display industry. (1) It is well known that there are many ways to clean substrates. Cleaning with aqueous solutions is among the most common and is generally regarded as chemically driven and mechanically assisted, with the various chemistries and mechanical assist methods specifically tailored to the type and size of material to be removed after their proper identification. The choice of solution chemistry is usually designed to target particle removal through an undercutting mechanism, while mechanical agitation and electrostatic repulsion between the surface and particle in liquid serves to keep the particle suspended in solution and off the surface. The methodology of cleaning proposes to target the removal of large particles first followed by smaller particles and finally metallic ions that may interfere with proper thin film transistor performance. (2) In a process flow, this is demonstrated mechanically, for example, using high-pressure sprays, brush cleaning, and ultrasonic frequency agitation in early steps to target µm-size particles, followed later by megasonic frequency agitation which targets nm-size particles before drying and inspection. Given constant mechanical action, this brief treatise serves to illustrate the use of different chemistries on display glass surfaces to determine the advantages of some choices over others.

2. Results

Corning EAGLE XG® or Lotus™ glass substrates were used in this study to demonstrate the effects of various cleaning procedures. These substrates were 180 mm x 230 mm and cut using the scribe and break technique. Cleaning took place using either a SSEC single panel single side spin cleaner (Solid State Equipment LLC) or a Batch Cleaner (Akrion). Particle density measurements were performed with a Toray HS830 particle counter (Toray Engineering Co., Ltd.). ESI/MS (electrospray ionization mass spectrometry) was used for identification of film residues.

One well-known consideration for effectively cleaning particles from glass substrates is to dislodge them by use of an aqueous chemistry that will partially etch or dissolve the surface of the substrate. This serves to undercut adhesion of particles directly at the interface with the glass. The dissolution rates of silicate glasses in aqueous solutions are also a strong function of solution pH, typically increasing exponentially as the pH becomes higher (more alkaline). This effect is demonstrated in Figure 1, which shows the dissolution rate of a representative display glass in several alkaline media. Many commercial detergents used with display glasses contain alkali hydroxides (strong bases, e.g. NaOH, KOH) as active ingredients to facilitate cleaning efficiency through etching, and the log-linear change in dissolution rate with strong-base concentration here is evident. Overlaid in the figure are also 2 commercial glass cleaning detergents, highlighting their strong cleaning power due in large part to their high etch rates. What may be not realized is the fact that the high concentrations of metallic ion component (e.g. Na^+ from NaOH) in such detergents require sufficient rinse so that the metal ions are not left adsorbed on the substrate surface. This effect is exemplified in Figure 2, where a total of 300 seconds rinse time with deionized water is necessary for a sample treated with Detergent B to reduce surface metallic ion concentrations to the same level as for the same glass cleaned in SC1 ($NH_4OH:H_2O_2:H_2O$) 1:2:80 with no rinse.

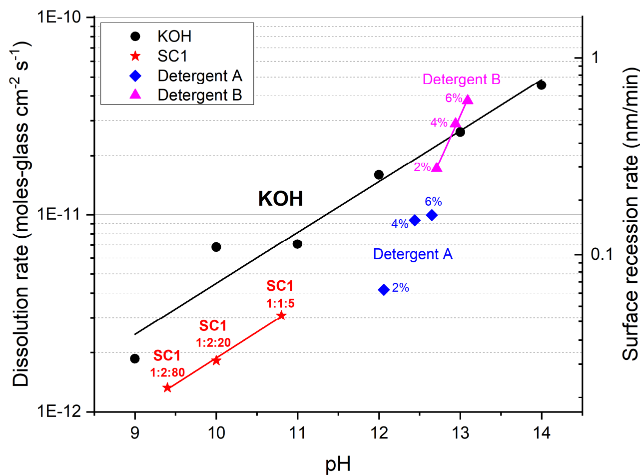

Figure 1. Dissolution rate as a function of pH for various alkaline chemistries.

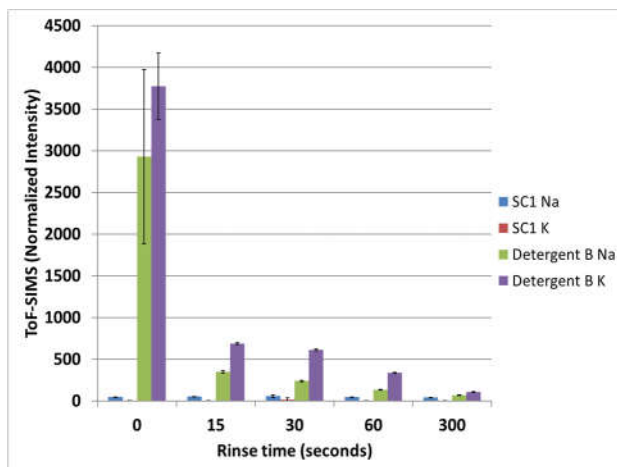

Figure 2. ToF-SIMS normalized intensity for sodium and potassium as a function of DI water rinse time in seconds. Here SC1 was 1:2:80 $NH_4OH:H_2O_2:H_2O$ applied to Lotus glass at 65° C for 1 minute followed by DI Water rinse time Detergent B exposure was at 2% concentration at 65°C for 1 minute followed by DI water rinse time.

The slower etch rate provided by SC1 chemistries, on the other hand, does not suffer from needing a long rinse time, as these chemistries do not inherently contain metallic ion components. Hence if the etch power is sufficient to remove said contaminants, it may be a better choice for shorter line distance.

With the SSEC cleaner, a comparison of SC1 chemistry with Detergent A indicated that broader distributions in particle density were found with Detergent A compared to SC1 as shown in Figure 3 as examined by the Toray instrument. Here HVS is spray and HB is horizontal brush.

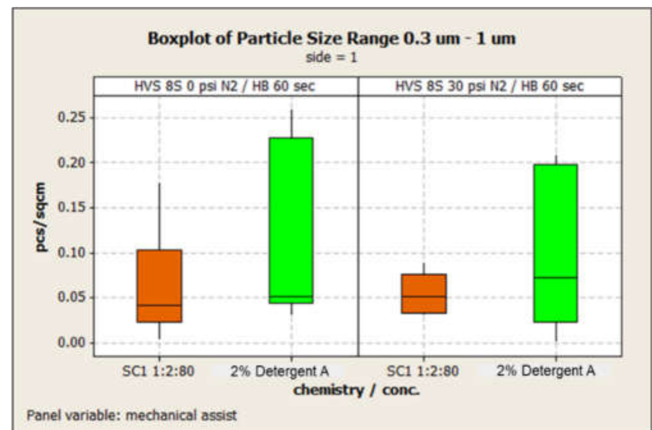

Figure 3. Particles/square cm as measured by Toray for either SC1 or detergent chemistries at different Spray (HVS) and Brush (HB) conditions.

Particle identification for organic residue was done by extracting the surface with chloroform followed by ESI/MS of the solvent for organic identification. The table below indicates that, for the recipes tried, Detergent A components were not detected for detergent recipes, but packing film residue was. These included the slip agents and antioxidants. The SC1 recipes tried, however, were able to detect only antioxidants.

recipe detail	chemical component	slip agent (ng/ml for 180 x 230 mm slide)	others	Detergent B Components
Surf Extra HVS/Surf HB	2% Detergent A	yes; 778.15		n/d
Surf Extra HVS/Surf HB	2% Detergent A	yes; 96.65		n/d
Surf HVS/Surf HB	2% Detergent A	n/d		n/d
Surf HVS/Surf HB	2% Detergent A	n/d		n/d
HVS w/surf	2% Detergent A	yes; 140.49	antioxidant	n/d
HVS w/surf	2% Detergent A	yes; 76.40	antioxidant	n/d
1:2:80 SC1 HVS/HB	$NH_4OH:H_2O_2:H_2O$	n/d		
1:2:80 SC1 HVS/HB	$NH_4OH:H_2O_2:H_2O$	n/d		
1:2:80 SC1 Extra HVS/HB	$NH_4OH:H_2O_2:H_2O$	n/d		
1:2:80 SC1 Extra HVS/HB	$NH_4OH:H_2O_2:H_2O$	n/d		
1:2:80 SC1 HVS/Extra HB	$NH_4OH:H_2O_2:H_2O$	n/d	antioxidant	
1:2:80 SC1 HVS/Extra HB	$NH_4OH:H_2O_2:H_2O$	n/d	antioxidant	

Table 1. ESI/MS of detected residues for different SC1 and detergent conditions

It should be noted that material choices are likewise critical during display line build as they may shed particles on the glass surface or interact with cleaning chemistries in ways that are deleterious. For example, in SC1 chemistries, the peroxide component provides oxidizing action that can help solubilize unwanted organic stains and residues. But, these components can also interact with metallic contact materials used on manufacturing lines. For example, tantalum can be used for SC1 megasonic shower heads. Analysis of one such showerhead revealed that the

majority was made of tantalum, and a minor component was made of antimony—a Group V element known to interfere with semiconductor device performance. Issues of tantalum corrosion in SC1 solution were studied by monitoring the oxidation rate of tantalum in SC1 with XPS during SC1 exposure at elevated temperatures and found to be significant (Table 2 and Figure 4) in accordance with literature. (3) It is recommended that preferred material choices could include coating the tantalum with an SC1 resistant material such as PFA.

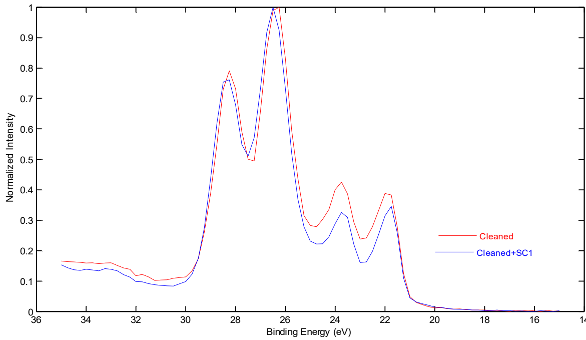

Figure 4. XPS spectra of Tantalum shower head as received or after exposure to SC1.

Treatment	Area	C	O	Ta
Cleaned	A1	36.5	46.7	16.9
	A2	31.6	50.1	18.3
Cleaned + 6 Hr SC1	A1	20.7	56.7	22.6
	A2	18.7	57.1	24.3

Table 2. XPS atom % detected for two different areas of tantalum shower head as a function of exposure to SC1 solution indicating oxidation.

3. Impact

Chemistry choices in display glass cleaning clearly affect glass surface chemistry and may impact TFT fabrication. We have shown that alkaline detergents—while largely effective at particle removal—can leave unwanted contaminant ions on the surface, as well as broader particle density distributions in comparison to alternative chemistries such as SC1. However, material choices used in line applications of SC1 must be critically examined as well so that they do not negatively impact performance.

4. References

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