Conductivity and pH Measurement

Flat Panel Display HF Etching Solutions

Hydrofluoric acid (HF) is used in flat panel display processing, glass etching and other industrial processes. The extremely corrosive and toxic nature of HF makes it difficult to handle, requiring special materials of construction. This is also true of the sensors needed for its measurement. The strong etching baths as well as the more dilute rinse waters and wastewater neutralization processes require careful selection of sensors for conductivity and pH.

Etch Baths

Hydrofluoric acid is commercially available at concentrations near 50%. In etching solutions this concentration must be diluted and maintained within close tolerances to achieve controlled etching rates and high yields. This concentration can be monitored using inductive conductivity instrumentation which allows measurement without any metal in contact with the fluid. The sensor consists of two adjacent coils encapsulated in a single polymer body. The first coil is energized with AC current. The fluid surrounding the doughnut shaped sensor induces

UPW UniCond and HF-resistant InPro 3252 pH sensor.

Vertical Text 24 pt

a signal into the second coil in proportion to the conductivity of the fluid. This signal is then measured, temperature compensated and provided for display and control. Inductive conductivity sensors using PFA (perfluoro-alkoxy) and PTFE (polytetrafluoroethylene) wetted materials withstand the severe conditions of HF-containing baths.

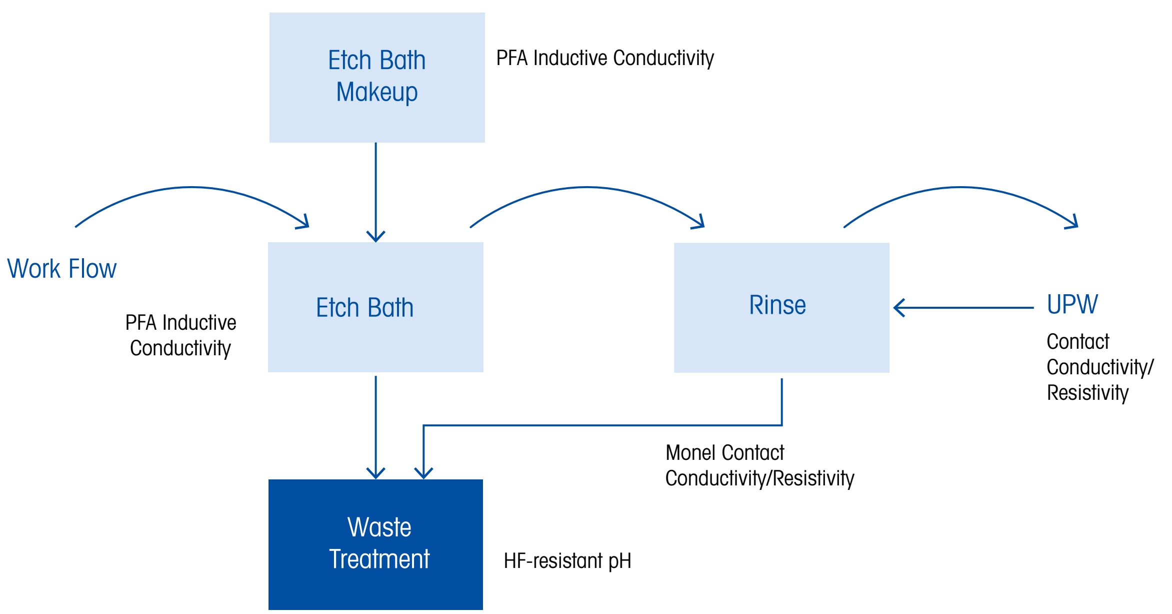
Rinse Water

FPD substrates and other products etched in hydrofluoric acid baths must be rinsed extensively before further processing. Usually this is done with ultrapure water. The initial rinse water will contain enough HF to be highly corrosive while the final rinse must reach ultrapure water levels of purity. To assure thorough rinsing, an ultrapure level contact conductivity/resistivity sensor must monitor the used water quality. At the same time, this sensor must withstand the initial acid conditions.

Resistivity sensors for monitoring etching rinse water are available with Monel® electrodes which have excellent resistance to HF, whereas standard stainless steel or titanium sensors are rapidly attacked. Monel sensors are calibrated and measure with the same high accuracy available with other Thornton ultrapure resistivity sensors and will tolerate occasional dumps of hydrofluoric acid etchant as well as the dilute rinse water. UniCond™ conductivity sensors measure over a wide range, allowing extended monitoring of HF rinsing processes.

Wastewater Treatment

The rinse waters and the etch baths themselves, when they are spent, must be treated before discharge or reclaim. This treatment typically consists of neutralization, coagulation and settling of the fluoride by adding calcium chloride, lime and/or limestone to produce insoluble calcium fluoride. The measurement of pH to control the neutralization is complicated by the corrosive nature of acidic fluoride solutions. HF attacks the glass membrane of most pH sensors as readily as it etches flat panel substrates. The rate of attack is dependent on fluoride concentration, pH and temperature as well as the glass composition. If the fluorides are cosistently neutralized upstream of the pH sensor, then there is less opportunity for attack.



Etch Bath Wafer Cleaning Process

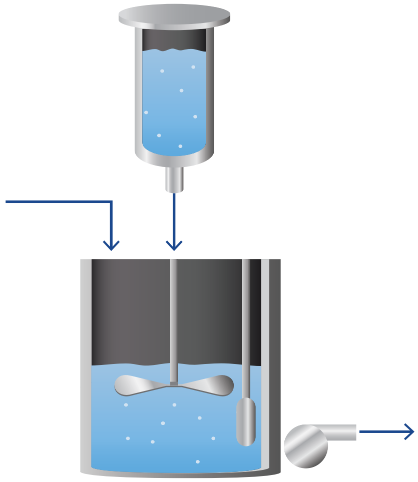


Figure 1A. Batch

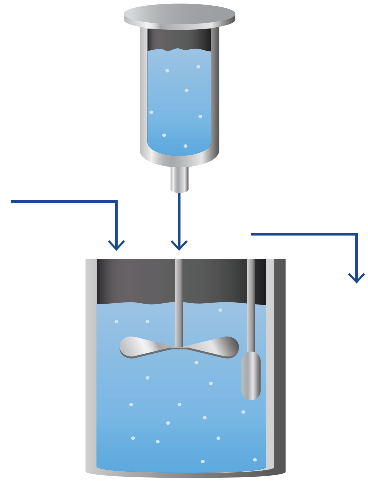


Figure 1B. Continuous

The exposure to acidic conditions may depend on the treatment strategy. If treatment is done in batches as in Figure 1A, with filling, neutralizing and pumping out, then the pH sensor could be exposed to hydrofluoric acid all through the long filling cycle. In those situations a special HF-resistant glass pH sensor may be needed to achieve greater resistance to hydrofluoric acid. On the other hand, if treatment is continuous with gravity overflow as in Figure 1B, then control could maintain the pH near neutral most of the time and the pH sensor would not be subjected to hydrofluoric acid. A conventional glass electrode should be satisfactory in this case unless there is poor mixing or frequent control upsets occur.

Fluoride treatment typically involves precipitation of calcium fluoride which can rapidly coat any kind of pH sensor as well as the process equipment itself. The pH sensor installation should be designed to enable easy access to the electrode for maintenance which usually includes cleaning with dilute hydrochloric acid (HCl) to dissolve the calcium scaling.

Figure 2. HF-resistant pH electrode for most HF neutralization processes

The pH vs. fluoride concentrations in Figure 3 shows the initial recommendation for sensor type for various operating conditions at 20°C (68°F). It is always desirable to use a conventional glass pH sensor which provides accurate measurement at moderate cost. The alternative is the HF-resistant glass sensor (Figure 2) which has a glass formulation more resistant to HF but is higher in cost. This figure is only a guide and cannot account for variations in temperature, additional materials present or other conditions which may affect the rate of attack of a glass sensor. Other factors may also be important in selecting the best sensor for a particular application, but this provides a starting point.

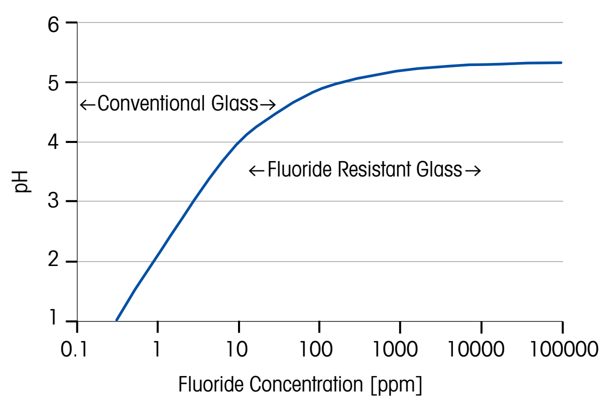


Figure 3. Selection of pH Sensor Type for Fluoride-Containing Processes at 20°C

Application Note

HF-Resistant Sensors
Inductive Conductivity for HF Etchant Concentration
52 005 424 7250 PFA Inductive Conductivity Sensor with 5 m (16 ft) cable
52 005 425 7250 PFA Inductive Conductivity Sensor with 10 m (33 ft) cable

Contact Conductivity with 0.1 cm-1 cell constant for HF Rinse Water
230-251 Monel conductivity sensor with 34 mm (1.35") insertion used with M800 Transmitter
230-261 Monel conductivity sensor with 132 mm (5.19") insertion used with M800 Transmitter
240-203 Monel conductivity sensor with 34 mm (1.35") insertion used with M300 Transmitter
240-204 Monel conductivity sensor with 132 mm (5.19") insertion used with M300 Transmitter
58 031 407 ISM Monel conductivity sensor with 34mm (1.35") insertion used with M800 and M300 ISM Transmitters

M300 ISM Transmitters
58 031 408 ISM Monel conductivity sensor with 132mm (5.19") insertion used with M800 and M300 ISM Transmitters

Glass pH Electrode for HF Neutralization
52 003 550 pH Electrode, 4262/120/Pt1000 VP HF Resistant, may be used with THORNTON housings and instruments including the M300 and M800 transmitters with preamplifier.

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