

The Use of Ozone in FPD Production

PROBLEM

The LTPS TFT (Low Temperature Polycrystalline Silicon Thin Film Transistor) process is a critical step in the production of flat panel displays (FPDs). In the LTPS TFT process, the cleanliness of the substrate prior to the transformation of silicon from an amorphous phase to a polycrystalline phase plays an important role in determining the ultimate electrical properties of the thin film transistor. In particular, metal and carbon contamination can have detrimental effects on transistor performance.

BACKGROUND

Flat Panel Displays and Thin Film Transistors

Display technology requires the fabrication of thin film transistors (TFTs) on glass substrates. These TFTs act as switches that turn the individual pixels in a display on and off. Historically, TFTs were developed for use with liquid crystal displays (LCDs), as shown in Figure 1. As display technologies have matured over the past decade, high-resolution LCD and organic light emitting diode (OLED) displays have begun to replace conventional LCDs as the preferred technology for some smartphone and other flat panel displays. The benefits of switching to high-resolution LCD and OLED technologies include greater power efficiency, brighter colors, and sharper images. Samsung is expected to supply Apple with 100 million OLED displays annually between 2017 and 2020. As well, high-resolution LCD and OLED technologies are now being employed for small/medium and flexible display applications.

Figure 2 shows the basic structures of LCD, high-resolution LCD and OLED displays. Each of these technologies employs TFTs to control pixel switching, with each pixel driven by TFT/capacitor circuitry located on what is known as the “backplane” of the display. In contrast to displays based on

LCD the OLED backplane requires at least one additional drive transistor. The electrical current through it determines the brightness of the light transmitted or emitted by each pixel.

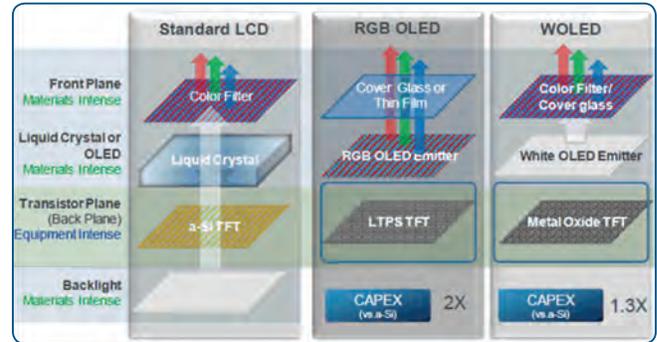


Figure 2. A comparison of the structures of LCD and OLED flat panel displays [2]

a-Si and LTPS TFTs

Conventional LCD displays use TFTs fabricated using amorphous silicon (a-Si) as the active semiconductor (see Figure 1). High-resolution LCD and OLED technologies employ a different TFT structure that uses low temperature polycrystalline silicon (LTPS) as the active semiconductor (certain high-resolution LCD technologies employ metal oxide, MO, active semiconductors, however this technology will not be discussed in this Applications Note and is not the standard technique).

Figure 3 illustrates the difference between amorphous, polycrystalline, and monocrystalline materials. Most readers will be familiar with monocrystalline silicon since that is the material from which the silicon wafers used for most electronic circuits are fabricated. In monocrystalline material, silicon exists as a single crystal with every atom fixed in an extended, ordered, three dimensional structure. In polycrystalline

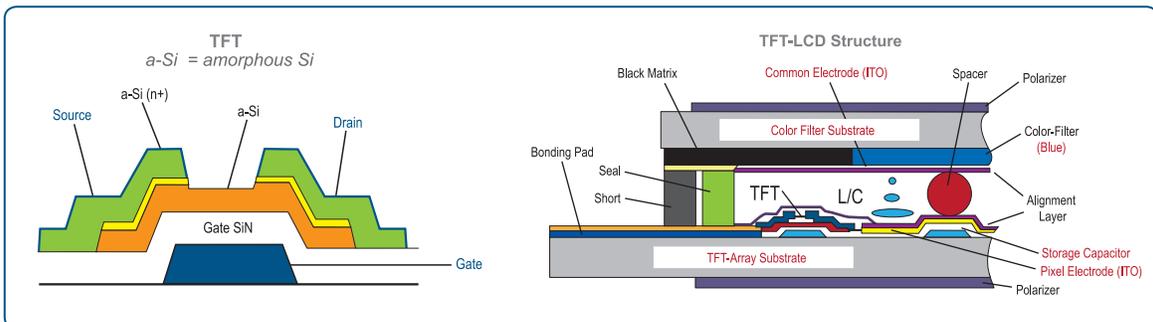


Figure 1. Thin film transistor (TFT) and its application in a conventional LCD display pixel [1]

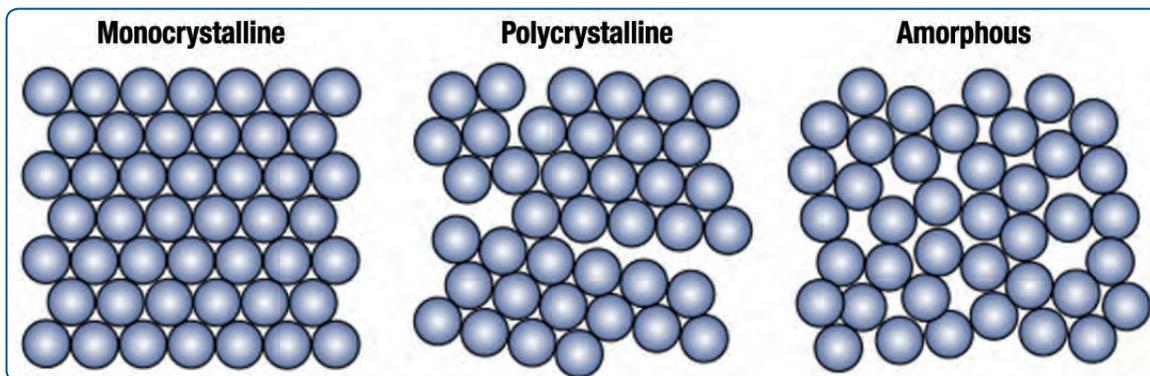


Figure 3. The atomic arrangement in monocrystalline, polycrystalline and amorphous states of matter.

material, such order is only present in small regions (known as domains or grains) that are packed tightly together to form a coherent thin film. The grain boundaries that exist between each domain impact the electrical properties of the film, degrading these properties in comparison with those of single crystal silicon. Amorphous material has neither short- nor long-range crystalline order. Compared to monocrystalline and polycrystalline silicon, amorphous silicon exhibits the poorest electrical properties especially in terms of electron mobility.

Even though a-Si's electrical properties are relatively poor, they proved adequate for the performance requirements of the TFTs employed in conventional LCD technology. The relatively low cost and simple process requirements for a-Si thin film deposition led a-Si devices to become the TFT technology of choice for standard LCDs. Recently, however, the consumer demand for higher resolution displays has led manufacturers to move to more advanced display technologies such as high-resolution LCD and OLED, at least for small and medium size displays.

LTPS Technology

Consideration of Figure 2 shows that advanced display technologies, both high-resolution LCD and OLED, require LTPS TFT technology (high-resolution LCD also utilizes MO TFT technology, but only to a very limited - ~1% - extent). LTPS TFT advantages over a-Si in these display technologies include much faster switching times (electron mobility in LTPS is > 100 x that in a-Si) and higher currents. The other major benefit of LTPS over a-Si is that the transistor size can be dramatically reduced while still providing the necessary power to drive the display. This allows significant reductions

in power requirements and/or greater resolution in high-resolution LCD and OLED displays.

LTPS, as the name suggests, produces a polycrystalline silicon thin film at temperatures significantly below those normally required for polycrystalline silicon deposition on glass. The term "low temperature" is, of course, relative. Conventional (high temperature polycrystalline silicon, HTPS) polycrystalline silicon deposition processes on glass or quartz require temperatures that range between 800 and 1000°C. Since conventional glass will begin to melt and flow at these temperatures, HTPS processes can only employ quartz substrates which limits the process to small panel application. The LTPS process, however, is performed at temperatures below 600°C. This allows LTPS to be used in much larger displays that use glass substrates. In the LTPS process a thin (~50 nm) layer of a-Si is first deposited on the substrate. This is subsequently annealed and crystallized using an excimer laser to convert the a-Si to a polycrystalline silicon film (Figure 4).

The excimer laser annealing (ELA) process is one of the most critical steps in the formation of LTPS. In a typical LTPS process, a 308 nm excimer laser beam is scanned over the thin a-Si film which absorbs the UV radiation, partially melting the surface of the film. Once the laser beam passes, the melted material solidifies, forming polycrystalline silicon in the process. Irradiation by the laser also transfers sufficient energy into the thin solid a-Si film that the remaining a-Si undergoes a transformation to crystalline material through a solid phase crystallization process in which crystalline silicon originating from the melt acts as a seed crystal.

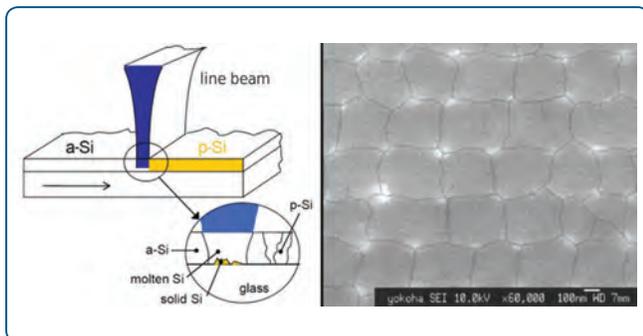


Figure 4. Laser annealing of a-Si to produce polycrystalline silicon [3]

The crystallization process and the electrical properties of the polycrystalline silicon films produced in LTPS technology strongly depend on the cleanliness of the substrate and the surface of the a-Si film. Both crystallization of silicon from the melted material and during the solid phase crystallization process depend on the purity of the silicon. If contamination is present, these residual impurities can easily diffuse throughout the thin a-Si film during ELA. Once crystallization has occurred, these impurities can act as traps for mobile electron charge carriers, degrading the device performance. As well, the presence of impurities can impact the crystallization process itself, producing less uniform polycrystalline and grain boundary characteristics which can, in turn, impact device yield. In particular, metal and carbon contamination which cause increased leakage currents must be eliminated for a reliable production of LTPS TFTs.

The use of ozonated water (DIO_3) for substrate cleaning has proven particularly effective in removing metal and carbon contamination on a range of substrates. Ozone (O_3) is the strongest commercially available oxidizing agent. It is an unstable oxygen compound produced when O_2 molecules are exposed to a high voltage electrical discharge. Its high electrochemical potential (e.g. 2.08 eV for ozone vs. 1.23 eV for the oxygen molecule) results in very fast reactions with molecules containing target contaminants such as carbon and metal atoms, either through direct reaction with the O_3 molecule or through the liberation of highly reactive atomic oxygen radicals which attack the target. Most organic compounds are rapidly oxidized by ozone, a characteristic that gives the compound its powerful properties.

Ozone generators have been available for well over a hundred years [4] and ozone use and handling are well understood. Ozone treatments have been applied across a broad spectrum of industrial applications, including water purification in semiconductor processing, municipal waste water treatment and medical disinfection [5] [6]. Simple injection of appropriate quantities of gaseous ozone into ultrapure water (UPW) called DIO_3 is all that is needed to produce an effective cleaning agent for metallic (it is often a combination with HF and/or HCl) and carbon contamination, making ozone a highly cost effective cleaning agent.

DIO_3 has found use in a number of processes requiring effective cleaning by oxidation. Within the semiconductor industry, it has proven as an effective and lower cost alternative to RCA and SPM solution cleaning processes. It has been shown to remove organic contamination (up to 20 ppm DIO_3) and metallic contamination (up to 30 ppm) and, in combination with HF/HCl, to be an effective agent for particle and metal removal.

SOLUTION

MKS Instruments Inc. offers the LIQUOZON® line of dissolved ozone delivery systems for use in applications requiring DIO_3 . These units have proven highly effective for DIO_3 -based substrate cleaning applications; MKS has been providing LIQUOZON DIO_3 systems to the FPD industry since 2003.

DIO_3 substrate cleaning has proven particularly useful in LTPS technology where 80% of yield decrease can be caused by contaminated surfaces prior to ELA. Cleaning a-Si with DIO_3 prior to ELA has been clearly shown to provide enhanced electrical performance in subsequent LTPS TFT devices.

Figure 5 shows a secondary ion mass spectrometry (SIMS) as a function of depth below a polycrystalline silicon/ SiO_2 surface. The scan demonstrates the effectiveness of DIO_3 cleaning in reducing carbon contamination. In this particular case, carbon contamination within the polycrystalline film was reduced by a factor of 3 using DIO_3 cleaning. This study also showed that DIO_3 had no influence on the nitrogen and oxygen concentrations in the polycrystalline silicon film [7].

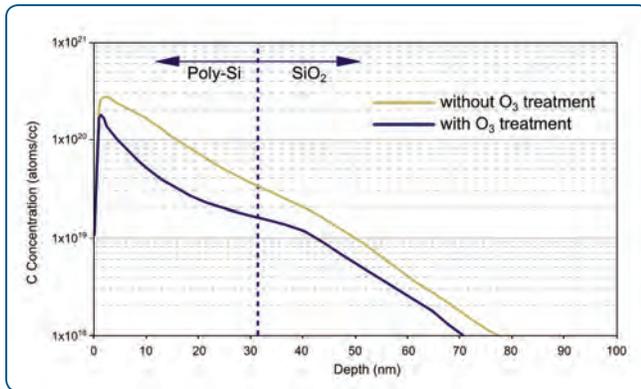


Figure 5. SIMS profile of carbon contamination with and without [7]

While the use of scanning electron microscopy (SEM) images for grain size determinations was unable to definitively show whether DIO₃ cleaning makes any significant difference to this thin film characteristic, qualitative examination of SEM photos suggests that grain size and uniformity becomes more regular when DIO₃ cleaning is employed prior to ELA. However, electron backscattering diffraction (EBSD) measurements have been able to determine that the average grain size in LTPS films is greater when the substrate/film undergoes a DIO₃ cleaning prior to ELA. Figure 6 shows one such determination in which the average grain size was increased by more than 25%. This difference is important for the LTPS TFT yield and functionality since a larger average grain size correlates with fewer uncontrolled grain boundary effects. Thus, the film uniformity can be drastically improved [7].

The effectiveness of DIO₃ cleaning in contaminant removal can also be demonstrated through a comparison of TFT performance for samples produced with and without a DIO₃ clean prior to ELA (Figure 7). The data in the graph in Figure 7 show that DIO₃ treatment prior to ELA drastically reduces the threshold voltage of LTPS TFTs. High mobility, low leakage currents and low threshold voltages, all of which are improved through DIO₃ cleaning, are desirable characteristics for high-resolution active matrix LCD and OLED display technology.

Finally, DIO₃ cleaning can represent a significant cost savings over conventional RCA and SPM cleaning technologies. As compared to RCA cleaning, DIO₃ procedures use less chemicals and DI water. This is because ozone has a higher oxidation-reduction potential than the active cleaning agents in RCA and SPM cleans; this translates to lower concentrations of oxidants needed to accomplish equivalent cleaning action. The higher oxidation potential also results in a higher removal rate for organic contaminants which translates to a high potential throughput rate in the cleaning process. As well, tighter concentration control is possible with DIO₃ which assures that only as much ozone as is needed is used in the cleaning procedure. All of these characteristics directly translate to a significantly lower Cost of Ownership for DIO₃ cleaning technology as compared with RCA and SPM cleans (Figure 8).

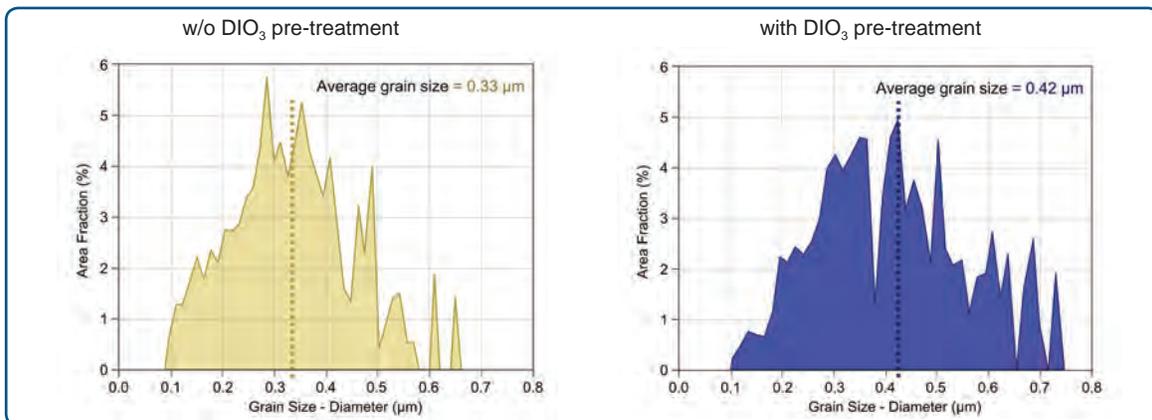


Figure 6. EBSD measurement of grain size distribution in LTPS with and without DIO₃ treatment prior to ELA [7]

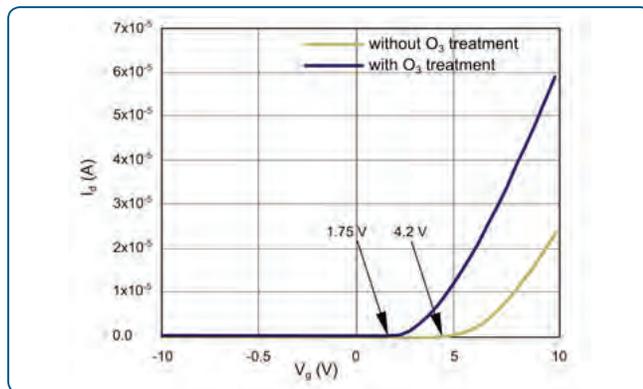


Figure 7. The effect of DIO_3 cleaning prior to ELA on TFT performance [7]

CONCLUSION

Current trends in flat panel display markets clearly show a move towards increased use of high-resolution LCD and OLED technology. This technology cannot be produced using standard a-Si TFT technology and the industry is therefore undergoing a shift to LTPS-TFT for switching and brightness control in advanced FPDs.

TFT electrical characteristics in devices fabricated using LTPS technology are critically dependent on the cleanliness of the substrate and a-Si film prior to excimer laser annealing. Contamination by metals and carbon, especially, degrade the performance of TFTs produced using LTPS.

DIO_3 has been demonstrated as an effective cleaning agent for the removal of metallic and carbon contamination in LTPS applications. DIO_3 cleaning prior to ELA reduces carbon contamination in the polycrystalline silicon film by a factor of three. Good evidence exists for a positive correlation between DIO_3 cleaning and increased and more uniform grain size in the polycrystalline silicon film.

Cleaning with DIO_3 prior to ELA yields TFTs with high electron mobility, lower leakage currents and lower threshold voltages, all highly desirable properties for TFTs in FPD applications.

Finally, the use of DIO_3 rather than RCA and SPM cleaning procedures results in a significant reduction in the CoO of the cleaning process used in FPD fabrication.

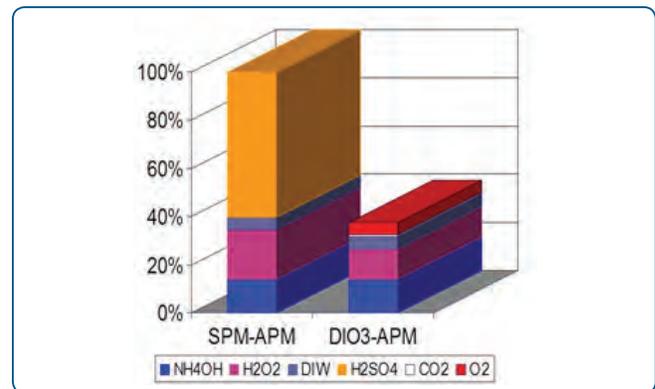


Figure 8. Detailed chemical cost per run comparison, SPM vs DIO_3 clean, spray tool [8]

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For more information on MKS Instruments' LIQUOZON® Ozone Delivery Technology, link to: <https://www.mksinst.com/product/category.aspx?categoryid=2>

For a general catalog of MKS products, go to <https://www.mksinst.com/>

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