

Chapter 2

Pre Treatment Processes of Amorphous Silicon Thin Films

2.1 Introduction

Recently the poly-crystalline Silicon thin film transistor (poly-silicon TFTS) was employed by the active devices in driver circuits of active matrix liquid crystal display (AM-LCD) and active matrix organic light emitting diode display (AM-OLED), all applications need the uniform film and larger poly-Silicon grain size where it should be fabricated on the glass under the fabrication temperature was less than 600°C. To attain this requirement, the laser annealing and thermal annealing crystallization had been investigated. We reported the XeCl excimer laser annealing and presented the uniform film for self-alignment grain structure with surface oxidation of amorphous. We established three conditions that included the HF + H₂O₂ water, HF + O₃ water, HF + UV exposure prior clean, respectively, and it was crystallized by the irradiation of XeCl excimer laser annealing with energy density 370mJ/cm² in N₂ ambient. The laser beam was uniformed by long and short homogenizers and was focused by 5 times lens on the surface of the sample with a size of 0.4×320 mm². The prior clean condition of HF clean was the base treatment process that would compare with other prior clean conditions. The other prior clean conditions were HF + H₂O₂ water, HF + O₃ water and HF + UV exposure prior clean

Among many crystallization techniques reported to date, excimer laser crystallization seems to be the most promising method. Poly-silicon thin film with large grain size could be

manufactured with suitable laser conditions, such as laser energy density, laser frequency, and laser energy. The crystallization mechanism of α -silicon by ELA at various energy regimes had been described [10], [11]. Three major regimes could be identified based on the thin film microstructure as a function of the incident laser energy density. First, in the low energy density regime, the grain size was found to increase with laser energy density. It could be associated with explosive crystallization followed by partial melting and regrowth of the thin film. Second, in the high energy density regime, corresponding to complete melting of the thin film, small fine grain size was observed and independent of the incident energy density. It was related to the substantial supercooling taking place before the onset of solidification due to homogeneous nucleation. At last, in the medium energy density regime, which was the transition regime between the first two, the largest grain sized poly-silicon could be acquired. The laser energy density was corresponding to nearly complete-melting of the poly-silicon thin film. The phenomenon occurs within a narrow process window, referred to as the super lateral growth (SLG) [12]. The laser-irradiated films were melted in liquid phase and solidify from the residual silicon seeds at the liquid-Si/oxide interface. Fig. 2-2 ~ 2-47 illustrate the mechanism of the ELA poly-silicon within different laser energy regions.

At present, pre treatment process had been done to investigate excimer laser crystallization of α -silicon thin films. In this chapter, we would compare the different prior clean condition in physical characteristics for poly-silicon thin film and electric characteristics for LTPS devices.

2.2 Experimental Procedure

A buffer layer of 50nm/150nm thickness of SiN_x/SiO_x [13] were deposited by plasma enhanced chemical vapor deposition (PECVD) means at 500°C on glass substrate. Amorphous silicon film of a 50nm thickness was deposited on buffer layer as the active layer by PECVD at 500°C with SiH₄ gas source then was heated at 500°C for one hour to remove the incorporated hydrogen in the film. After dehydrogenation, first procedure was prior clean

treatment with HF clean then established three surface treatment conditions that included the H₂O₂ water, O₃ water, UV exposure prior clean, respectively, and it was crystallized by the irradiation of XeCl excimer laser annealing with energy density 370mJ/cm² in N₂ ambient. The first condition was surface cleaning with O₃ water which concentration was 20ppm, the second condition was surface cleaning with H₂O₂ water which concentration was 30%, the third condition was surface cleaning with UV light exposure which wave length was 254um, and all of these conditions could advance the surface oxidation of α -silicon thin films, it had the difference at long time or short time treatment. Crystallization was carried out by excimer laser annealing with wavelength of 308 nm in N₂ ambience [14] at room temperature. The laser beam was uniformed by long and short homogenizers and was focused by 5 times lens on the surface of the sample with a size of 0.4×320 mm². The optical system of ELA was shown in Fig. 2-1. Top-gate, poly-silicon TFTs was fabricated with conventional processing. The polycrystalline layer was tailored into active islands. Next, PR coating and patterned then n⁺ ion doping of PH₂⁺ ion implantation with the concentration of 6×10¹⁴ cm⁻², then 1000Å TEOS gate oxide was deposited using PECVD, then PR coating and patterned, then LDD ion doping of PH₂⁺ ion implantation with the concentration of 2×10¹³ cm⁻² was carried out to form the n-type source and drain region, then PR coating and patterned, then p⁺ ion doping of BF₂⁺ ion implantation with the concentration of 1×10¹⁵ cm⁻² was carried out to form the p-type source and drain region, than rapid thermal annealing was performed to activate the implanted dopants and recrystallize the source and drain region at temperature 650°C. 2000Å Mo gate electrode was deposited using PVD. Then, a 3000Å/500Å PECVD SiO_x/SiN_x was deposited as passivation layers. After contact holes opening, Ti/Al/Ti was deposited by thermal evaporation and patterned to form the electrical connecting pads [15].

The transfer characteristics of the poly-silicon TFTs were measured by HP4156 semiconductor parameter analyzer. The device parameters including the field-effect mobility, the subthreshold swing, the threshold voltage, the off current and the on/off current ratio were extracted from the measured characteristics.

The base treatment process of HF clean had three parameters of experiment, it was included the clean time 0sec, 30sec, 90sec and 150sec and excimer laser parameters were included energy 950mJ, frequency 300Hz, power 285W, scan speed 6mm/sec, pitch 0.02mm, beam width 0.4mm and energy density range from 330mJ /cm² to 430mJ/cm². The treatment clean process of O₃ clean had six parameters of experiment, it was included the clean time 0sec, 50sec, 100sec, 300sec, 500sec and 900sec and excimer laser parameters were included energy 950mJ, frequency 300Hz, power 285W, scan speed 6mm/sec, pitch 0.02mm, beam width 0.4mm and energy density range from 330mJ /cm² to 440mJ/cm².

The treatment clean process of H₂O₂ clean had seven parameters of experiment, it was included the clean time 0sec, 30sec, 180sec, 300sec, 420sec, 540sec and 900sec and excimer laser parameters were included energy 950mJ, frequency 300Hz, power 285W, scan speed 6mm/sec, pitch 0.02mm, beam width 0.4mm and energy density range from 330mJ /cm² to 440mJ/cm².

The final treatment clean process of UV exposure clean have four parameters of experiment, it was included the clean time 0sec, 200sec, 400sec and 600sec and excimer laser parameters were included energy 950mJ, frequency 300Hz, power 285W, scan speed 6mm/sec, pitch 0.02mm, beam width 0.4mm and energy density range from 330mJ /cm² to 440mJ/cm².

Cross section-view transmission electron microscopy (TEM) was used to determine the grain boundary shape and size. Surface roughness of the as deposited and excimer laser annealed poly-silicon thin films had been investigated by atomic force microscopy (AFM).

2.3 Results and Discussion

2.3.1 The Prior Clean of HF + H₂O₂ Water

The pre treatment clean process of α -silicon thin films with surface oxidation clean that need to be treated by HF 1% for 30sec. Because of the surface was oxidized by oxidizer only, it was included the H₂O₂ water 30%, O₃ water 20ppm and UV exposure with wavelength

254nm. The base treatment clean process of HF 1% clean time was defined by grain size distribution versus laser energy densities as shown in Fig. 2-2 ~ 2-4. The base pre treatment process time was included 30, 90 and 150 sec. The Fig. 2-2 was shown the average grain size distribution of HF 1% pre treatment clean. The pre treatment clean time was zero the average grain size was larger than other pre treatment clean time when laser energy densities were from 330 to 380mJ/cm². The second large grain size was pre treatment clean of HF 1% for 30sec; if clean time was increased more long the grain size became smaller in high laser energy densities form 400 to 430 mJ/cm². The Fig. 2-3 was shown the maximum grain size distribution of HF 1% pre treatment clean. The sample was no clean having larger grain size; this condition was like the minimum grain size distribution as shown in Fig. 2-4. The base clean function could rid of particle and oxide from surface and improve the surface contact quality, so the optimization of base pre treatment clean process time was 30sec with HF 1%, and grain size was about 0.44um at the energy density 410 mJ/cm². In the Fig. 2-5 was shown the pre treatment clean of H₂O₂ 30% water clean after laser irradiation, the average grain size distribution versus laser energy densities. It was no pre treated by H₂O₂ 30% water had larger grain size in high energy density about 430 mJ/cm². It meant the surface oxidation of a-silicon that was formed the oxidative layer not complete oxidization. So it did not have the oxidative layer to reserve the heating of laser energy and retard the super cooling taking place before the onset of solidification due to homogeneous nucleation. In the low energy density region, the grain size was found to increase with laser energy density and pre treatment clean time from 180 to 900 seconds. In the medium energy density region, which was the transition region between the partial melting and complete melting that could induce larger grain with the pre treatment clean time for 30 seconds. The maximum grain size distribution had larger grain with the high energy densities from 410 to 440 mJ/cm²; nevertheless the minimum grain size distribution had larger grain with the medium energy densities from 370 to 410 mJ/cm² as shown in Fig. 2-6, 2-7. In this region the average grain size distribution with pre treatment clean time 420 seconds had larger grain than others in energy density 400 mJ/cm², but the uniformity of poly crystallization film was not so better,

so the optimization of pre treatment clean process time was 420 seconds with H₂O₂ 30% in energy density 370 mJ/cm², and grain size was about 0.3μm.

2.3.2 The Prior Clean of HF + O₃ Water

The pre treatment clean process with O₃ water 20ppm was obtained the different situation in average grain size distribution with pre treatment clean process of H₂O₂ water 30%. It was same condition without any oxidative pre treatment clean before mention. In the low and medium energy density regions of average grain size distribution of pre treatment clean with O₃ water 20ppm had obviously variation, when energy density below 370 mJ/cm² the grain size variation small, when energy density over this value the grain size became larger; this situation was like base pre treatment clean of HF 1%, it was shown in Fig. 2-8. The energy densities of three regions were same as conditions of pre treatment clean of H₂O₂ water 30%. The maximum and minimum grains size distribution had larger grain with the high energy densities regions was like the region of pre treatment clean of H₂O₂ water 30%, as shown in Fig. 2-9, 2-10. In the minimum grain size distribution with pre treatment clean time 500 seconds had larger grain than others in energy density 400 mJ/cm², but in the average grain size distribution with pre treatment clean any time except 0 and 50 seconds had larger grain so the optimization of pre treatment clean process time was 100 seconds with O₃ 20ppm in energy density 400 mJ/cm², and grain size was about 0.35μm.

2.3.3 The Prior Clean of HF + UV Exposure

The average grain size distribution of pre treatment clean process with UV exposure was shown in Fig. 2-11, the medium energy density region was 360 to 390 mJ/cm², it was different from before pre treatment clean process that the medium energy density region was shifted forward 10 mJ/cm², it meant the surface oxidative speed of α-silicon was more fast than others, so it had the oxidative layer to reserve the heating of laser energy and retard the super cooling taking place in the small energy densities region. It was shown in Fig. 2-12, the maximum grain size distribution had same condition in larger grain with the high energy

densities from 390 to 440 mJ/cm². The minimum grain size distribution had larger grain with the medium energy densities from 350 to 410 mJ/cm² as shown in Fig. 2-13. This medium region was shifted forward 20 mJ/cm². The average grain size distribution had larger grain size and uniform poly film with the high energy density 390 mJ/cm² and UV exposure time was 200 seconds, so the optimization of pre treatment clean process time was 200 seconds with UV exposure in energy density 390 mJ/cm², and grain size was about 0.35 μ m.

2.3.4 Physical Characteristics

(A) Scanning Electron Microscope

The grain size of the ELA poly-silicon thin film could be measured by using SEM. In order to distinguish the individual grain structure, the ELA poly-silicon thin film was immersed in the Secco etching solution [16], which etched the grain boundaries more quickly than the interior parts of the grains. Fig. 2-14 ~ 2-47 was shown the SEM micrographs of the ELA poly-silicon film after Secco etching for 60seconds. The excimer laser energy densities were adjusted from 330 to 440 mJ/cm². In addition, different pre clean treatment conditions were also influence during ELA process. As shown in Fig. 2-14, the applied laser energy densities were 330 to 380 mJ/cm². The laser energy 950mJ, frequency 300Hz, power 285W, scan speed 6mm/sec, pitch 0.02mm, beam width 0.4mm and pre treatment clean with HF 1% for 30seconds no large grains were observed, As shown in Fig. 2-15, increased the laser energy densities from 390 to 440 mJ/cm², the grains structure were unregulated and non uniform in high energy densities, so the energy densities more high the grain size more large and non uniform. Fig. 2-16 and 2-17 were shown the different pre treatment clean time with HF 1% for 90sec and same conditions before mention, the grains structure had no obviously difference. Fig. 2-18 and 2-19 were shown the pre treatment clean of HF 1% for 150sec and had same conditions grain structures.

The Fig. 2-20 and 2-21 were shown the different pre treatment clean time with O₃ water 20ppm for 50sec, the grain structure had a little regularization that had one dimension structure to be named the 1D self-alignment and direction was same as laser scanning

direction. The laser energy densities were focused in the medium energy density region, which was the 390 and 400 mJ/cm²; the largest grain sized poly-silicon could be acquired. The grain size was about 0.3um. If the pre treatment clean time was increased the grain structure had more regularization, it meant the surface oxidative condition of α -silicon could decide the grain structure. The pre treatment clean time was enough the grain structure was regularization in optimization energy density; in this case, the O3 water clean time was 50 seconds in energy density 400 mJ/cm² had regularization grain structure, as shown in Fig. 2-22 ~ 2-29.

The Fig. 2-30 and 2-31 were shown the different pre treatment clean time with H2O2 water 30% for 30sec, the grain structure was like the pre treatment clean of HF 1% condition and grain size was large when energy density over 390 mJ/cm², the clean time was increased the grain structure was more regularization; in this case the clean time was 300 seconds at least, as shown in Fig. 2-32 ~ 2-41.

The Fig. 2-42 and 2-43 were shown the different pre treatment clean time with UV exposure for 200sec, the 1D self-alignment grain structure was observed in energy density 380 mJ/cm². So if the surface had complete oxidation, the 1D self-alignment grain structure occur in optimization energy density; in this case the exposure time was 200 seconds at least in the energy density 380 mJ/cm², as shown in Fig. 2-44 ~ 2-47.

(B) Atomic Force Microscopy

The atomic force microscopy (AFM) was shown in Fig. 2-48 ~ 2-50. The base pre treatment clean of HF 1% for 30seconds was shown the mean roughness and maximum roughness in the energy densities 310, 360, 400 mJ/cm², respective. The applied laser energy density was 310 mJ/cm² and the mean roughness was 2.45nm, maximum roughness was 21.12nm, the applied laser energy density was 360 mJ/cm² and the mean roughness was 1.53nm, maximum roughness was 14.67nm, the applied laser energy density was 400 mJ/cm² and the mean roughness was 2.9nm, maximum roughness was 39.31nm, as shown in Fig. 2-48. It was observed the less roughness in optimization grain size condition.

In the Fig. 2-49, the pre treatment clean of O3 20ppm for 100seconds was shown the mean roughness and maximum roughness in the energy densities 300, 340, 360 mJ/cm², respective. The applied laser energy density was 300 mJ/cm² and the mean roughness was 6.48nm, maximum roughness was 58.87nm, the applied laser energy density was 340 mJ/cm² and the mean roughness was 8.72nm, maximum roughness was 82.89nm, the applied laser energy density was 360 mJ/cm² and the mean roughness was 5.99nm, maximum roughness was 63.52nm. The optimization grain size of O3 pre clean was more roughness.

In the Fig. 2-50 the pre treatment clean of UV exposure for 400seconds was shown the mean roughness was 7.55nm, the maximum roughness was 61.74nm in the energy density 300 mJ/cm², the mean roughness was 7.49nm, the maximum roughness was 77.61nm in the energy density 340 mJ/cm², the mean roughness was 6.08nm, the maximum roughness was 69.82nm in the energy density 360 mJ/cm², this condition was same as O3 pre treatment clean.

(C) Transmission Electron Microscopy

The micro-structural morphologies such as the grain size, inter- and intra-grain defect density, and grain orientation could be investigated from the TEM images and the electron diffraction patterns. As depicted in cross-section TEM images, the invert V-shaped, crystalline structure was observed for the poly-silicon thin film after excimer laser irradiation. Fig. 2-51 is shown cross-section TEM micrographs of the ELA poly-Silicon thin films. The invert V-shaped grain structures in the ELA poly-silicon thin films are the locations of grain boundary that was compared with Fig. 2-48 ~ 2-50 of atomic force microscopy (AFM). The roughness shape was similar to those invert V-shaped of the ELA poly-silicon thin films. Hence the roughness shape was the location of grain boundary.

2.3.5 Electrical Characteristics

Fig. 2-52, the field effect mobility (μ_{FE}) versus clean time, base pre treatment clean of HF 1% was shown the clean time more long the μ_{FE} had a little degradation. The pre

treatment clean time was 30seconds that mean value of μ_{FE} was $125 \text{ cm}^2/\text{V}\cdot\text{s}$ for n-type LTPS TFT and p-type was $92 \text{ cm}^2/\text{V}\cdot\text{s}$ in energy density $420 \text{ mJ}/\text{cm}^2$. The threshold voltage of base pre treatment clean of HF 1% was depicted the variation in different clean time, it had no treatment clean that threshold voltage was shifted to positive about 4V for n-type LTPS TFT and the p-type threshold voltage was -1V . The clean increased to 150seconds the threshold voltage was shifted to negative about 1.2V for n-type LTPS TFT and the p-type threshold voltage was -4.2V ; so the better clean time for base treatment clean of HF 1% was 30seconds, as shown in Fig. 2-53. The file transfer characteristics of ELA LTPS TFT using base pre treatment clean with HF 1% for 30seconds in energy density $420 \text{ mJ}/\text{cm}^2$. Some important electrical characteristics of LTPS TFTs were also listed, it was included the $W/L = 6\mu\text{m}/12\mu\text{m}$, $V_d=0.1\text{V}$, $V_t -3.4\text{V}$, $U_{fe} 90 \text{ cm}^2/\text{V}\cdot\text{sec}$, $I_{off} 1.87\text{E}-13\text{A}$, SS 0.45 for p-type LTPS TFT and $V_t 2.5\text{V}$, $U_{fe} 126 \text{ cm}^2/\text{V}\cdot\text{sec}$, $I_{off} 1.00\text{E}-14\text{A}$, SS 0.71 for n-type, as shown in Fig. 2-54 and 2-55.

Fig. 2-56, the field effect mobility (μ_{FE}) versus clean time, the pre treatment clean of H₂O₂ 30% was shown the clean time more long the μ_{FE} was increased. The pre treatment clean time was 420seconds that μ_{FE} was $137 \text{ cm}^2/\text{V}\cdot\text{s}$ for n-type LTPS TFT at mean value and p-type was $103 \text{ cm}^2/\text{V}\cdot\text{s}$ in energy density $400 \text{ mJ}/\text{cm}^2$. The threshold voltage for pre treatment clean of H₂O₂ 30% was depicted the variation in different clean time, in any clean time the threshold voltage was shifted to positive value except the no pre treatment clean, as shown in Fig. 2-57. In the Fig. 2-58, the transfer characteristics of p type ELA poly-Silicon TFTs with H₂O₂ pre treatment clean for 420 sec in laser energy density $400\text{mJ}/\text{cm}^2$ had data listed $W/L = 6\mu\text{m}/12\mu\text{m}$, $V_d= 0.1\text{V}$, $V_t -2.2\text{V}$, $U_{fe} 104 \text{ cm}^2/\text{V}\cdot\text{sec}$, $I_{off} 1.20\text{E}-13\text{A}$, SS 0.37. The transfer characteristics of n type were drawn in Fig. 2-59, $V_t 4.2\text{V}$, $U_{fe} 135 \text{ cm}^2/\text{V}\cdot\text{sec}$, $I_{off} 1.53\text{E}-13\text{A}$, SS 0.44.

Fig. 2-60, the field effect mobility (μ_{FE}) versus clean time, the pre treatment clean of O₃ water 20ppm was shown the clean time 100 seconds the μ_{FE} was maximum. The μ_{FE} was $135 \text{ cm}^2/\text{V}\cdot\text{s}$ for n-type LTPS TFT at mean value and p-type was $101 \text{ cm}^2/\text{V}\cdot\text{s}$ in energy density $400 \text{ mJ}/\text{cm}^2$. The threshold voltage for pre treatment clean of O₃ water 20ppm was depicted the variation in different clean time, in any clean time the threshold voltage was shifted to

positive value except the no pre treatment clean and clean 50seconds only, this condition was same as pre treatment clean of H₂O₂ 30%, as shown in Fig. 2-61. In the Fig. 2-62, the transfer characteristics of p type ELA poly-Silicon TFTs with O₃ pre treatment clean for 400 seconds in laser energy density 400mJ/cm² had data listed W/L = 6μm/12μm, V_d= 0.1V, V_t -1.9V, U_{fe} 88 cm²/V•sec, I_{off} 1.03E-13A, SS 0.16. The transfer characteristics of n type were drawn in Fig. 2-63, V_t 2.9V, U_{fe} 134 cm²/V•sec, I_{off} 2.87E-13A, SS 0.52.

Fig. 2-64, the field effect mobility (μ_{FE}) versus clean time, the pre treatment clean of UV exposure with wavelength 254nm was shown the exposure time 200seconds the μ_{FE} was maximum. The μ_{FE} was 148 cm²/V*s for n-type LTPS TFT at mean value and p-type was 110 cm²/V*s in energy density 400 mJ/cm². The threshold voltage for pre treatment clean of UV exposure was depicted the variation in different clean time, the V_{tn}-V_{tp} was small with exposure time 200seconds, as shown in Fig. 2-65. In the Fig. 2-66, the transfer characteristics of p type ELA poly-Silicon TFTs with UV exposure pre treatment clean for 200seconds in laser energy density 400 mJ/cm² had data listed W/L = 6μm/12μm, V_d= 0.1V, V_t -1.3V, U_{fe} 102 cm²/V•sec, I_{off} 1.07E-13A, SS 0.16. The transfer characteristics of n type were drawn in Fig. 2-67, V_t 3.2V, U_{fe} 147 cm²/V•sec, I_{off} 1.71E-13A, SS 0.36.

2.4 Conclusions

From the results of material analysis and device characterization, the relation between electrical characteristics of LTPS TFTs and pre treatment processes conditions with laser annealing conditions had been identified. It was found that caused the surface oxidation of α-silicon thin films by pre treatment process and laser energy density had a deep influence on the resulting poly-silicon grain structure and electrical characteristics of LTPS TFTs. It was included the different methods of pre treatment process, the first method was surface cleaning with O₃ water which concentration was 20ppm, the second method was surface cleaning with H₂O₂ water which concentration was 30%, the third method was surface cleaning with UV light exposure which wave length was 254um, and all of these methods could advance the surface oxidation of α-silicon thin films, it had the difference at long time or short time

treatment. When surface of α -silicon thin films was completely oxidized by pre treatment process then treated by ELA, the LTPS thin films would be fabricated with grain size about 0.3 μ m, grain shape like square and uniform distribution on surface, but the surface was more roughness, this structure was named 1D self-alignment grain structure that was produced in optimization energy density region and direction was same as laser scanning direction. The pre treatment clean condition had 1D self-alignment grain structure, it was included the O₃ water clean time 50 seconds at least, H₂O₂ clean time 300 seconds at least and UV exposure time was 200 seconds at least. The optimization condition of every pre treatment clean was decided in this situation, the LTPS TFTs fabricated by ELA with optimization laser energy density, the field effect mobility of 130 and 90 cm²/V*s could be achieved for n-channel and p-channel ELA LTPS TFTs, respectively. The thresholds voltage had different shift owing to the difference surface oxidation on α -silicon thin films. The better condition for pre treatment clean of UV exposure was obtained in field effect mobility (μ_{FE}) and threshold voltage. The UV exposure was induced the O₃ gas in atmosphere, this situation would advance the surface oxidation of α -silicon thin films and the oxidative layer will reserve the heating of laser energy, so grain size was larger than other pre treatment clean condition and μ_{FE} was 148 cm²/V*s at mean value.