In-Situ and Ex-Situ Measurements on Silicon Thin Films Fabricated by Excimer Laser Annealing

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Abstract. The phase transitions occurring at the surface of amorphous silicon and a-Si/SiO\textsubscript{2} interface of the sample during XeF\textsubscript{2} excimer laser annealing has been investigated by non-intrusive in-situ real-time optical reflectivity and transmissivity measurements with nanosecond time resolution. Five distinct regimes were demonstrated on the basis of various excimer laser fluences. The structural transformation scenario of silicon films based on the recrystallization mechanism is proposed to interpret the formation of the grain microstructure. The ex-situ microstructural characterizations of excimer laser-irradiated region as a function of various excimer laser energy densities were characterized by scanning electron microscopy and micro-Raman scattering measurements. A super-lateral growth length of approximately 1\,\mu m was obtained in a 90-nm-thick a-Si film by a single excimer laser pulse without any substrate heating. Micro-Raman scattering measurements as a function of various excimer laser energy densities were also carried out.

1. Introduction

Excimer laser annealing (ELA) of amorphous silicon (a-Si) thin films has emerged as a promising method for fabricating polycrystalline silicon (poly-Si) thin-film transistors (poly-Si TFTs) in the context of active-matrix liquid-crystal displays (AMLCDs) \cite{1}. ELA is superior to other annealing approaches such as solid-phase crystallization (SPC) \cite{2} and metal-induced crystallization (MIC) \cite{3} mainly because it is a low-thermal-budget processing technique allowing the use of inexpensive glass substrates. Further, this method can produce large grained poly-Si with a low dislocation density. It is necessary to realize the phase transformation mechanism of silicon films for fabricating good quality poly-Si films during ELA. The accurate phase transformation mechanisms involved in the process are not well understood even if investigations of ELA of thin amorphous Si films have been widely performed in the past several years \cite{4}, especially for back side ELA. Many research groups have extensively studied the mechanism of XeCl ELA of a-Si prepared by low pressure chemical vapor deposition (LPCVD) \cite{5}. The recrystallization mechanism of plasma-enhanced chemical-vapor-deposition (PECVD)-grown amorphous silicon films, however, is less studied in this respect. Accordingly, a-Si films prepared by PECVD were used in this study. A non-invasive in-situ time–
resolved optical reflection and transmission (TRORT) [6-8] monitoring system combining two continue wave He-Ne probe lasers, a digital oscilloscope and three photodectors is utilized to interpret the structural transformation dynamics of a-Si films during XeF ELA using three types of optical measurements including front side reflectivity, front side transmissivity and back side reflectivity. The melt-mediated transformation scenarios of the Si thin films were determined in terms of various excimer laser energy densities. The resulting poly-Si films of the XeF excimer laser-irradiated region were characterized using field emission scanning electron microscopy (FE-SEM) and micro-Raman scattering measurements.

2. Experiment

2.1. Sample preparation

The glasses (NEG OA10, Nippon Electronic Glass) were used as substrates in this work. Silane-based a-Si films of 90 nm-thick were deposited on 0.7 mm-thick glass substrate covered with a 300-nm thick SiO₂ layer by PECVD using an AKT 1600 cluster tool. These samples were then dehydrogenated by performing a thermal treatment in an argon atmosphere at approximately 550°C for two hours to reduce the content of hydrogen to prevent the ablation caused by sudden hydrogen eruption during ELA.

2.2. Excimer laser annealing system

The sample was held in self-closing tweezers at the end of the cantilever beam fixed on the x-y precision translation stage. The x and y axis displacement of the two stages can accurately be controlled (resolution 0.625μm) using a LabVIEW™ based (National Instruments Inc.) custom design interface in order to yield large area crystallization. The movement of the focusing lens mounted on the z-axis stage was precisely controlled to adjust the laser energy density during ELA. All the experiments were performed at room temperature and atmospheric pressure. The a-Si thin films was irradiated by a XeF excimer laser beam (LAMBDA PHYSIK COMPex 102, wavelength =351nm, pulse duration= 25ns, repetition rate=1Hz). The beam slit of 4mm×15mm was also used to increase the intensity uniformity within a shot, rather than using the beam homogenizer. The output energy of the laser light was monitored with a laser power meter (Vector H410 SCIENTECH, Inc.), and calibrated every time just before using the XeF excimer laser.

2.3. Thin film analysis

In order to analyze the phase transformation of a-Si/SiO₂ interface, the front He-Ne probe laser had a 45° angle of incidence from the normal of the sample's surface, while the back He-Ne probe laser had a 37° angle of incidence from the normal of the sample's surface. The fast digital storage oscilloscope (Lecroy WS-454, bandwidth =500 MHz, maximum sample rate= 2GS/s) was used to record the reflective and transmissive spectra data simultaneously with a time resolution of 1 ns. A BK7 beam splitter(R : 90±3%,d2”x t 0.25”) was used to reflect 10 % of the excimer laser beam to a triggering Si PIN photodetor in order to trigger the digital storage oscilloscope during XeF ELA. Figure 1 shows the three configurations of front side reflectivity (FSR), front side transmissivity (FST) and back side reflectivity (BSR) in the back side ELA. The utilization of the three configurations provides complementary information in-time and depth concerning the melting and recrystallization process for analyzing the structural transformation dynamics of PECVD-grown silicon films during XeF ELA. After ELA, the extensive microstructural analysis and grain size of the excimer laser-irradiated region were carried out using FE-SEM (Oxford JEOL JSM-6500F) operated at an acceleration voltage of 15 kV (resolution 1.5nm). The micro-Raman scattering measurements of the irradiated region of the sample were obtained at room temperature using a Renishaw inVia micro-Raman-spectroscopy in back-scattering mode operated at 3mW. The system is equipped with an optical microscope for focusing the 514.5 nm (spot size=5 μ m, resolution=2 cm⁻¹) excitation line from the Ar⁺ laser beam onto the sample.
3. Results and discussions

3.1. Phase transformation scenarios
Following ELA at laser energy density range from 90 mJ/cm² to 250 mJ/cm², the experimental results can be divided into five distinct regimes based on the different laser energy densities: heating of the Si films, partial melting, near-complete melting, complete melting, and ablation of the Si films. At a laser energy density of 75 mJ/cm², the reflectivity and transmissivity spectrum exhibited an abrupt drop, followed by a relaxation to the initial value indicating that the a-Si did not melt and the a-Si film was merely undergoing heating and cooling during ELA. The changes in the TRORT spectra are governed by the increase in the extinction coefficient and the temperature-dependent optical constants of Si [9]. No poly-Si films in the sample were observed using FE-SEM and micro-Raman scattering measurements. Therefore, the laser energy density of 75 mJ/cm² is well under the threshold for surface melting of a-Si films in this study.

As to the above surface melting threshold of a-Si films, two distinct processes take place during the crystallization of a-Si films using pulsed XeF excimer laser irradiation. One is the melting of the amorphous material following the absorption of the laser light and the other is the nucleation and subsequent growth of poly-Si grains as the sample cools. The formation of nuclei is a crucial step for the phase transition. Evidence from these two distinct steps of laser energy density of 190 mJ/cm² during ELA is shown in Figure 2. The data are normalized to the initial a-Si reflectivity. The sample initially absorbs the XeF excimer laser irradiation (from point A to point B). Most of the laser beam energy is absorbed at a shallow depth of approximately 20 nm into the top a-Si film [9]. The sample starts to melt indicated by point B. This is attributed to the formation of the melted liquid Si layer on the sample (from point C to point D). The reflectivity increases because the reflectivity of Si changes from 32% to 76% upon melting during the phase transition from solid to liquid, which exhibits the metallic behavior [10]. In addition, the refractive index (n) linearly decreases with the temperature for He-Ne laser. Between point D and point E the reflectivity decreases, indicating the solidification process. This result is in good agreement with the observation of amorphous germanium (a-Ge) during ELA by Mulato et al. [11]. The melt-phase duration is indicated at intervals between point B and point E. The surface reflectivity and interface reflectivity increase and the transmissivity decrease following the XeF excimer laser irradiation. The “top-hat” profile is observed both in the surface reflectivity spectrum and the interface reflectivity spectrum. The interface reflectivity remains approximately 40 ns in the plateau before decreasing upon solidification. However, the surface reflectivity only remains at approximately 25 ns in the plateau before decreasing upon solidification. The melt-phase duration is approximately 50 ns and 60 ns for surface and interface, respectively. Point E is defined as

![Figure 1](image-url)
the completion of solidification. The sample is completely transferred to poly-Si at point F. The resolidification velocity of the surface (line L1) is faster than the interface (line L2) of the silicon film. The recalescence phenomenon is observed in the surface spectrum at mark a. The recalescence phenomenon [12] indicates the reheating and remelting processes produced by the release of the solidification heat during the bulk solidification of the primary melted layer. The maximum reflectivity ($m_r$), the final reflectivity ($f_r$) are also shown in this figure. The resolidification velocity of the interface is deeply affected by this recalescence phenomenon. This behavior is manifested in line L3. The recalescence phenomenon is also observed in the interface spectrum at mark b. The original resolidification velocity of the transmission spectrum is shown in line L5. The resolidification velocity of the transmission spectrum is deeply affected by this recalescence phenomenon. This behavior is manifested in line L6. These results reveal that the solidification of the silicon films is derived from the surface of the sample. The front reflectivity measurement was carried out without the aperture in order to evaluate the effect of scattering by the evolving surface morphology. However, no appreciable scattering was detected as a result of transient melting and crystallization. Except for the a-Si films, the recalescence phenomena are also observed for a-Ge films both upon picosecond [13] and nanosecond laser-pulse-induced melting of the surface [14]. In addition, reflectivity spectra shows that the explosive crystallization (EC) phenomenon always precedes complete melting of the film. Hence, complete melting should occur close to the melting point of c-Si, not a-Si. Following TRORT spectra analysis, the resulting recrystallization model of 90 nm-thick PECVD-grown a-Si thin films at laser energy density of 190 mJ/cm$^2$ is summarized in Figure 3.

![Figure 2](image-url)

**Figure 2.** Surface reflectivity, interface reflectivity and transmissivity of the sample during XeF ELA as a function of time.
3.2. Grain size analysis

FE-SEM micrographs of excimer laser-irradiated region with obvious grain boundaries, obtained by delineating defects using Secco etching, show a high uniformity of poly-Si grains. Grain size as a function of various laser energy densities is shown in Figure 4. In the partial melting regime (100 mJ/cm$^2$ ~ 200 mJ/cm$^2$), there is an increase in the grain size with increase in laser energy density. The longest melt-phase duration is approximately 110ns at a laser energy density of 200 mJ/cm$^2$, but the grain size is not at the maximum in terms of homogeneous random nucleation by supercooling in the complete melting regime. The grain size, however, reaches the maximum because of super-lateral-growth (SLG) nucleation in the near-complete melting regime at a laser energy density of 190 mJ/cm$^2$. It is remarkable that the maximum size of the average grain reaches approximately 1μm. The SLG phenomenon is also observed both in femtosecond laser annealing (FLA) [15] and XeCl ELA [16]. In the complete melting regime (200 mJ/cm$^2$ ~ 225 mJ/cm$^2$), the disk-shaped microstructural feature was observed and was surrounded the small poly-Si (smaller than 100 nm), which can be attributed to the fact that the supercooling associated with short pulses causes homogeneous random recrystallization from more nucleation sites. When the laser fluence exceeds 225 mJ/cm$^2$, the laser fluence is excessive and causes partial evaporation of the Si thin films. As expected, measurements shows that the dependence of grain size of PECVD-grown silicon on the crystallization excimer energy densities exhibits characteristics similar to other work on LPCVD-grown silicon[16], with two distinct regimes (the low energy density and high energy density regimes) clearly discernable. In the low energy density (ED) regime (100 mJ/cm$^2$ < ED < 190 mJ/cm$^2$), grain sizes slowly increase because the melt depth increases with increasing excimer laser energy density. On the other hand, in the high energy density regime (190 mJ/cm$^2$ < ED < 225 mJ/cm$^2$), grain size is not affected by variations in excimer laser energy density because the crystallization mechanism is not the same.
3.3. Micro-Raman analysis

The sharp and symmetric peaks indicate that the microstructure of the a-Si films has changed to poly-Si films because the sharp peak was centered at 510 ~ 520 cm\(^{-1}\). Raman intensity increases at first with energy density and then saturates. The intensity, however, decreases at excimer laser energy densities above 190 mJ/cm\(^2\). On the other hand, the full width at half maximum (FWHM) first decreases with energy density, and then increases. Figure 6 shows the FWHM of the micro-Raman scattering spectra for the poly-Si films. The FWHM of the micro-Raman scattering spectra reaches the minimum level at a laser energy density of 190 mJ/cm\(^2\). Such a difference can be attributed to the grain size effects or to the existing internal strain [17]. The sharp peaks of the sample were centered at a range from 514 to 516 cm\(^{-1}\). The crystalline volume fraction of the XeF ELA poly-Si films is approximately 100% because no amorphous component was observed in the micro-Raman scattering spectrum, which is exceedingly different from the SPC poly-Si films [2]. This result reveals that ELA is a very powerful technology for producing the crystallized poly-Si by melt regrowth of silicon films. These results are believed to give complementary information about the manufacturing of coarse-grained poly-Si by XeF ELA.

![Figure 4](image1.png)

**Figure 4.** Variation in average grain size as a function of various laser energy densities

![Figure 5](image2.png)

**Figure 5.** Micro-Raman scattering spectra of the sample which were prepared by XeF excimer laser annealing with laser energy densities ranging from 100 mJ/cm\(^2\) to 225 mJ/cm\(^2\).
4. Conclusion
The TRORT optical diagnostics offers great promise for understanding the mechanism of laser recrystallization since it is capable of making very fast measurements. The precise phase transformation mechanisms were presented for PECVD-grown 90 nm-thick a-Si thin films on glass substrate by non-intrusive in-situ real-time optical reflectivity and transmissivity measurements at visible wavelength with nanosecond time resolution during back side ELA. The largest grain size (~1μm) in the SLG regime at a laser fluence of 190–200 mJ/cm² in the air at room temperature was observed in this study, which is 3.57 times the maximum grain size fabricated by the blue FLA at room temperature [18]. The FWHM of the micro-Raman scattering spectra reaches the minimum at a laser energy density of 190 mJ/cm², which can be attributed to the grain size effects or to the existing internal strain. These positive findings can provide the recrystallization mechanism of the silicon films can be manifested using the in-situ real-time optical measurement and provide high throughput of the ELA during in-line large area flat panel display fabrication using poly-Si TFTs. In additional to the structural transformation dynamics measurements of silicon films, this system could also be utilized to monitor other kinds of thermodynamics on precision superalloy manufacturing such as nickel-based superalloy welding, titanium-based superalloy welding, and Inconel 738 superalloy welding.

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References
[1] M. Matsumura 2005 Future prospect of LTPS Technologies Digest of technical papers 1-4 The twelfth international workshop on Active-Matrix Liquid-Crystal Display (AM-LCD) Kanazawa Japan
[2] T.Toyama, R. Muhida, T. Harano, T.Sugano, M. Okajima and H. Okamoto 2003 Solid Phase Crystallization in Initial Growth Region of Polycrystalline Silicon Layer During Deposition at 180°C by Plasma Chemical Vapor Deposition Japanese Journal of Applied Physics 42 L1347-L1349
[3] H. Kirimura, Y. Uraoka, T. Fuyuki, M. Okuda and I. Yamashita 2005 Study of low-temperature crystallization of amorphous Si films obtained using ferritin with Ni nanoparticles Applied Physics Letters 86 262106-262109
[4] G. K. Giust and T. W. Sigmon 1997 Microstructural characterization of solid-phase crystallized amorphous silicon films recrystallized using an excimer laser Applied Physics Letters 70 767-769
[5] Y. F. Chong, H. L. Gossmann, M. O. Thompson, S. Yang, K. L. Pey and A. T. S.Wee 2004
Time-resolved reflectance studies of silicon during laser thermal processing of amorphous silicon gates on ultrathin gate oxides. *Journal of applied physics* 95 6048-53

[6] C. C. Kuo, W. C. Yeh, C. B. Chen and J. Y. Jeng 2006 Nanosecond Time Resolution In-situ Optical Reflection and Transmission Measurements during XeF Excimer Laser Interaction with Amorphous Silicon Thin Films. *Material Science Forum* 505-507 337-342.

[7] C. C. Kuo, W. C. Yeh, C. B. Chen and J. Y. Jeng Monitoring the explosive crystallization phenomenon of silicon thin films during short pulse duration XeF excimer laser annealing using real-time optical diagnostic measurements. *Thin Solid Films* Accepted

[8] C. C. Kuo, W. C. Yeh, C. B. Chen and J. Y. Jeng 2005 Evidence of explosive crystallization during excimer laser crystallization by time-resolved optical diagnostic measurement using He-Ne probe laser. *Digest of the technical paper* 191-194 The twelfth international workshop on Active-Matrix Liquid-Crystal Display (AM-LCD) Kanazawa, Japan

[9] D. H. Auston, C. M. Surko, T. N. C. Venkatesan, R. E. Slusser and J. A. Golovchenko 1978 Time-resolved reflectivity of ion-implanted silicon during laser annealing. *Applied Physics Letters* 33 437-440

[10] D. von der Linde and N. Fabricius 1982 Observation of electronic plasma in picosecond laser annealing of silicon. *Applied Physics Letters* 41 991-993

[11] M. Mulato, D. Toet, G. Aichmayr, P. V. Santos and I. Chambouleyron 1997 Laser crystallization and structuring of amorphous germanium. *Applied Physics Letters* 70 3570-72.

[12] J. Armengol, F. Vega, N. Chaoui, J. Solis, and C. N. Afonso 2003 Recalescence after bulk solidification in germanium films melted by ns laser pulses. *Journal of Applied Physics* 93 1505-10

[13] J. Siegel, J. Solis, and C. N. Afonso Slow interfacial amorphization of Ge films melted by ps laser pulses. *Journal of Applied Physics* 84 5531-5537, 1998.

[14] J. Siegel, J. Solis, and C. N. Afonso 1999 Recalescence after solidification in Ge films melted by picosecond laser pulses,” *Applied Physics Letters* 75 1071-73

[15] J. M. Shieh, Z. H. Chen, B. T. Dai, Y. C. Wang, A. Zaistev and C.L. Pan 2004 Near-infrared femtosecond laser-induced crystallization of amorphous silicon. *Applied Physics Letters* 85 1232-34

[16] J. S. Im, H. J. Kim and M.O.Thompson 1993 Phase transformation mechanisms involved in excimer laser crystallization of amorphous silicon films. *Applied Physics Letter* 63 1969-71

[17] S.A. Lyon, R.J. Nemanich, N.M. Johnson and D.K. Biegelsen 1982 Microstrain in laser-crystallized silicon islands on fused silica. *Applied Physics Letters* 40 316-318

[18] Y. C. Wang, K. W. Chen, C. L. Pan, J. M. Shieh, Z. H. Chen and B. T. Dai 2005 Blue Femtosecond Laser-Induced Crystallization of Amorphous Silicon for TFT Applications. *Proceeding of Optics and Photonics (Taiwan)* 35-37 Taiwan December 16-17