Crystallization to polycrystalline silicon thin film and simultaneous inactivation of electrical defects by underwater laser annealing

Emi Machida,^{1,2} Masahiro Horita,^{1,3,a)} Yasuaki Ishikawa,^{1,3} Yukiharu Uraoka,^{1,3} and Hiroshi Ikenoue⁴

¹Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan

²Research Fellowships of the Japan Society for the Promotion of Science, Japan Society for the Promotion of Science, 1-8 Chiyoda, Tokyo 102-8472, Japan

³Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Honcho, Kawaguchi, Saitama 332-0012, Japan

⁴Graduate School of Information Science and Electrical Engineering, Kyushu University, 744 Motoooka Nishi-ku, Fukuoka 819-0395, Japan

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We propose a low-temperature laser annealing method of a underwater laser annealing (WLA) for polycrystalline silicon (poly-Si) films. We performed crystallization to poly-Si films by laser irradiation in flowing deionized-water where KrF excimer laser was used for annealing. We demonstrated that the maximum value of maximum grain size of WLA samples was 1.5 μm , and that of the average grain size was 2.8 times larger than that of conventional laser annealing in air (LA) samples. Moreover, WLA forms poly-Si films which show lower conductivity and larger carrier life time attributed to fewer electrical defects as compared to LA poly-Si films. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4772513>]

Thin film transistors (TFTs) have been generally used for pixel switching devices of active matrix-flat panel displays such as liquid crystal displays and organic light emitting diode displays. In particular, the polycrystalline silicon (poly-Si) TFT has greater field-effect mobility ($>50\text{ cm}^2/\text{V s}$)¹⁻⁴ than other channel materials such as amorphous silicon (a-Si), oxide, and organic ($<10\text{ cm}^2/\text{V s}$), and the p-channel TFT can be fabricated by using poly-Si because of its high hole mobility.⁵ Thus, the poly-Si has the applicability not only to the high-performance pixel switching devices but also to the driver circuit or memory, that is, the system-on-panel display⁶ can be realized. In recent years, several studies have been conducted in order to achieve further low-temperature fabrication of poly-Si TFTs for the use of flexible plastic substrates.⁷⁻¹¹ Poly-Si thin films are generally formed by excimer laser annealing (ELA) using a-Si films on the glass substrate as a starting material.¹ However, laser crystallized poly-Si films still contain a huge amount of electrical defects and these electrical defects degrade the device performance.^{12,13} Inactivation treatment of electrical defects such as hydrogenation by forming gas annealing (FGA) is usually conducted after crystallization, but this process needs substrate temperature around 400 °C¹⁴ and this is too high to use the plastic substrates because the glass transition temperature of typical plastic films such as polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) is lower than 160 °C. Therefore, low-temperature annealing technique for the inactivation treatment is needed to realize poly-Si TFT fabrication on the plastic substrates. Here, we propose an underwater laser annealing (WLA): a laser annealing technique for low-temperature fabrication of poly-Si TFTs. We think that WLA could achieve low-temperature crystallization because of the cooling effect of the sample surface by

additional thermal diffusion to flowing water. Moreover, it is expected that WLA has a capability for inactivation of electrical defects at the same time as crystallization. After pulse laser irradiation in water, a water vapor layer is generated on the Si surface where this water vapor contains some active species such as hydrogen, oxygen, and hydroxyl. H₂O molecules will be chemically dissociated by heat energy, and electrical defects within the poly-Si films might be terminated by the formation of Si-H, Si-O, or Si-OH bonds. WLA process is one of the strong candidates for low-temperature inactivation technique, but we must note that the timing of WLA during the TFT fabrication process is very important for effective inactivation of electrical defects within the channel layer. Inactivation treatment is generally performed at the end of TFT fabrication process. Although active species have to diffuse into gate-electrode and gate-insulator to reach channel layer, a heating time of the pulse laser is much shorter than that of FGA. Therefore, it is very important to inactivate electrical defects within the poly-Si film at the same time as crystallization. We performed the crystallization to poly-Si films by WLA and evaluated their crystallinity, impurity within the poly-Si films, and electrical properties. From these experiments, we clarified the impact of WLA on grain growth and simultaneous inactivation of electrical defects while crystallization.

A-Si films (50 nm) were deposited on quartz glass substrates by low-pressure chemical vapor deposition (LPCVD) at 560 °C. Subsequently, the crystallization to poly-Si was carried out with KrF excimer laser (Gigaphoton). The laser beam has the wavelength of 248 nm, the pulse duration around 55 ns, and the repetition rate of 100 Hz. The laser energy density and the number of laser beam shots were changed to 500–800 mJ/cm² and 5–30 shots/location, respectively. The beam size on the substrate surface was 360 μm $\times$ 830 μm . In the WLA, the laser beam was irradiated

^{a)}Electronic mail: horita@ms.naist.jp.

FIG. 1. (a) Grain size dependence of poly-Si films formed by LA or WLA on the laser energy densities and SEM images of (b) LA and (c) WLA poly-Si films formed at the number of shots of 10 shots/location and the laser energy density of 650 mJ/cm². The solid line in Fig. 1(a) shows the fitted curve of average grain size plots of LA poly-Si and the dashed lines show that of WLA poly-Si films. The average grain sizes were calculated from 100 grains of each film.

to the substrate surface through the quartz window, which prevents a ruffle, and the flowing deionized-water (DI-water) layer. We also performed conventional laser annealing in air (LA) for comparison of irradiation medium. In the LA, the laser beam was irradiated in the laser annealing system without flowing water. The grain size of poly-Si films was estimated by scanning electron microscopy (SEM; JEOL, JSM-7400F) measurements of the poly-Si film surface. After performing selective etching of grain boundaries by Secco-etching solution¹⁵ and deposition of 10-nm thick platinum (Pt) to prevent electrically charge of poly-Si surface, SEM measurements were carried out. Defect passivation effect of WLA was evaluated by the microwave photo conductivity decay (μ -PCD) measurements. We obtained the peak reflectivity of microwave instead of the excess carrier lifetime, because the lifetime of poly-Si thin film is around several hundred picoseconds and too short for precise evaluation. Impurity such as hydrogen and oxygen within the poly-Si films was measured by secondary ion mass spectroscopy (SIMS; ULVAC-PHI ADEPT-1010) using the Cs⁺ primary ion. Electrical properties of the poly-Si films were measured by conductive-atomic force microscopy (C-AFM; Shimadzu, SPM-9600) measurements.¹⁶ The C-AFM measurements were performed with a platinum-iridium (Pt-Ir)-coated cantilever at a constant sample voltage (V_{sub}) of -2.0 V. Before C-AFM measurements, native oxide and/or thermally oxidized SiO₂ films on the poly-Si films were removed using a buffered hydrogen fluoride (BHF) solution for 10 s to eliminate the influence of oxide layer on the conductivity. Surface morphology and corresponding current images were simultaneously obtained by C-AFM at room temperature in air ambient. The sample holder, to which the V_{sub} was applied, was

electrically connected to the poly-Si film by a conductive paste. Thus, the V_{sub} was applied between the cantilever and the poly-Si films surface.

Figure 1 shows the relationship between laser energy density and the average grain size, and SEM images of crystallized poly-Si films by LA or WLA. The maximum and average grain sizes of WLA poly-Si were larger than those of LA poly-Si in all irradiation conditions. We focused on the grain size of poly-Si films formed at the number of shots of 10 shots/location because the grain growth of both poly-Si films was most promoted at that number of shots. In the LA, the average grain size remained at small value less than 200 nm despite the maximum grain size enlarging with the increasing of laser energy densities. As shown in Fig. 1(b), there are many small grains whose size is around 100 nm in the LA poly-Si film even though the maximum grain size reached 0.9 μm . In contrast, the average grain size of WLA poly-Si increased as well as the maximum grain size, with the increasing of laser energy densities. The maximum values of maximum and average grain size of WLA poly-Si films were 1.6 and 2.8 times larger than that of LA poly-Si films, that is, WLA achieves giant and uniform grain growth as shown in Fig. 1(c). These results indicate that irradiation medium of laser annealing is very important to promote grain growth. We speculated that the difference of irradiation medium effect and a change in temperature distribution within the Si films. In order to evaluate the difference of temperature distribution between WLA and LA poly-Si films, we observed surface morphology of the poly-Si films which suffers considerable damage due to high-energy laser irradiation in air or water.

Figures 2(a) and 2(d) show SEM images of LA and WLA sample surfaces which have thermal damage by high-

FIG. 2. (a) and (d) SEM images of annealed Si film surface after high-energy laser irradiation in (a) air or (d) water. The laser irradiation conditions are the number of shots = 100 shots/location, the laser energy density = 600 mJ/cm². (b), (c) and (e), (f) Schematic illustration of formation mechanism of considerable damage such as agglomeration of molten Si.

FIG. 3. Depth profiles of (a) ^1H and (b) ^{18}O within the precursor a-Si, WLA poly-Si, and LA poly-Si. The average grain sizes of WLA and LA poly-Si films were 197 nm, the number of shots was 10 shots/location, and the laser energy density of measured LA and WLA poly-Si samples was 600 mJ/cm^2 and 700 mJ/cm^2 , respectively.

energy laser irradiation. While both samples suffered from considerable irradiation damage such as partially removing or thinning of Si layer by vaporization of molten Si, damage formation mechanism was absolutely different. The absorption coefficient of the laser beam ($\lambda = 248 \text{ nm}$) for LPCVD a-Si is $\sim 10^6 \text{ cm}^{-1}$, and thus the penetration length into the a-Si is approximately 7 nm.¹⁷ In the LA, the highest point of temperature locates at the Si film surface. Therefore, the high-energy laser irradiation causes the vaporization of molten Si from surface side, and the vaporized Si atoms exert a reaction force, which cause agglomeration of molten Si, as shown in Figs. 2(b) and 2(c). On the other hand, the SEM image of WLA samples showed the evidence of vaporization from inside film. In the WLA, surface temperature is reduced due to the presence of flowing water, and irradiation energy diffuses from the Si surface into the water in addition to the thermal diffusion into the SiO_2 film. Therefore, high-energy laser irradiation in water causes vaporization from the inside

film as shown in Figs. 2(e) and 2(f). From these results, it is considered that the temperature distribution within the Si film is homogenized by the presence of flowing water on the Si films, resulting in decreasing of nucleation density because a nucleation starts from the minimum point of temperature such as Si/buffer SiO_2 interface. Decreasing of nucleation density brings in an enhancement of grain growth. Consequently, we conclude that the temperature distribution within the Si film is homogenized in the case of WLA, and this effect leads to giant and uniform grain growth.

Next, we focused on the impurity of hydrogen and oxygen within the Si layer. Figure 3 shows the depth profiles of (a) ^1H and (b) ^{18}O within the precursor a-Si film and crystallized poly-Si films (we measured ^{18}O as oxygen owing to too high detector responses of SIMS against ^{16}O). Detected counts of oxygen of a-Si, WLA, and LA poly-Si layers were at the same level. On the other hand, counts of hydrogen from the WLA poly-Si layer were much larger than those from the LA poly-Si and precursor a-Si layers. Estimated hydrogen concentration at the WLA poly-Si surface and 20 nm deep was $3 \times 10^{20} \text{ atoms/cm}^2$ and $2 \times 10^{20} \text{ atoms/cm}^2$, respectively, and these values are almost the same level as poly-Si films after FGA (H_2 gas concentration: 10%, substrate temperature: 400°C , processing time: 1 h). These results indicate that hydrogen in water vapor generated by WLA diffuses into the Si films, as well as FGA, although short heating time and low-substrate temperature as compared to FGA. We thought that this hydrogen will inactivate electrical defects such as dangling bonds in the poly-Si films, and WLA poly-Si films have better electrical characteristics than LA poly-Si films. Next, we observed local electrical properties of crystallized poly-Si films to discuss the improvement effect of electrical characteristics by hydrogen within the poly-Si films.

We conducted C-AFM measurement of poly-Si films formed by WLA or LA. Before the C-AFM measurements, we removed the SiO_2 layer on the poly-Si surfaces. Therefore, even if the oxidation occurs during laser annealing, the

FIG. 4. Surface topography and current images of (a)-(c) LA and (d)-(f) WLA poly-Si films during four times scanning at the V_{sub} of -2.0 V at the selfsame measurement area. White dotted line in surface topography images shows grain boundaries of poly-Si film surface. The I_{avg} of the LA poly-Si film at 1st and 4th scan were 4.7 pA and 3.7 pA , respectively. The I_{avg} of the WLA poly-Si film at 1st and 4th scan were 2.2 pA and 1.8 pA , respectively. The average grain sizes of both poly-Si samples were 197 nm, the number of shots was 10 shots/location, and the laser energy density of measured LA and WLA poly-Si samples were 600 mJ/cm^2 and 700 mJ/cm^2 , respectively.

oxide layer does not affect the C-AFM measurements. Since applying the negative bias voltage to poly-Si substrates, the current flows from poly-Si surface to the cantilever by electron detrapping. Figure 4 shows surface topography and current images of (a-c) LA and (d-f) WLA poly-Si films during four times C-AFM scanning in the same area. At the first scan, current flowed in the entire area of LA poly-Si surface includes grain and grain boundary, and average current (I_{avg}) reduced significantly as the number of scan increases. In the case of LA, it is expected that there are many electrical defects not only at grain boundaries but also inside of grains, and current flows through these defect sites to the cantilever due to the electron detrapping.¹⁶ With increasing number of scan, defect sites charge positively and amount of current reduces. On the other hand, the I_{avg} of the WLA poly-Si was much smaller than that of the LA poly-Si sample, and current mainly flowed at grain boundaries. It is considered that electrical defects in the poly-Si films are inactivated by hydrogen supplied from water vapor, and the I_{avg} became smaller as compared to LA.

We conducted μ -PCD measurements of WLA and LA poly-Si films which were used for C-AFM measurements to evaluate defects within poly-Si films. The peak reflectivity of microwave from WLA poly-Si was 15% larger than that of LA poly-Si although these poly-Si have the same average grain size. The microwave reflectivity is proportional to the excess carrier lifetime, that is, higher peak reflectivity confirms fewer electrical defects within WLA poly-Si. Consequently, we concluded that WLA forms poly-Si films which have not only much better crystallinity but also fewer electrical defects as compared to LA.

In conclusion, we proposed and demonstrated WLA as the low-temperature crystallization method for a-Si thin films. We also crystallized the a-Si films by ordinary LA and compared their grain size, impurity, and electrical properties. As the results, crystallization to poly-Si films was achieved by WLA. The maximum value of maximum grain size of WLA samples was 1.5 μm , and that of the average grain size was 2.8 times larger than that of LA samples. It is considered that WLA promotes giant and uniform grain growth by decreasing surface temperature and homogenization of temperature distribution. In addition, WLA poly-Si films contain more hydrogen than LA poly-Si films and have fewer defect sites attributed to electrical defects. The peak reflectivity of microwave, which is proportional to the excess carrier lifetime,

from WLA poly-Si was 15% larger than that of LA poly-Si although both poly-Si have the same average grain size. Hydrogen in water vapor generated by WLA inactivates electrical defects, and WLA poly-Si indicated much better electrical properties than LA poly-Si films. Hydrogen concentration of WLA poly-Si films was the same level as FGA poly-Si films. Although processing time is short and substrate temperature is low, as compared to the case of FGA, we succeeded in the diffusion of hydrogen to poly-Si layer and improvement of its electrical properties. We believe that WLA is very promising technique for low-temperature fabrication technique of poly-Si TFTs, and electrical devices using WLA poly-Si films as active layer must have excellent electrical properties.

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- ¹T. Sameshima, S. Usui, and M. Sekiya, *IEEE Electron Device Lett.* **7**, 276 (1986).
- ²S. Uchikoga and N. Ibaraki, *Thin Solid Films* **383**, 19 (2001).
- ³S. Jin Park, Y. Mi Ku, E. Hyun Kim, J. Jang, K. Hyung Kim, and C. Ok Kim, *J. Non-Cryst. Solids* **352**, 993 (2006).
- ⁴K. Yamasaki, E. Machida, M. Horita, Y. Ishikawa, and Y. Uraoka, *Jpn. J. Appl. Phys., Part 1* **51**, 03CA03 (2012).
- ⁵W.-J. Nam, H.-J. Lee, H.-S. Shin, S.-G. Park, and M.-K. Han, *Jpn. J. Appl. Phys., Part 1* **45**, 4389 (2006).
- ⁶M. Furuta, S. Maegawa, H. Sano, T. Yoshioka, Y. Uraoka, H. Tsutsu, I. Kobayashi, T. Kawamura, and Y. Miyata, in *Euro Display '96* (Society for Information Display, 1996), p. 547.
- ⁷M. Cheol Lee, S. Myeon Han, S. Hyuk Kang, M. Young Shin, and M. Koo Han, *Tech. Dig. of Int. Electron Devices Meet.* **8-10**, 8.7.1 (The Institute of Electrical and Electronics Engineering, 2003).
- ⁸Y. C. Wu, T. C. Chang, P. T. Liu, Y. C. Wu, C. W. Chou, C. H. Tu, J. C. Lou, and C. Y. Chang, *Appl. Phys. Lett.* **87**, 143504 (2005).
- ⁹D. P. Gosain, T. Noguchi, and S. Usui, *Jpn. J. Appl. Phys., Part 2* **39**, L179 (2000).
- ¹⁰G. Kawachi, T. Aoyama, A. Mimura, and N. Konishi, *Jpn. J. Appl. Phys., Part 1* **33**, 2092 (1994).
- ¹¹D. Min Kim, D. Sup Kim, and J. Sang Ro, *Thin Solid Films* **475**, 342 (2005).
- ¹²H. Lin, C. Hung, W. Chen, Z. Lin, H. Hsu, and T. Hunag, *J. Appl. Phys.* **105**, 054502 (2009).
- ¹³S. Inoue, M. Kimura, and T. Shimoda, *Jpn. J. Appl. Phys., Part 1* **42**, 1168 (2003).
- ¹⁴W. B. Jackson, N. M. Johnson, C. C. Tsai, I.-W. Wu, A. Chiang, and D. Smith, *Appl. Phys. Lett.* **61**, 1670 (1992).
- ¹⁵F. Secco d' Aragona, *J. Electrochem. Soc.* **119**, 948 (1972).
- ¹⁶E. Machida, Y. Uraoka, T. Fuyuki, R. Kokawa, T. Ito, and H. Ikenoue, *Appl. Phys. Lett.* **94**, 182104 (2009).
- ¹⁷E. D. Palik, *Handbook of Optical Constants of Solids* (Academic, New York, 1985).