Crystallization of amorphous-Si using nanosecond laser interference method

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Funding information
Ministry of Trade, Industry and Energy, Republic of Korea, Grant/Award Number: 20184030201910; Future Growth Engine Program, Grant/Award Number: 10079974

Abstract
Laser crystallization of a 50-nm thick amorphous-Si (a-Si) thin film on glass substrate was examined by a Nd:YAG (λ = 1064 nm) nanosecond laser and a two-beam laser interference method. In spite of the low absorption rate of the laser wavelength in the a-Si, crystallized Si ripple patterns were observed following a single laser pulse irradiation. The atomic force microscope (AFM) measurement revealed that surface ripple arrays are protruded as high as 120 nm at the positions corresponding to the maximum laser intensity and the ripples are composed of narrow double peaks with a separation of 1 μm. Raman image mapping was used to plot the spatial distribution of the crystallized Si phase. It was found that a 1064-nm-wavelength nanosecond laser could crystallize an a-Si thin film into polycrystalline-Si (pol-Si) by nonlinear absorption under high laser energy irradiation.

KEYWORDS
recrystallization, semiconducting silicon, single crystal growth, surface structure

1 INTRODUCTION

Laser annealing, including the activation of ultra-shallow junction in semiconductor devices or low-temperature polysilicon (LTPS) process in display or solar cell devices is a widely used technique in Si-based devices.1–3 The LTPS process is a well-established method to obtain polycrystalline-Si (pol-Si) grains from amorphous-Si (a-Si).3–6 Currently, the LTPS process is performed using a 308-nm wavelength XeCl excimer laser, converting the a-Si to uniform pol-Si grains of approximately 300 nm.3–6 Solid-state lasers of 355 nm or 532 nm wavelengths have also been explored as alternatives to excimer lasers, owing to their quite stable operation and achievable output, which is as high as that of excimer lasers.7–9 However, since the LTPS method involves quite complicated processes like light absorption, heat transfer, solid-to-liquid phase changes, and cooling process within tens of nanoseconds, it is difficult to form uniform and well-ordered poly-Si grains in a large area.2–9

Compared with a laser annealing process that irradiates a laser to a substrate at a uniform intensity, one feature of the laser interference process is that the laser intensity is periodically modulated; thus, periodic surface textures can be formed conveniently.10–14 There have been several reports on laser interference processes, such as periodic patterning on Si wafers with lasers of 355 nm and 1064 nm wavelengths and pol-Si crystallization of a-
Si thin films on glass substrate with a 532-nm wavelength laser.\textsuperscript{10–14} However, it is known that it is difficult to use a 1064-nm wavelength laser for processing a-Si thin films because of extremely low absorption coefficients of a-Si and crystalline Si.\textsuperscript{15} Carius et al conducted a laser crystallization experiment using a laser with a wavelength of 1064 nm on an a-Si thin film with a thickness of approximately 500 nm and suggested that crystallization could be achieved by the nonlinear absorption of the laser.\textsuperscript{16} Actually, it was reported that the absorption coefficient of Si could increase at high laser intensity, assisted with two-photon absorption process.\textsuperscript{17,18}

In this work, we report on the laser-induced crystallization of an a-Si thin film on glass substrate using a two-beam laser interference method. Although the absorption rate of the Nd:YAG ($\lambda = 1064$ nm) solid state laser was quite low, the poly-Si ripple structures were formed periodically after a single laser pulse irradiation. The spatial surface modulation and the section of the crystallized Si phase across the ripple arrays were examined by atomic force microscope (AFM) measurement and Raman spectra image mapping. From these results, it was concluded that the 1064-nm wavelength nanosecond laser crystallized a-Si thin film into poly-Si as expected, due to the nonlinear absorption from the irradiation by a very high intensity laser.

2 EXPERIMENTAL DETAILS

A 50-nm thick a-Si film was deposited on a 300-nm thick oxide layer, which was deposited on a glass substrate by plasma enhanced chemical vapor deposition. The hydrogen in the a-Si layer was removed by thermal annealing at 350°C for 30 min. The Q-switched diode-pumped solid-state (DPSS) Nd:YAG laser (EKSPLA, NL303) with a wavelength of 1064 nm was used for the annealing process. Sinusoidal light modulations were created to a spot of $2 \times 2$ mm$^2$ by interfering two laser beams of equal intensity split by a Fresnel biprism. The laser pulse frequency was 10 Hz and the pulse duration time was 5 ns. A single laser beam was irradiated on a substrate with a laser energy density in the range of 2–2.5 J/cm$^2$, while the optimum laser energy was chosen by AFM and Raman spectra analysis.

3 RESULTS AND DISCUSSION

Figure 1 shows an optical microscope image of the Si thin film surface annealed by a single laser irradiation with an energy density of 2.2 J/cm$^2$, where periodic poly-Si stripe arrays were formed. The stripe positions and the line spacing of about 6.4 μm correspond to the maxima and the period in the interference laser beam, respectively.

Figure 2 shows AFM images of the annealed Si surface with top view Figure 2A and perspective view Figure 2B. Figure 2C shows a cross-sectional profile of the area represented by dotted lines in Figure 2A. The periodic lines are formed at the highest intensity of the laser interference. The protrusion height was approximately 120 nm and the full width at half maximum (FWHM) was approximately 1.5 μm. According to the theory of laser crystallization, ripples are known to appear at the highest intensity of the laser; however, in this experiment, it was observed that the ripples were composed of two peaks at approximately 1 μm intervals with a dimple depth of approximately 30 nm, as shown in Figures 2B and 2C. Owing to the short pulse duration time of approximately 5 ns, the melt-Si under the solidification process has not enough time to form grain boundary near the ripples position. The intermediate region between ripples is slightly curved downward where the laser energy is not sufficient to melt the Si layer, and an a-Si phase still exists without melting and crystallization process.\textsuperscript{10,13}

To characterize the crystallinity of the Si layer, confocal Raman spectroscopy was used and the Raman shift and peak intensities were analyzed to determine the degree of crystallization of the annealed Si surface. In general, the Raman peaks of the a-Si and crystal Si were observed at approximately 470 cm$^{-1}$ and approximately 520 cm$^{-1}$, respectively.\textsuperscript{19–21} In the case of the laser annealed Si, a peak at 520 cm$^{-1}$ or less was observed depending on the Si grains. It is known that a Raman peak at near 500 cm$^{-1}$ corresponds to micro crystalline-Si (micro-Si) or poly-Si.\textsuperscript{19–21}

The signal wavelength used in this Raman measurement was 532 nm. When the intensity of the Raman signal is high, the Raman laser is absorbed in the a-Si, resulting in a self-annealing effect, which leads to an undesired...
Therefore, it is necessary to examine the selfannealing effect first for various Raman laser intensities. Figure 3 compares the Raman spectra of the a-Si surface with laser intensities in the range of 16 to 100%. In this measurement, the maximum Raman laser intensity and the beam diameter were 15.8 mW and 2.8 μm, respectively, which corresponds to an energy density of 256 kW/cm². For easy comparison, each curve was shifted equally in the vertical direction. For a laser intensity up to 32% of the maximum intensity, corresponding to 96 kW/cm², the Raman spectra of the a-Si phase were obtained, where the maximum peak near 470 cm⁻¹ is known as the transversal optical mode of the Si–Si vibrations in the a-Si phase. However, for laser intensity over 40% of the maximum intensity, an additional peak appeared near 500 cm⁻¹, corresponding to the poly-Si or micro-Si phase. Furthermore, the central peak intensity was increased and its position shifted from 501 cm⁻¹ to 506 cm⁻¹ as the Raman laser power increased. Considering that the Raman peak of the crystalline Si is 520 cm⁻¹, the Raman laser itself crystallizes the a-Si above 40% of the maximum laser intensity. Therefore, we measured the Raman spectra with an intensity of less than 32% of the maximum laser power.

In Figure 4C, the Raman spectra of the annealed a-Si surface are plotted for the middle of ripples (Figure 4A) and on a ripple (Figure 4B). The two curves are represented as dotted and solid lines, where the curve in Figure 4A is plotted with a five times magnification for comparison. We observed that the Raman peak on a ripple has a maximum at 506 cm⁻¹, while the Raman peak at middle position of ripples has a similar shape to that of the a-Si Raman spectra, except for a small side lobe at 506 cm⁻¹, which is a contribution from a small fraction of crystallized Si phase in the vicinity of the middle position. As the Raman peak of 506 cm⁻¹ is less than that of the crystal Si of 520 cm⁻¹, the ripples are expected to be micro- or poly-Si phases. Considering that the current wavelength of 1064 nm corresponds to an extremely weak absorption rate in an a-Si or crystalline Si, the direct
absorption of the laser beam is possibly limited.\textsuperscript{15} Instead, the laser energy is absorbed by the nonlinear effect because of the high laser energy density of 2.2 J/cm\textsuperscript{2}.\textsuperscript{16–18}

Raman image mapping method was used to obtain the spatial distribution of the crystallinity of the Si. As the Raman peaks of a-Si and crystalline Si can be observed at approximately 470 cm\textsuperscript{-1} and approximately 520 cm\textsuperscript{-1}, respectively, the Raman image mapping can be used to determine the degree of crystallization at each position by constructing an image of the position and the intensities of peaks. Figure 5A shows a Raman image of the crystalline Si peak at the annealed surface following laser irradiation. The scan area and scan step were 32 $\mu$m $\times$ 20 $\mu$m in the horizontal and vertical directions and 0.2 $\mu$m, respectively, for the laser energy of 96 kW/cm\textsuperscript{2}. It is noted that Figure 5A is plotted for the maximum Raman peak intensity between 490 cm\textsuperscript{-1} and 530 cm\textsuperscript{-1} to identify local position where crystalline Si phase is dominant. As expected, the peaks are repeated according to the laser interferometric interval of 6.4 $\mu$m. In the middle of the peak, the Raman peak of the crystalline Si is nearly zero, indicating that it corresponds to the a-Si region. Figure 5B shows the a-Si region, which is obtained when the Raman peak positions were in the range of 470 to 490 cm\textsuperscript{-1}. It can be seen that the a-Si region is formed only within less than a width of 1.5 $\mu$m of the middle position. As can be seen in Figure 5A, the intensity of the crystalline Si peak gradually increases as it moves away from the middle position and finally forms two maximum peaks near the positions of the highest laser intensity. This result is different from the previous results where two grains from both directions meet to form a single ripple shaped by lateral solidification.\textsuperscript{10,16} Owing to the sinusoidal laser interference, the thermal gradient to the lateral direction becomes significant. Since the lateral solidification will be mostly affected by the lateral cooling rate, or in other word, periodic length of laser interference, it is expected that double peaks could form near the confluence of the two grains as a result of the cooling process and vary depending on the laser interference beam profile.

The average of the Raman peak is plotted to compare the degree of crystallization with the position in Figure 6 A, which reveals double peaks similar to the AFM result in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.jpg}
\caption{Raman spectra of the annealed a-Si surface: A, At the middle position of the ripples and B, On the ripple line. The Raman intensity of (a) is plotted with 5 times magnification for comparison.}
\end{figure}
Figure 2. However, the FWHM of the Raman peak is approximately 3 μm, which is twice as large as the 1.5 μm value of the AFM data. Therefore, it can be expected that the actual Si crystallization begins to form before the protruded region. Figure 6B shows the average Raman peak profiles, indicated by ①, ②, and ③ in Figure 6A. For a better comparison, the results of ② and ③ shown with two times magnification. The peak at position ③ (black line) is similar to the Raman peak of the a-Si, whereas at position ② (red line), the peak shows a small intensity at 510 cm⁻¹, indicating that the a-Si and crystalline Si phases coexist. It was clearly found that the maximum Raman peak was formed at position ①, where most of the crystalline Si is formed.

4 CONCLUSIONS

In conclusion, we examined the crystallization of an a-Si thin film by using a 1064-nm nanosecond laser interference method. The annealed surface forms regular stripe ripples at the positions where the laser energy is maximal. The crystallinity of the patterns was analyzed by AFM and Raman spectra measurements, revealing that the stripe patterns were almost crystallized with double peak formations, while normal a-Si region existed only within a width of less than 1.5 μm of the middle position.
ACKNOWLEDGMENTS

This work was supported by the Future Growth Engine Program (10079974, Development of core technologies on materials, devices, and processes for TFT backplane and light emitting front plane with enhanced stretchability above 20%, with application to stretchable display) funded by the Ministry of Trade, Industry and Energy (MOTIE, Korea).

This work was further supported by “Human Resources Program in Energy Technology” of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and financial resources were granted by the Ministry of Trade, Industry and Energy, Republic of Korea (No. 20184030201910).

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How to cite this article: Kang MJ, Kim M, Hwang ES, Noh J, Shin ST, Cheong B-H. Crystallization of amorphous-Si using nanosecond laser interference method. J Soc Inf Display. 2019;27:34–40. https://doi.org/10.1002/jsid.745