Crystallization of Silicon Thin Films by Infrared Semiconductor Laser Irradiation

T. Haba¹, T. Sameshima¹ and N. Sano²

¹Tokyo University of Agriculture and Technology, 2-24-16, Naka-cho, Koganei, Tokyo, 184-8588, Japan
²Hightec Systems Corporation, 3-9-15, Shin Yokohama, Kohoku-ku, Yokohama, Kanagawa, 222-0033, Japan
E-mail: tsamesim@cc.tuat.ac.jp

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Abstract.
We report the crystallization of 40-nm-thick hydrogenated amorphous (a-Si:H) silicon films using 976-nm continuous wave (CW) infrared semiconductor laser with photo absorption of 200-nm-diameter carbon particles. Laser beam was focused to the surface of carbon particles with area of 500 by and 15 µm. Laser irradiation for 50 µs at a power of 14 W heated the surface region to about 300 K, which was estimated by analysis of spectra of light emission caused by laser irradiation when quartz substrates were placed on carbon particles. The silicon thin films coated with SiOₓ films were contacted to carbon particles. Laser irradiation for 50 µs at laser power 12 W initiated crystallization. The crystallization volume ratio (CVR) increased to 1 as the laser power increased to 14 W. The repetition of laser irradiation was also effective to increase CVR and make it uniform.

Introduction

Polycrystalline silicon films have been applied to various kinds of devices such as thin film transistors (TFTs) and solar cells. Laser crystallization processes using pulsed excimer lasers have been widely adopted for the mass production of low-temperature polycrystalline silicon (LTPS) TFTs used for switching transistors of pixels and the peripheral driver circuits of liquid crystal displays (LCDs) [1,2]. However, thin silicon film has a low optical absorbance in the near-infrared region. Therefore, infrared lasers have not been used for the crystallization of silicon films. We have proposed silicon crystallization using diamond-like carbon (DLC) films as photo absorption layers by irradiation using a infrared laser [3,4]. DLC has outstanding properties of high hardness, thermal conductivity, wear-resistance, thermal durability and chemical inertness. Therefore, it is widely utilized for technological and industrial applications such as wear resistant and protective hard coats. DLC has also interesting optical properties, which are low refractive indices from 1.3 to 1.9 and high extinction coefficients from 0.8 to 0.9 for wavelengths from 250 to 1100 nm. Therefore, a high power laser diodes with wavelengths of 800 –1000 nm can be used for the crystallization of silicon films with the assistance of DLC. The power of continues wave (CW) semiconductor laser is stable and easily modulated by the electrical current. In particular, they have a markedly high durability with a lifetime longer than
10,000h. A laser annealing system with a laser power much higher than that of conventional excimer lasers used for mass production of LCD panels will be established using commercially available cheap laser diodes with an energy conversion efficiency above 40%.

In order to look for a further possibility of crystallization process using a combination of infrared laser with carbon, we report in this paper, crystallization of silicon films using carbon particles mechanical contacting silicon samples. We demonstrate crystallization conditions of the laser power and the laser dwell time. We also report crystalline properties using Raman scattering and temperature increase in carbon particles by laser heating.

**Experimental**

Figure 1 shows experimental steps for the present method. 40-nm-thick undoped hydrogenated amorphous silicon (a-Si:H) films with a hydrogen concentration of 16% were formed on quartz glass substrates by plasma enhanced chemical vapor deposition. 200-nm-thick SiO$_x$ films were subsequently formed on the a-Si:H films using Polysilazane precursor heated at 260 $^\circ$C with 1.3x10$^6$ Pa H$_2$O vapor for 3h. A stainless-steel container with a diameter of 6 cm and a depth of 1 cm was prepared. It was filled with carbon particles with a mean diameter of 200 nm. The top surface of samples was carefully and mechanically contacted with no substantial air gaps. The samples were placed a moving stage for laser irradiation. During samples moving, the samples were irradiated with 976 nm infrared semiconductor line beam laser from the rear side of the transparent substrates. Line beam laser was focused at the top surface of the samples with a 500-μm-width and 15-μm-length. The laser dwell time was given by a laser beam length divided by the sample velocity. It ranged from 3 ms to 15 s. Carbon particles absorbed a laser light and were heated themselves. The heating energy propagated to the samples and silicon films were heated. There must be small air gaps among carbon particles. If thermal diffusion length in air during laser heat duration for example 100 μs is much larger than the gaps, silicon films would be heated uniformly. The thermal diffusion length was estimated 47μm in the case of laser irradiation for 100 μs and thermal diffusion coefficient of air of 0.217 cm$^2$/s [5]. We believe that there is a possibility of uniform heating and crystallization of silicon films using carbon particles when they are closed packed. Carbon particles can effectively absorb the infrared light because the optical reflectivity at the surface of carbon surface was low about 10% due to a low refractive index [6]. Moreover, there is light scattering in the case of carbon particles. However, there was a reflection loss at the quartz glass/Si layer interface when the laser light was irradiated from the rear side. Because the reflectivity was 35% at 976 nm for quartz glass/40-nm-a-Si layer, we interpret the optical absorption efficiency was about 60% for the present experimental system.
In order to estimate temperature increase of carbon particles by laser heating, black body radiation was observed using multichannel spectrometer from 250 to 800 nm, as shown by insert in Fig. 2. Quartz substrates were placed on carbon particles. Laser beam was irradiated at a dwell time of 50 μs by sample moving and at different laser powers ranging from 8 to 14 W. Light emission from quartz/carbon interfaces were measured using spectrometer during laser irradiation.

**Results and discussions**

Figure 2 shows spectra of light emission at dwell time of 50 μs and at laser power of 8 and 14 W. The sensitivity of the detector was calibrated. The emission showed a broad spectra and its intensity increased as the wavelength increased. It was also increased as the laser power increased. The emission spectra was analyzed by black body radiation model using Planck’s radiation equation, $I=8πhc^2 \times \frac{1}{e^{hc/\lambda kT}-1}$, where $h$ is Planck’s constant, $c$ is the light velocity, $\lambda$ is the wavelength, $k$ is the Boltzmann’s constant and $T$ is temperature. The emissivity of carbon particles was supposed to be 1. Calculated spectra reasonably explained characteristics of experimental spectra. The fitting calculated spectra to experimental spectra gave temperature each laser irradiation condition, as shown in Fig. 2. Figure 3 summarizes temperature of carbon particles as a function of laser power at dwell time of 50 μs. The temperature increased from 2865 to 3000 K as laser power increased from 8 to 14 W. It is important that laser heating of carbon particles at temperature higher than the melting point of silicon was achieved. Quartz substrates were not broken by laser irradiation. They kept the smooth surface after laser heating.

Figure 4 shows Raman scattering spectra of 40-nm-thick silicon films irradiated for dwell time 50 μs and at different laser powers ranging from 11 to 14 W. The crystalline silicon phonon peaks were observed around wavenumber of 515 cm$^{-1}$ in the most of region irradiated with laser beam above 12 W. Crystalline silicon peak was observed in only partial regions at 11 W. We interpret a threshold laser power of crystallization of 12 W in this case. The silicon films were crystallized by heat diffusion from carbon particles heated by laser irradiation. The peak of crystalline silicon increased and the peak of amorphous silicon around wavenumber of 480 cm$^{-1}$ decreased as laser power increased from 12 to 14 W. The line shape of
crystalline peak was sharp with a band width of 7 cm\(^{-1}\) at 14 W and no amorphous peak was observed. Surface roughness was observed in the case of laser irradiation at 14 W. It probably resulted from movement of silicon atoms during melting of silicon films caused by high power laser irradiation. On the other hand, no surface roughness was observed below 13 W. We interpret that silicon films were probably crystallized in the solid state.

Figure 5 shows CVR distribution in the normal direction of laser scanning of silicon films at dwell time of 47 \(\mu\)s, at 13 W and repetition of laser irradiation from 1 and 3 times. The average CVR increased as number of laser scans increased. Moreover fluctuation of CVR became low in the case of 3 times laser irradiation. The result shows carbon particles played a role of heating source at every laser irradiation occasion. Total heating duration increased and crystallization proceeded. We believe that there was a possibility of moving of carbon particles during laser irradiation because high thermal energy. The results of Fig. 5 indicates that the average moving distance of carbon particles was much smaller than heat diffusion length and that carbon particle contributed multiple heating of silicon films. There is therefore a possibility that silicon film with high uniformity of CVR can be achieved by overlapping irradiation.

![Fig.4. Raman scattering spectra of 40-nm-thick silicon films irradiated for dwell time 50 \(\mu\)s and at different laser powers ranging from 11 to 14 W](image)

![Fig.5. CVR distribution in the normal direction of laser scanning of silicon films at dwell time of 47 \(\mu\)s, at laser power of 13 W and repetition of laser irradiation from 1 and 3 times](image)
Summary

Rapid thermal crystallization of silicon films by CW infrared semiconductor laser irradiation using carbon particles as photoabsorption layer was investigated. The photoabsorption layers were fabricated by stainless-steel container filled with carbon particles with a mean diameter of 200 nm. Quartz substrates were placed on carbon particles and irradiated with 976-nm infrared semiconductor line beam laser at dwell time of 50 μs and at different laser powers ranging from 8 to 14 W. During laser irradiation, spectra of light emission were observed using multichannel spectrometer from 250 to 800 nm. Temperature of carbon particles were estimated by fitting spectra. The temperature increased from 2865 to 3000 K as laser power increased from 8 to 14 W. 40-nm-thick undoped hydrogenated amorphous silicon (a-Si:H) films were formed on quartz glass substrates by plasma enhanced chemical vapor deposition. 200-nm-thick SiOx films were subsequently formed on the a-Si:H films using Polysilazane precursor heated at 260 °C with 1.3x10⁶ Pa H₂O vapor for 3h. The top surface of samples was contacted to carbon particles. The samples were irradiated by laser from the rear side of the transparent substrates. Raman scattering spectra were measured in order to investigate crystallization of silicon films. Crystallization of silicon films were confirmed at dwell time of 50 μs and at laser power of 12 W. Crystalline volume ratio (CVR) increased as laser power increased. CVR of 1 was achieved at dwell time of 50 μs and laser power of 14 W. The average CVR increased and fluctuation of CVR became low as number of laser scans increased. This result shows carbon particles played a role of heating source at every laser irradiation occasion.

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References