Crystallization of Silicon Thin Films by Infrared Semiconductor Laser Irradiation Using Carbon Particles

T. Sameshima [*], K. Kogure [*], S. Yoshidomi [*], T. Haba [*], M. Hasumi [*] and N. Sano [**]

[*] *Tokyo University of Agriculture and Technology, 2-24-16, Naka-cho, Koga nei, Tokyo, 184-8588, Japan*
Email: tsamesim@cc.tuat.ac.jp
[**] *Hightec Systems Corporation, 3-9-15, Shin Yokohama, Kohoku-ku, Yokohama, Kanagawa, 222-0033, Japan*

We report the crystallization of 40-nm-thick hydrogenated amorphous silicon films using 940-nm continuous wave infrared semiconductor laser with 200 nm diameter carbon particles as photo absorption. The laser beam was focused to 100 μm diameter at the surface of carbon particles. Laser irradiation at 25 W heated the carbon surface region to about 3430 K, which was estimated by analysis of spectra of light emission caused by laser irradiation when quartz substrates were placed on the surface of carbon particles. The silicon films coated with SiO_2 films were crystallized by laser irradiation for 170 μs at 25 W. The crystallization volume ratio was 0.53. Crystallization over 1.1 mm area was also demonstrated by laser irradiation at 25 W.

Keywords: Carbon Optical absorption, Semiconductor laser, Optical reflectivity, Raman scattering

1. Introduction

Laser-induced rapid crystallization using pulsed excimer lasers has been widely used for fabricating polycrystalline silicon (poly-Si) films, which have been applied to thin film transistors (TFTs) and solar cells. Laser-induced rapid crystallization has an advantage of a low processing temperature. It allows to fabricate poly-Si TFTs at 300°C, which is suitable for fabricating switching transistors of pixels and peripheral driver circuits of liquid crystal displays (LCDs) [1-5]. However there have been problems of a low laser power of excimer laser at most 400 W and high maintenance cost because of toxic gases.

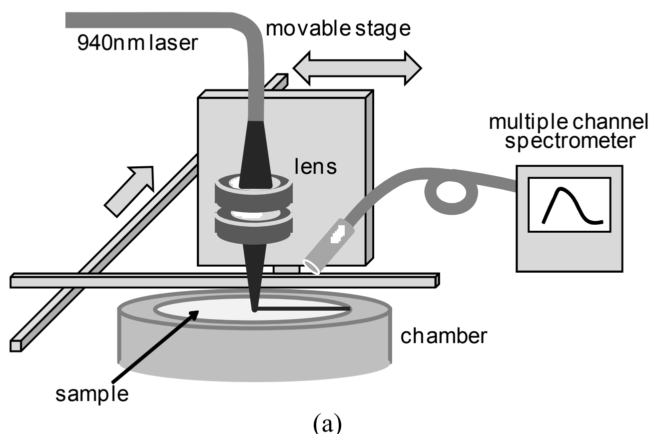
We have developed continuous wave (CW) infrared semiconductor laser annealing using carbon layer as an optical absorption layer.[6-8] Infrared semiconductor lasers with a power of 10 kW and a high conversion efficiency of 50% are available. A high power laser is attractive for rapid laser annealing with a short tact time. In order to achieve rapid annealing using CW laser, we have developed optics shaping a narrow and uniform line laser beam with a length of 15 μm and a rapid movement system at 1 m/s. A laser intensity of 500 kW/cm^2 and 15 μs rapid irradiartion have been achieved at the sample surface [9].

In order to solve a problem of low optical absorbance of silicon in the infrared region, we have used carbon as a photo absorption layer [10]. Carbon, especially diamond like carbon (DLC), has outstanding properties of high hardness, good thermal conductivity, wear resistance, thermal durability and chemical inertness. Therefore, it has been 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. When carbon films are formed on siliocn, laser diodes with wavelengths of 800 –1000 nm can be used for the crystallization of silicon films. Carbon films absorb laser light and heat themselves to a high temperature and also heat adjacient silicon films by heat diffusion. At present sputtering mtehod for carbon film formation has been well established in the industry field. Moreover, it is necesarry to look for a further possibility of crystallization process using a combination of infrared laser with carbon for low cost processing.

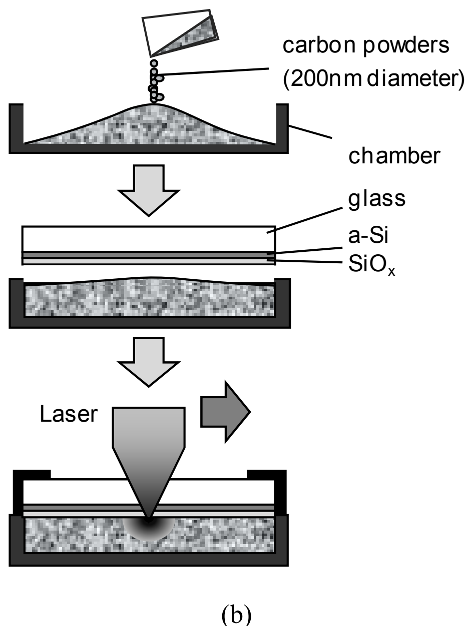
In this paper, we report crystallization of silicon films using carbon particles. We report heating properties to a high temeprature about 3400 K of carbon particles by laser irradiation by observing light emission from carbon particles. We also discuss crystallization conditions of the laser power and the laser dwell time. We also report crystalline properties including crystalline volume ratio using Raman scattering method.

2. Experimental Details

Figure 1(a) shows an experimental apparatus. An infrared semiconductor laser beam with a wavelength of 940 nm and a power of 25 W was introduced by an optical fiber. The optical fiber and optics with lens were mounted on the X-Y mobile stage. The laser was moved at 1 m/s at maximum in the X-direction. It was also moved in the Y-direction with a step. Laser light was focused by lens to a spot with a Gaussian-like intensity distribution with a diameter of 100 μm. A stainless-steel chamber with a diameter of 6 cm and a depth of 1cm was filled with carbon particles with a mean diameter of 200 nm, as shown in Fig. 1(b). The top surface of samples was carefully placed on the surface of carbon particles by a mechanically stress with no substantial air gaps. The samples were irradiated with 940 nm infrared semiconductor laser beam from the rear side of the transparent substrates. Carbon particles absorbed laser light and heated themselves. The heating energy propagated to the samples and silicon films were heated by the heat diffusion. 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)



(b)

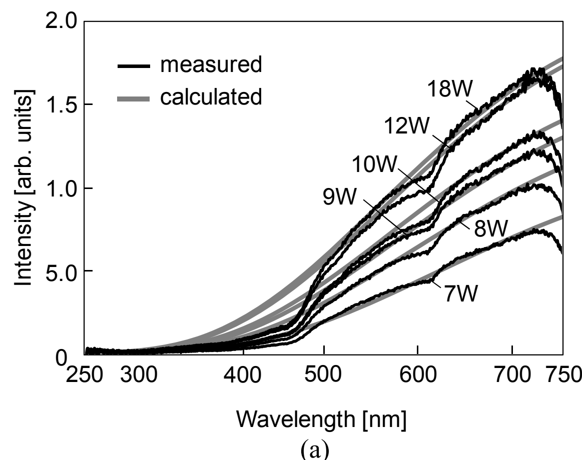
Fig.1: Experimental apparatus with a 940 nm infrared semiconductor laser (a) and image of laser annealing of samples using carbon particles as photo-absorption.

a low refractive index [10]. Moreover, there is light scatter 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 940 nm for quartz glass/40-nm-a-Si layer, we interpret the optical absorption efficiency was about 60% for the present experimental system.

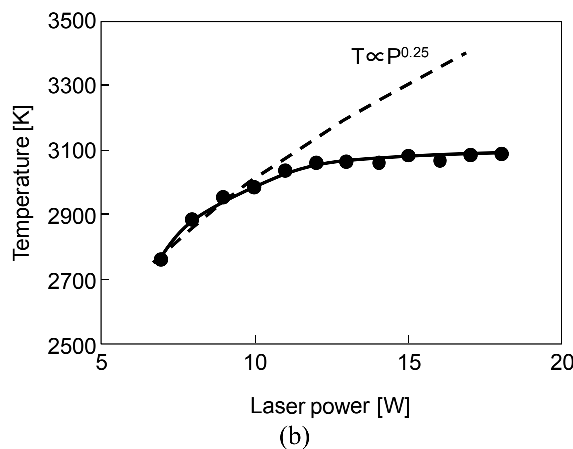
In order to estimate temperature increase of carbon particles by laser heating, light emission from carbon surface was observed using multichannel spectrometer from 250 to 750 nm, as shown in Fig. 1(a). Quartz substrates were placed on the surface of carbon particles. Light emission from quartz/carbon interfaces was measured using spectrometer during laser irradiation with different laser powers ranging from 7 to 25 W. The sensitivity of the detector with different wavelengths was calibrated using a black body furnace. The emission spectra was analyzed by black body radiation model using Planck's radiation equation, I= $8\pi hc\lambda^{-5}[\exp(hc/\lambda kT)-1]^{-1}$, where h is Planck's constant, c is the light velocity, λ is the wavelength, k is the Boltzmann's constant and T is absolute temperature. The emissivity of carbon particles was supposed to be 1. For experiment of laser crystallization, 40-nm-thick undoped hydrogenated amorphous silicon (a-Si:H) films with a hydrogen concentration of 20 % 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 liquid. The samples were then heated at 260°C with 1.3×10^6 Pa H_2O vapor for 3h for formation of SiO_2 films from Polysilazane layers.

3. Results and discussions

Figure 2 shows spectra of light emission with different laser powers (a) when the infrared laser was focused to the surface of carbon particles though a quartz substrate for 1 s, and temperature as a function of laser power (b). The emissions showed broad spectra and the emission intensity increased as the wavelength increased. It also increased as the laser power increased. The emission spectra were analyzed by the black body radiation theory using Planck's radiation equation. The fitting calculated spectra to experimental ones shown in Fig. 2(a) gave most possible temperature as a function of laser power, as shown in Fig. 2 (b).The temperature increased from 2750 to 3050 K as laser



(a)

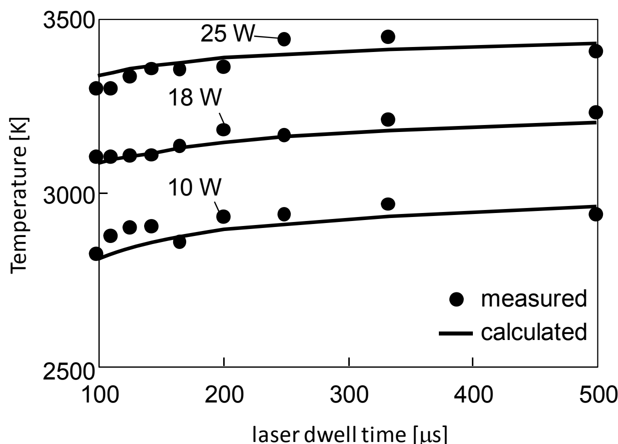


(b)

Fig.2: light emission spectra for laser irradiation for 1 s with different laser powers (a), and temperature as a function of laser power (b)

power increased from 7 to 11 W. It is important that carbon particles were heated to temperature higher than the melting point of silicon (1680 K). Behavior of temperature increase was almost proportional to laser power to the power of one fourth. It means that light emission occurred according to Stefan-Boltzmann law. On the other hand, temperature almost leveled off at 3050 K for laser power above 12 W. This saturation was probably caused by substantial dissipation of heating energy through explosively movement of carbon particles or distortion of glass substrate. Small holes at the carbon surface and small grooves at the surface of quartz substrate were observed by naked eyes after laser irradiation above 16 W.

Figure 3 shows temperature as a function of laser dwell time when the infrared laser was moved at velocities ranging from 10 to 100 cm/s at different powers of 10, 18 and 25 W. Temperature slightly increased as the laser dwell time increased from 100 to 500 μs for every laser power. The maximum temperatures of 2960, 3200 and 3430 K were obtained for the cases of 10, 18, 25 W irradiation, respectively. The maximum temperatures for 18 and 25 W were higher than the maximum temperature, 3050 K, for the case of stationary irradiation for 1 s. No damage was observed in the carbon particles and quartz substrate. Carbon particles did not substantially moved and heating energy was effectively kept. Solid curves were temperatures calculated including heat energy losses by black body radiation and heat diffusion. In the short laser dwell time lower than 200 μs, heat diffusion was important and temperature was decreased by heat conduction to carbon and glass substrate. On the other hand, the highest temperature was almost governed by radiation energy loss in the case of



the laser dwell time longer than 200 μs because of spatial limitation of heat conduction.

Fig.3: Temperature as a function of laser dwell time when the infrared laser was moved at velocities ranging from 10 to 100 cm/s at different powers.

Figure 4 shows Raman scattering spectra with different dwell times when the laser beams at 25 W were irradiated and moved one way. The color of the silicon films were changed by laser irradiated for line-shape regions with a width of about 100 μm as shown by inset of Fig.4. Raman scattering was measured at the middle points of laser irradiated regions. The crystalline silicon phonon peaks appeared around wavenumber of 519 cm^{-1} for a laser dwell time of 143 μs. The intensity of crystalline silicon phonon peak increased as the laser dwell time increased. The silicon films were crystallized by heat diffusion from carbon particles heated by laser irradiation.

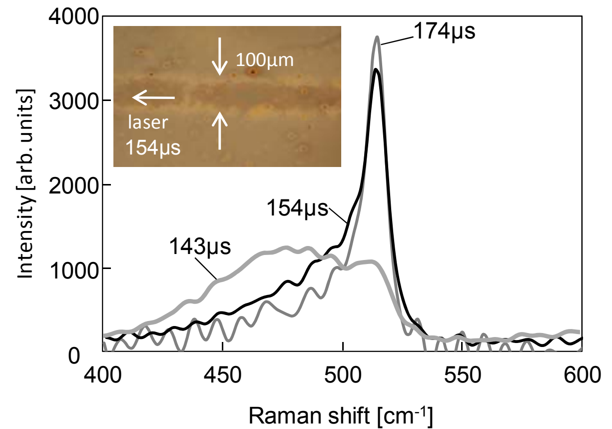


Fig.4: Raman scattering spectra with different dwell times when the laser beam at 25 W was irradiated and moved one way. Inset represents a photo of silicon surface laser irradiated for 154 μs.

Figure 5 shows crystalline volume ratio as a function of the laser dwell time when laser beam at 18 and 25 W was irradiated to samples. The crystalline volume ratio was obtained by analysis of Raman scattering spectra assumed by three phonon bands of crystalline at 519 cm^{-1}, nano-crystalline at 500 cm^{-1} and amorphous at 480 cm^{-1}. It was estimated intensity ratio of the crystalline band to those of total three bands. The crystalline volume ratio increased from 0.03 to 0.53 as the laser dwell time increased from 143 to 175 μs in the case of 25 W. Laser irradiation with a high laser intensity $2.1x10^5$ W/cm^2 (25 W case) heated carbon particles to a high temperature and achieved crystallization of silicon with a short dwell time. Surface roughness was observed in the case of laser irradiation longer than 180 μs. It probably resulted from that silicon films were melted and significant movement of silicon atoms occurred on the glass substrate. On the other hand, a long heating duration of 440 μs was necessary to crystallize silicon films at 18 W. It indicates that heating carbon to very high temperature is important to crystallize silicon films by heat conduction from carbon particles.

Figure.6 shows crystalline volume ratio distribution over 1.1 mm measured in the normal direction of laser scanning. 1.1 mm region was irradiated by laser beam at 25 W. Laser irradiation was repeated in the plus or minus at 60 cm/s in the X direction with a dwell time of 150 μs. It paused at edges a little before moving again in the opposite direction. During the pause, the laser beam was moved stepwise by 50 μm in the Y direction. Overlapping

rate was 50%. The average crystalline volume ratio was 0.45. The crystalline volume ratio distributed from 0.3 to 0.58. While this demonstration shows a possibility of

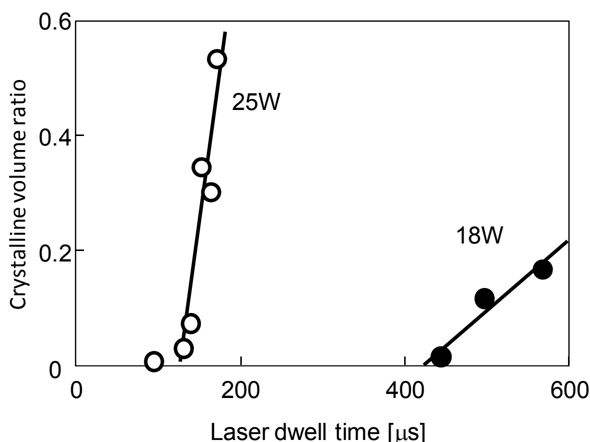


Fig.5: Crystalline volume ratio as a function of the laser dwell time with different laser powers of 18 and 25 W.

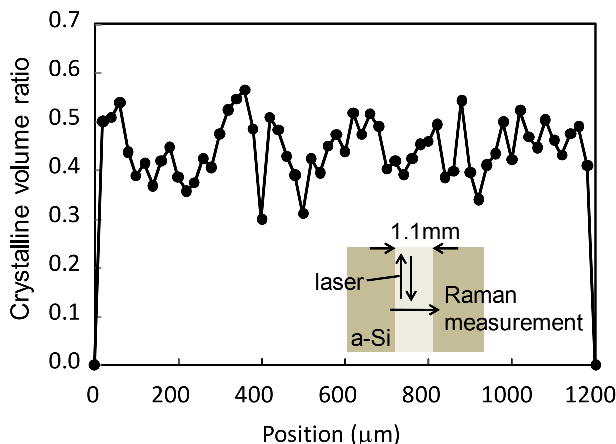


Fig.6: Crystalline volume ratio distribution over 1.1 mm measured in the normal direction of laser scanning region at 25 W as shown in inset.

crystallization of silicon film over a large area, there is a problem in uniformity of the crystalline volume ratio. Carbon contact to silicon should be further improved.

4. Summary

Rapid thermal crystallization of silicon films by CW infrared semiconductor laser irradiation using carbon particles as photo absorption was investigated. A stainless-steel chamber was filled with carbon particles with a mean diameter of 200 nm. Quartz substrates were placed on carbon particles and irradiated with 940 nm infrared semicon ductor laser at a diameter of 100 μm. During irradiation and movement of laser, spectra of light emission from the carbon surface were observed using multichannel spectrometer from 250 to 750 nm. Temperature of carbon particles were estimated by fitting spectra. The temperature increased to 3430 K at a laser power of 25 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 SiO_x films were subsequently formed on the a-Si:H films using Polysilazane precursor heated at 260°C with 1.3×10^6 Pa H_2O vapor for 3h. The top surface of silicon films 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 longer than 143 μs for a laser power of 25 W. The crystalline volume ratio was 0.53 in the case of 170 μs dwell time. This result shows that carbon particles can play a role of a good heating source for crystallizing silicon films.

Acknowledgments

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