Formation of Si Nano-Crystals by Millisecond Annealing of SiO_x Films using Thermal Plasma Jet

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Abstract

Rapid thermal annealing of SiO_x films on quartz substrate in millisecond time domain has been performed by thermal plasma jet irradiation. The relationship between the surface temperature during the annealing measured by an optical probe method and the formation of Si crystals has been investigated. By annealing the SiO_x films at a temperature higher than 1390 K, a clear peak associated with crystalline Si TO phonons become observable in Raman scattering spectra. The SiO_x films annealed under such conditions exhibit dot-like surface morphology with the typical diameter of 10 ~ 20 nm. When annealing the films at a temperature as high as 1690 K, clear dot structures with the height and the density of 23 nm and 2.7 X 10^{10} cm^{-2}, respectively, have been observed. These results indicate that by annealing the SiO_x films at high temperatures, formation of Si nano-crystals in millisecond time domain is achievable.

Introduction

Formations of Si nano-structures such as pores [1], wires [2] and dots [3] have attracted much attention because one can expect the impact of the introduction of their quantum effects into the conventional Si metal-oxide-semiconductor field effect transistors (MOSFETs), which significantly improve the functionality of the devices [4,5]. It has been reported that Si nano-crystals precipitate by annealing Si rich oxide (SiO_x , $x<2$) films with a temperature as high as 1000C and durations as long as 30 min [6,7]. This is a very simple technique to form Si nano-crystals with relatively uniform size distribution. The authors have developed a millisecond annealing technique using thermal plasma jet [8]. Using this annealing technique, one can raise the surface temperature more than 1000 K with in several ms [9]. By applying this annealing technique, we have successfully crystallized amorphous Si films on glass substrate and fabricated high performance thin film transistors (TFTs) with the field effect mobility of 62 $cm^2V^{-1}s^{-1}$ [10].

In this study, we applied the plasma jet annealing technique to SiO_x films and investigated the change in the film property as a function of annealing temperature. It is demonstrated that precipitation of Si nano-crystals is achieved by this annealing technique.

Experimental

A thermal plasma source was developed as schematically shown in Fig. 1. The W cathode and the water-cooled Cu anode separated by 1 mm from each other are connected to a power supply. Arc discharge was performed by supplying DC biases of 13.9 to 14.3 V and 150 A between the electrodes with an Ar gas flow of 7 to 8 L/min. The thermal plasma jet was formed by blowing out the arc plasma through a nozzle with the diameter of 4 mm. SiO_x films were formed on quartz substrate by vacuum evaporation of SiO powder with the thickness of 680 nm. The specimen was linearly moved by a motion stage in front of the plasma jet with scanning speed ranging from 500 to 1200 mm/s. The distance between the plasma source and the specimen was set at 3 mm. In order to measure the surface temperature of quartz substrate during the plasma jet annealing, the reflectivity of the quartz substrates was monitored simultaneously by irradiating them with a laser light (λ=532 nm) from the backside of the quartz substrate and detecting the reflected light intensity by a photo-diode through a band pass filter (see Fig. 1). The

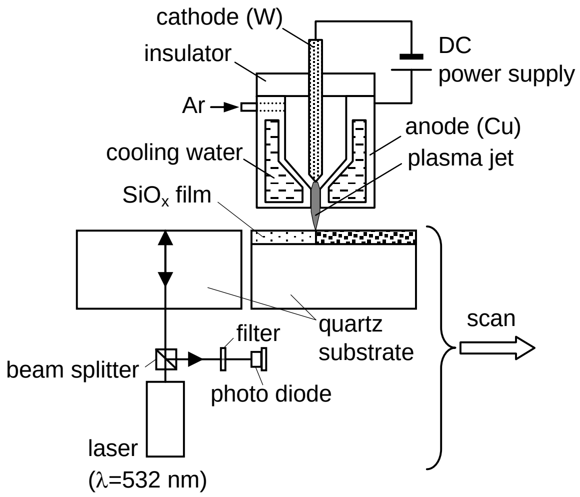

Fig. 1. Schematic diagram of annealing experiment using arc discharge thermal plasma jet. The surface temperature during annealing is measured by the optical probe method using laser light irradiated from the backside of quartz substrate.

details of the measurement have been reported elsewhere [9]. The measurement system was set on a motion stage and moved together with the specimen in front of the plasma jet as shown in Fig. 1. Raman scattering spectra were obtained from the annealed specimens using the excitation laser wavelength of 532 nm to examine the existence of Si crystals. The surface morphology of the films was observed by an atomic force microscopy (AFM) using tapping mode.

Results and Discussion

The Raman scattering spectra of the SiO_x films before and after the annealing under different scan speeds are shown in Fig. 1. Since the SiO_x films have weak absorption of the light at the wavelength of 532 nm, the observed spectra include both the signals from SiO_x film and quartz substrate. The broad peak around 420 cm^{-1} and relatively sharp peaks at 495 (D_1) and 600 cm^{-1} (D_2) are from quartz substrate [11]. By annealing the SiO_x films at a temperature higher than 1390 K, we observed significant change in film color from initial brown to bright yellow. In the Raman scattering spectrum of this film, a clear peak associated with crystalline Si TO phonons is observed at the peak position of 523 cm^{-1} as shown in Fig. 1. We observed this peak in all specimens annealed at higher temperatures. These results indicate that Si in crystalline phase is formed in the SiO_x films within 5 ms by annealing the films at temperatures higher than 1390 K.

From the AFM observation of the films annealed at high temperatures, we found fine dot-like structure with the typical size ranging from 10 ~ 50 nm. In SiO_x films annealed at a temperature as higher as 1690 K, we observed very uniformly dispersed nano-structures as shown in Fig. 3. The dot height is about 20 nm and the density is 2.7 X 10^{11} cm^{-2}.

These results confirm that the formation of Si nano-crystals in SiO_x films using millisecond annealing technique. The high density and good uniformity of the formed Si nano-crystals indicate that the present nano-structure formation technique is quite promising.

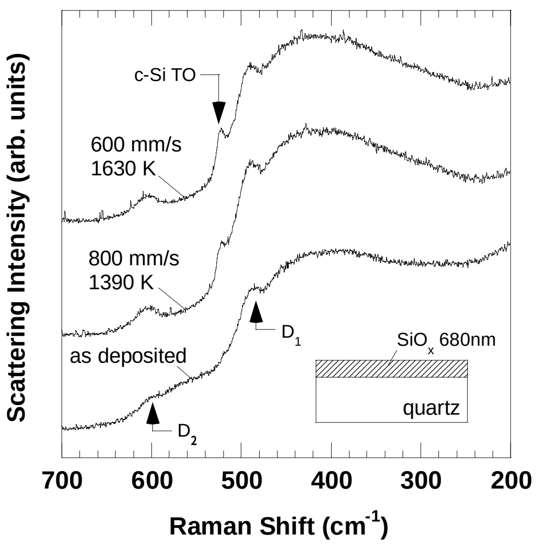

Fig. 2. Raman scattering spectra of SiO_x films before and after the plasma jet annealing.

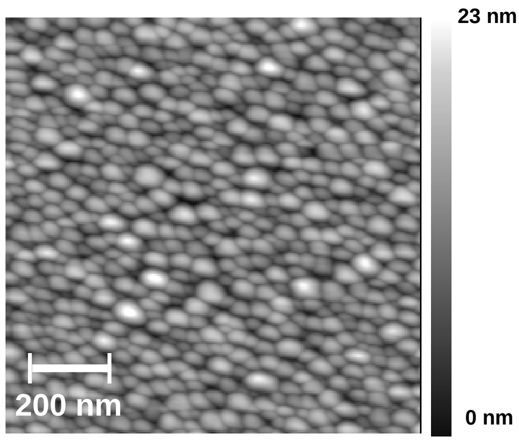

Fig. 3. AFM image of a SiO_x films annealed by the plasma jet with the temperature as high as 1,690 K.

Conclusions

By annealing the SiO_x films within 5 ms at a temperature higher than 1390 K, formation of Si nano-crystals has been confirmed. The dot size ranges from 10 to 50 nm, and the density as high as 2.7 X 10^{11} cm^{-2} has been obtained.

References

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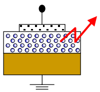
Background (I)

- Si nano-crystals embedded in SiO_2



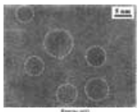
⇨ Opto-electronic devices

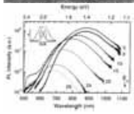
Advantages

- compatibility with Si process
- good Si/SiO_2 interface

[1] D. J. DiMaria *et. al.*, J. Appl. Phys. 56 (1984) 401.

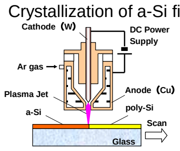
- Process technology of Si nano-crystal formation
  - Ion implantation to SiO_2 films
    Annealing：1100ºC、30~240 min in N_2
    [2] G.-R. Lin *et. al.*, J. Appl. Phys. 97 (2005) 094306.
  - SiO_x film（vacuum evaporation）
    Annealing：1030ºC 60 min in N_2
    [3] D. Nesheva *et. al.*, J. Appl. Phys. 92 (2002) 4678.
  - Size control of Si nano-crystals
    Annealing：：1000ºC、~30 min in O_2
    [4] M. L. Brongersma *et. al.*, Appl. Phys. Lett. 72 (1998) 2577.





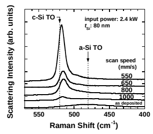
Background (II)

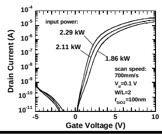
- A millisecond rapid thermal annealing using thermal plasma jet
  - Heating substrate surface up to 1600K within ms
  - Crystallization of a-Si films and application to TFT fabrication [5,6]



Advantages

- **simple, high power**
- **large area processing**





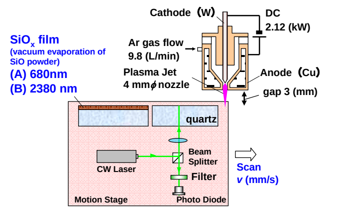
[5] H. Kaku *et.al.* Appl. Surf. Sci. 244 (2005) 8.
[6] S. Higashi *et.al.* Jpn. J. Appl. Phys. 44 (2005) L108.

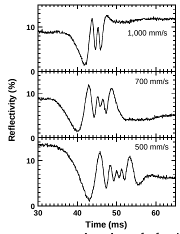
Objectivres

- Investigate the Si nano-crystal formation by annealing SiO_x films with plasma jet
- Clarify the crystallization temperature

Experimental (I)

- Annealing of SiO_xfilms and temperature measurement

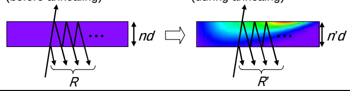




temperature dependence of refractive index [7]

$$\frac{dn_{quartz}}{dT} = 1.2\times10^{-5}$$

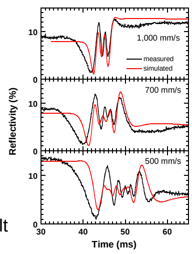
(before annealing) (during anneaing)



[7] J. H. Wray *et.al.* J. Opt. Soc. Am. 59 (1969) 774.

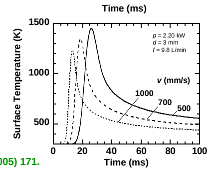
Experimental (II)

- Temperature Analysis [8]
  - 2-d Heat Diffusion Simulation
    > Effective power transfer efficiency : ε (%)
    > Width of plasma jet : *w* (mm)
  - Optical Simulation
    > $dn_{quartz}/dT = 1.2\times10^{-5}$
    > Multiple reflection & interference
  - Comparison with Experimental Result
  - Temperature Profile



Characteristic annealing parameters

v (mm/s)	T_{max} (K)	$R_{Heating}$ (K/ms)	$R_{Cooling}$ (K/ms)
1,000	1,300	340	147
700	1,430	244	103
500	1,560	197	81



[8] T. Okada *et.al.* Dig. Tech. Pap. AM-LCD 05 (Kanazawa, 2005) 171.

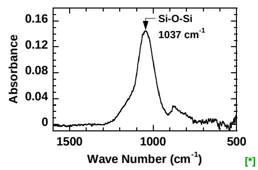
SiO_x Film Composition

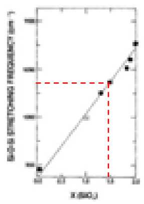
- From deposition condition…

	High residual pressure (1×10^{-3} Pa)			Low residual pressure (2×10^{-4} Pa)			
V_d (nm/s)	0.2	3.0	6.0	0.2	1.0	3.0	6.0
x	1.7	1.3	1.15	1.6	1.4	1.2	1.1

[3] D. Nesheva *et. al.*, J. Appl. Phys. 92 (2002) 4678.

- From FTIR measurement…





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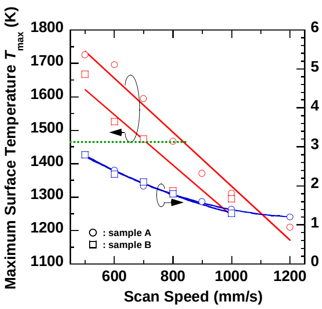
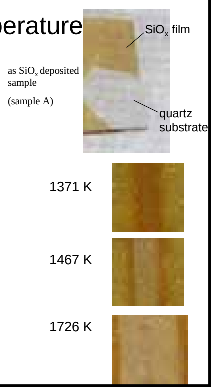
SiO_x x: 1.4~1.5

Experimental Results (I)

- Annealing condition and Temperature

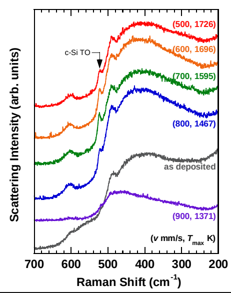




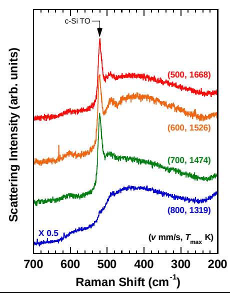
Experimental Results (II)

- Raman scattering spectra from SiO_x films before and after annealign (λ_{exc}=532 nm)

sample A 680nm



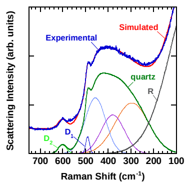
sample B 2380nm

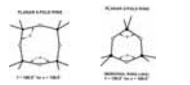


Experimental Results (III)

- Deconvolution (sample A)

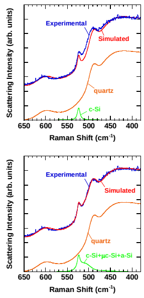
①quartz substrate



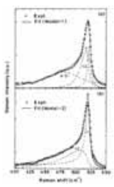


D_1:planner 4 member D_2:planner 3 member

②quartz＋SiO_x (after annealing)



Annealed sample is consisting of c-Si + μc-Si (+ a-Si ?)



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[11] M. N. Islam et. al. Appl. Phys. Lett. 78 (2001) 715.

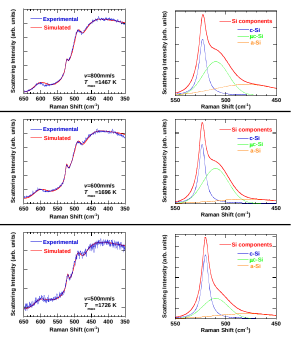
Experimental Results (IV)

- Deconvolution (sample A)

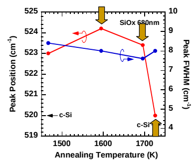
1467 K

1696 K

1726 K



annealing temperature and c-Si peak



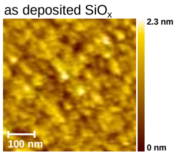
Si crystals formed below 1726K have compressive strain

Si crystals formed at 1726K is strain relieved

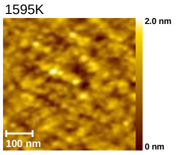
Experimental Results (V)

- Surface morphology of films (sample A)

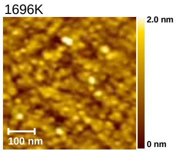
as deposited SiO_x



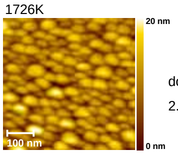
1595K



1696K



1726K



dot density

2.7 X 10^{11} cm^{-2}

Conclusions

- By annelaing SiO_xfilms within 2 ms at temperature higher than 1470 K, Si nano-crystals are formed.
- Raman scattering spectra obtained from annealed SiOx films show crystalline, micro-crystalline (or amorphous) Si phonon bands.
- By annelaing SiO_xfilm at a temperature as high as 1730 K, 20nm sized Si nano-crystals are obtained with the density as high as 2.7 X 10^{11} cm^{-2}.