Title	Flash-Lamp-Crystallized Polycrystalline Silicon Films with High Hydrogen Concentration Formed from Cat-CVD a-Si Films
Author(s)	Ohdaira, Keisuke; Tomura, Naohito; Ishii, Shohei; Matsumura, Hideki
Citation	Thin Solid Films, 519(14): 4459-4461
Issue Date	2011
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/9833
Rights	NOTICE: This is the author's version of a work accepted for publication by Elsevier. Keisuke Ohdaira, Naohito Tomura, Shohei Ishii and Hideki Matsumura, Thin Solid Films, 519(14), 2011, 4459-4461, http://dx.doi.org/10.1016/j.tsf.2011.01.313
Description	

Flash-Lamp-Crystallized Polycrystalline Silicon Films with High Hydrogen Concentration Formed from Cat-CVD a-Si Films

Keisuke Ohdaira[1,2], Naohito Tomura[1], Shohei Ishii[1], and Hideki Matsumura[1]

[1]Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

[2]PRESTO, Japan Science and Technology Agency (JST), 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

Abstract

We investigate residual forms of hydrogen (H) atoms such as bonding configuration in poly-crystalline silicon (poly-Si) films formed by the flash-lamp-induced crystallization of catalytic chemical vapor deposited (Cat-CVD) a-Si films. Raman spectroscopy reveals that at least part of H atoms in flash-lamp-crystallized (FLC) poly-Si films form Si-H_2 bonds as well as Si-H bonds with Si atoms even using Si-H-rich Cat-CVD a-Si films, which indicates the rearrangement of H atoms during crystallization. Peak desorption temperature during thermal desorption spectroscopy (TDS) is as high as 900 ºC, similar to reported value for bulk poly-Si.

Keywords

Crystallization, Flash Lamp Annealing, Polycrystalline Silicon, Solar Cell, Catalytic CVD, Hydrogen, Thermal Desorption Spectroscopy, Raman Spectroscopy

1. Introduction

Thin-film polycrystalline silicon (poly-Si) formed on low-cost substrates is a promising material for next-generation solar cell because of its advantages of low material usage, high stability against light soaking, and high performance. One of the methods of forming such thin poly-Si films is crystallization of precursor a-Si films by annealing. It has been demonstrated that poly-Si films formed by solid-phase crystallization through hour-order furnace annealing can be processed to solar cells with conversion efficiency of more than 10%, which indicates the feasibility of this concept [1]. To realize higher throughput, rapid annealing techniques should be applied instead of time-consuming furnace annealing.

Flash lamp annealing (FLA) is a millisecond-order annealing technique using pulse emission from a Xe lamp array [2, 3], and can realize selective and sufficient heating of micrometer-order-thick a-Si films and avoid thermal damage to entire low-cost glass substrates. We have clarified that poly-Si films more than 4 μm thick can be formed on quartz and soda lime glass substrates [4, 5]. No serious dopant diffusion occurs during the flash-lamp-induced crystallization process [6], and diode and solar cell operations have been demonstrated using flash-lamp-crystallized (FLC) poly-Si films [7]. Catalytic chemical vapor deposition (Cat-CVD) is suitable as a method of preparing precursor a-Si films for this purpose. This is because Cat-CVD can provide a-Si films with low film stress [8], which results in the deposition of a-Si films more than 4 μm thick without Si film peeling during deposition. Another advantage of Cat-CVD for this purpose is the formation of a-Si films with moderately low hydrogen (H) contents, which leads to the prevention of Si film peeling during deposition [9]. Interestingly, H atoms in a-Si films do not severely desorb during FLA, and we can form FLC poly-Si films with H contents on the order of 10^{21} /cm^3 [10, 11]. The remaining H atoms can be utilized for the passivation of dangling bonds in FLC poly-Si films [10-13]. We believe that the suppression of H desorption is due to explosive crystallization, that is, lateral crystallization with velocity on the order of m/s triggered by the release of latent heat [14, 15]. Fundamental understanding of the residual forms of H atoms in FLC poly-Si films is important for the realization of more effective H passivation using remaining H atoms. In this study, we have investigated the residual forms of H atoms such as band configuration in FLA poly-Si films on the basis of Raman spectroscopy and thermal desorption spectroscopy (TDS).

2. Experimental details

We first deposited a Cr film 200 nm thick on 20×20×0.7 mm^3-sized quartz substrates by sputtering, followed by the deposition of 4.5 μm-thick a-Si films by Cat-CVD. Detailed deposition conditions for a-Si films have been summarized elsewhere [16].

FLA was performed under a fixed condition with pulse duration of 5 ms and irradiance of approximately 20 J/cm^2. Typical spectrum of flash lamp light can be seen elsewhere [3]. Only one shot of flash lamp pulse was irradiated for each sample, and no additional heating was supplied. No dehydrogenation process was performed prior to FLA. Typical surface image and Raman spectrum of an FLC poly-Si film are shown in Fig. 1.

TDS was performed both for an FLC poly-Si film and a precursor a-Si film. Each sample was put on a holder in a high vacuum chamber (~10^{-8} Pa), and heated by infra-red radiation from underneath at a heating rate of 10 °C/min from room temperature to 1190 °C. Temperature was checked and controlled using a thermocouple embedded in the holder. Amount of desorbed H_2 as a function of temperature was detected with a quadrupole mass spectrometer. Relative amounts of Si-H, Si-H_2 and H-H bonds in a-Si and poly-Si films were evaluated by Raman spectroscopy using a 632.8 nm light from a He-Ne laser.

3. Results and Discussion

Figure 2 shows the concentrations of H atoms in a precursor a-Si film and an FLC poly-Si film estimated by TDS and secondary ion mass spectroscopy (SIMS) for comparison. The TDS measurement reproduced H concentration in both films previously obtained by SIMS [10,11], which indicates the accuracy of these measurements. From these results, H contents are estimated to be 8% both for a-Si and FLC poly-Si films, which is much larger than that obtained from the peak area of the Si-H wagging mode in Fourier-transform infrared (FT-IR) spectrum (3-4%) of Cat-CVD a-Si films. Similar tendency has been reported by other groups investigating Cat-CVD a-Si films [17], and this phenomenon might be a character of Cat-CVD a-Si films having H distribution different from plasma-enhanced CVD films [18].

Figure 3 shows TDS spectra of a precursor Cat-CVD a-Si film and a FLC poly-Si film. One can see a clear peak at ~650 ºC, which is typically observed in TDS spectra of H_2 from CVD a-Si films [19]. On the other hand, the spectrum of a FLC poly-Si shows no clear desorption signals less than 600 °C, while the spectrum has a peak temperature around 900 ºC. These features are completely different from that of an a-Si film, and are rather similar to that of bulk poly-Si [20].

Figure 4 shows Raman spectra of a precursor a-Si film and a FLC poly-Si film for the observation of Si-H, Si-H_2, and H-H signals. The Si-H peak, at ~2000 cm^{-1}, can be mainly seen in the spectrum of an a-Si film, whereas the Si-H_2 peak, located at ~2090 cm^{-1}, also appears after crystallization by FLA. On the other hand, H-H peak (~4158 cm^{-1} [21]) is not clearly observed in the Raman spectrum of an FLC poly-Si film. These facts indicate that H atoms move and rearrange during FLA, and the final bond configurations are mainly Si-H and Si-H_2. We can imagine that the formation of Si-H_2 bonds is unlikely inside crystalline Si grains, and most of them would exist at grain boundaries and/or other defective parts.

One may expect that H atoms bonded to Si atoms as Si-H and Si-H_2 will easily desorb at 600 °C or less, as is the case for H atoms in a-Si films. However, surprisingly, we can clearly see Si-H and Si-H_2 signals in the Raman spectrum of an FLC poly-Si film annealed at 700 °C for 30 min under N_2 atmosphere, as shown in Fig. 4(b). Their signal intensities are slightly smaller than the as-crystallized ones, but almost comparable. This means that most of H atoms forming Si-H and Si-H_2 bonds in FLC poly-Si films do not completely desorb even at 700 °C, which is consistent with the result of TDS measurement. Kisielowski-Kemmerich *et al.* have mentioned that the peak temperature of as high as 900 °C for bulk poly-Si is due to the existence of defective parts such as grain boundaries and/or dislocations [20]. This situation is also applicable to FLC poly-Si films, which contain a number of 10-nm-sized fine grains [14]. It is unlikely that the bonding energies of Si-H and Si-H_2 in FLC poly-Si films are widely different from those in a-Si films. Thus, the higher desorption temperature of H atoms in FLC poly-Si films could be due to the trapping of temporarily unbonded H atoms at defective parts which suppresses the outgassing of H atoms. Unbonded H atoms would again form Si-H and Si-H_2 bonds during cooling process. Further investigation will be necessary for the clarification of the characteristics of H desorption mechanisms.

Finally we will discuss the impact of H residual forms on the termination of dangling bonds by remaining H atoms. As mentioned above, grain boundaries could act to suppress H desorption even at considerably high temperatures, which enables the efficient rearrangement of H atoms during post-annealing of FLC poly-Si films. Furthermore, since crystallization process by FLA is so immediate, unbonded H atoms may also exist in FLC poly-Si films, although we have not confirmed their existence because they cannot be detected by Raman spectroscopy. They could move to grain boundaries or other defective parts during post-annealing, and would contribute to the termination of Si dangling bonds, resulting in the significant improvement of minority carriers lifetime and defect density reported previously [10, 11, 13].

4. Summary

H atoms in Cat-CVD a-Si films rearrange to form Si-H and Si-H_2 bonds during crystallization triggered by FLA. Most of H atoms do not desorb even annealing at 700 °C, and the peak desorption temperature is at around as high as 900 °C. This phenomenon could be explained by the trapping of H atoms at grain boundaries or other defective parts, which would leads to effective defect termination during post furnace annealing.

Acknowledgments

The authors would like to thank T. Owada and T. Yokomori of Ushio Inc. for their expert operation of FLA. The authors also acknowledge T. Yoshida of JAIST for his technical support for our experiment. This work was supported by JST PRESTO program.

References

1. M.J. Keevers, T.L. Young, U. Schubert, M.A. Green, 22nd European Photovoltaic Solar Energy Conference, Milan, Italy, September 3-7, 2007, p. 1783.
2. B. Pécz, L. Dobos, D. Panknin, W. Skorupa, C. Lioutas, N. Vouroutzis, Appl. Surf. Sci. 242 (2005) 185.
3. H. Habuka, A. Hara, T. Karasawa, M. Yoshioka, Jpn. J. Appl. Phys. 46 (2007) 937.
4. K. Ohdaira, Y. Endo, T. Fujiwara, S. Nishizaki, H. Matsumura, Jpn. J. Appl. Phys. 46 (2007) 7603.
5. K. Ohdaira, T. Fujiwara, Y. Endo, S. Nishizaki, H. Matsumura, Jpn. J. Appl. Phys. 47 (2008) 8239.
6. K. Ohdaira, T. Fujiwara, Y. Endo, K. Shiba, H. Takemoto, S. Nishizaki, Y.R. Jang, K. Nishioka, and H. Matsumura, 33rd IEEE Photovoltaic Specialists Conference, San Diego, U.S.A., May 11-16, 2008.
7. K. Ohdaira, T. Fujiwara, Y. Endo, K. Shiba, H. Takemoto, H. Matsumura, Jpn. J. Appl. Phys. 49 (2010) 04DP04.
8. A.H. Mahan, Thin Solid Films 501 (2006) 3.
9. K. Ohdaira, K. Shiba, H. Takemoto, T. Fujiwara, Y. Endo, S. Nishizaki, Y.R. Jang, H. Matsumura, Thin Solid Films 517 (2009) 3472.
10. K. Ohdaira, H. Takemoto, K. Shiba, H. Matsumura, Appl. Phys. Express 2 (2009) 061201.
11. K. Ohdaira, H. Takemoto, T. Nishikawa, H. Matsumura, Current Appl. Phys. 10 (2010) S402.
12. K. Brendel, N. H. Nickel, K. Lips, W. Fuhs, Mat. Res. Soc. Symp. Proc. 762 (2003) 69.

13. K. Ohdaira, T. Nishikawa, S. Ishii, N. Tomura, K. Koyama, H. Matsumura, Proc. 5th World Conf. Photovoltaic Energy Conversion (in press)

14. K. Ohdaira, T. Fujiwara, Y. Endo, S. Nishizaki, H. Matsumura, J. Appl. Phys. 106 (2009) 044907.

15. K. Ohdaira, T. Nishikawa, K. Shiba, H. Takemoto, H. Matsumura, Phys. Status Solidi C 7 (2010) 604.

16. K. Ohdaira, S. Nishizaki, Y. Endo, T. Fujiwara, N. Usami, K. Nakajima, H. Matsumura, Jpn. J. Appl. Phys. 46 (2007) 7198.

17. D.M. Goldie, S.K. Persheyev, J. Mater. Sci. 41 (2006) 5287.

18. A.H. Mahan, S.P. Ahrenkiel, R.E.I. Schropp, H. Li, D.S. Ginley, Thin Solid Films 516 (2008) 529.

19. P.J. Jennings, J.C.L. Cornish, B.W. Clare, G.T. Hefter, D.J. Santjojo, Thin Solid Films 310 (1997) 156.

20. C. Kisielowski-Kemmerich, W. Beyer, J. Appl. Phys. 66 (1989) 552.

21. K. Murakami, N. Fukata, S. Sasaki, K. Ishioka, M. Kitajima, S. Fujimura, J. Kikuchi, H. Haneda, Phys. Rev. Lett. 77 (1996) 3161.

Figure captions

Fig. 1 (a) Typical surface image and (b) Raman spectrum of an FLC poly-Si film.

Fig. 2 H concentration in a precursor Cat-CVD a-Si film and an FLC poly-Si film estimated by TDS and by SIMS [10, 11]. In the TDS measurement, H concentrations were simply estimated using total amounts of effused H_2 molecules and the volumes of Si films.

Fig. 3 TDS spectra of a precursor Cat-CVD a-Si film and a FLC poly-Si film.

Fig. 4 Raman spectra of a precursor a-Si film and a FLC poly-Si film for the observation of (a) Si-H and Si-H_2 bonds and (b) H-H bonds.

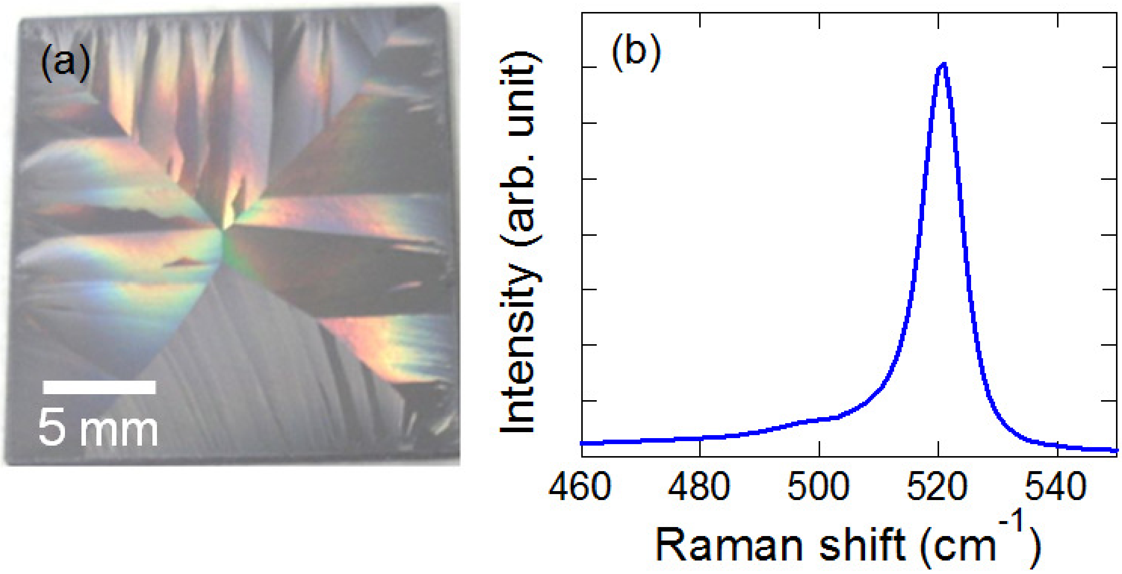

Figure 1 K. Ohdaira *et al.*,

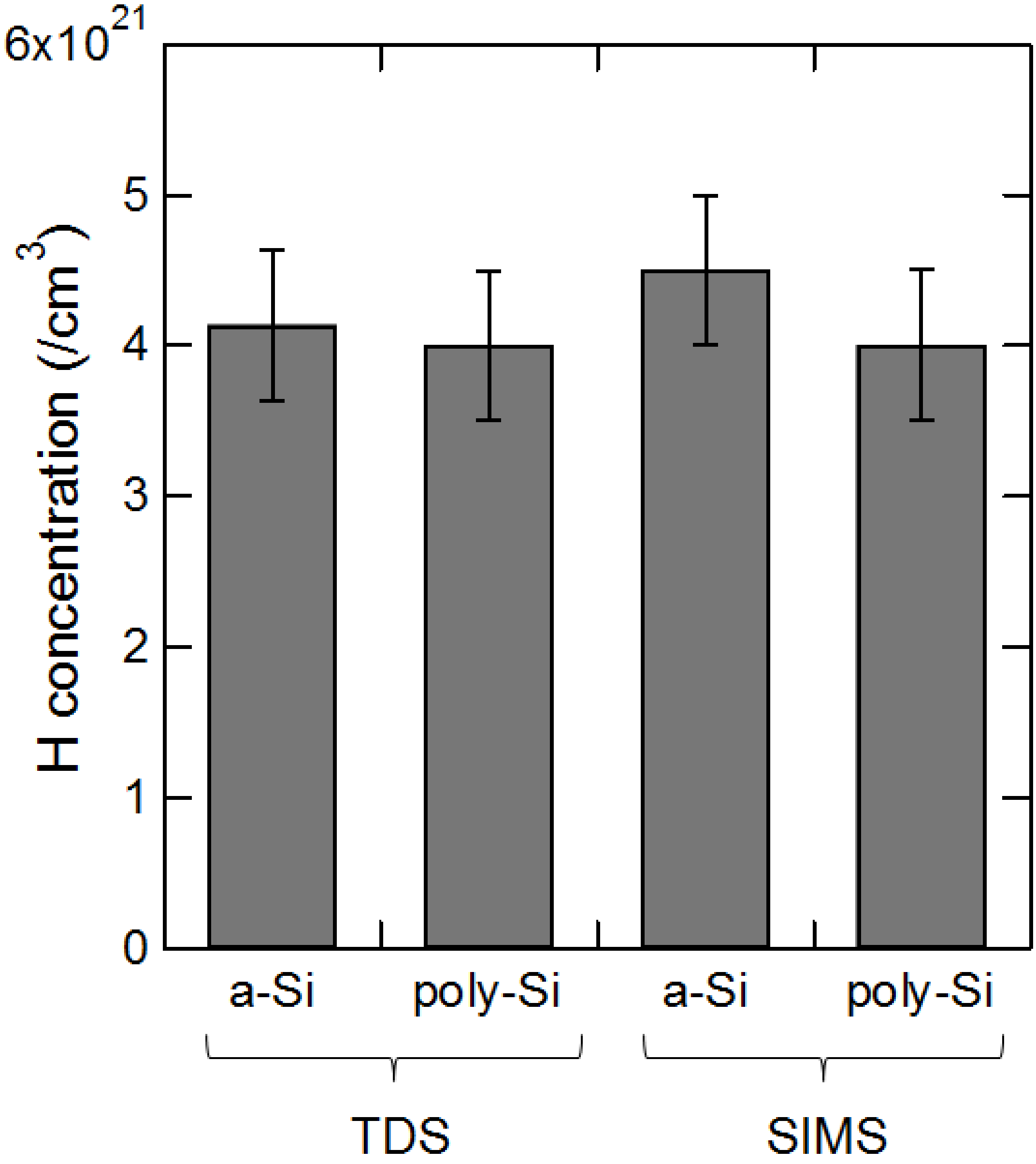

Figure 2 K. Ohdaira *et al.*,

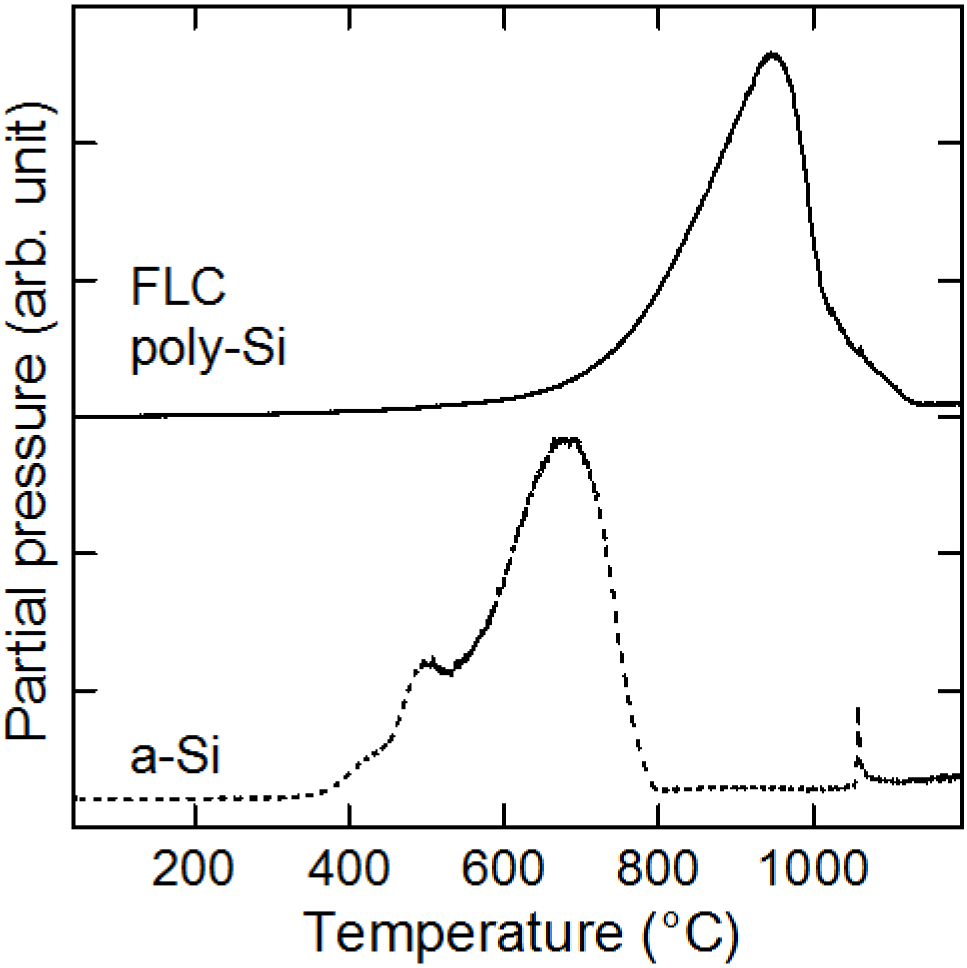

Figure 3 K. Ohdaira *et al.*,

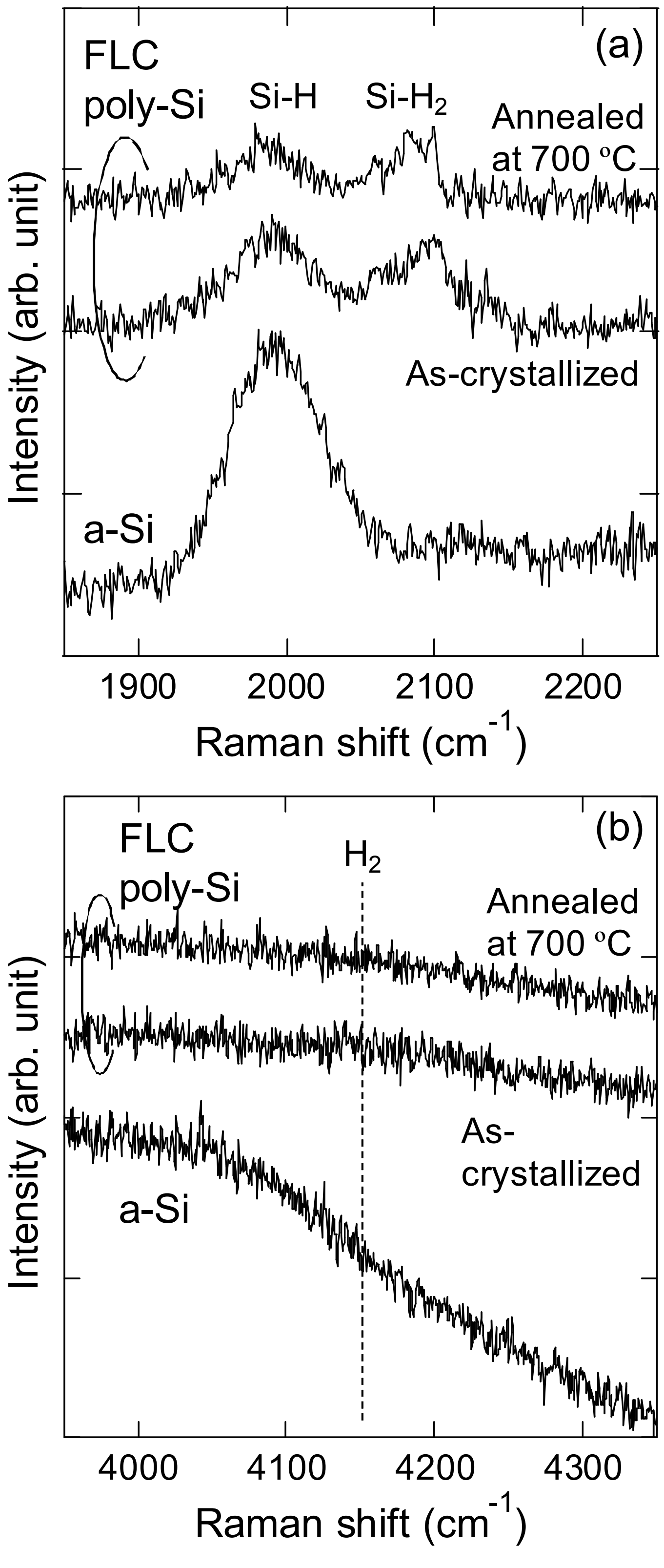

Figure 4 K. Ohdaira *et al.*,