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Description	

**High-Quality Polycrystalline Silicon Films with Minority Carrier
Lifetimes over 5 μ s Formed by Flash Lamp Annealing of Precursor
Amorphous Silicon Films prepared by Catalytic Chemical Vapor
Deposition**

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Polycrystalline silicon (poly-Si) films with a thickness over 1 μ m are formed by the flash lamp annealing (FLA), with a duration of less than 10 ms, of precursor amorphous silicon (a-Si) films prepared by catalytic chemical vapor deposition (Cat-CVD) on quartz substrates. Thicker a-Si films can be crystallized under lower lamp irradiance, which can be understood by considering both the total generated heat in the a-Si films and the thermal diffusion into the quartz substrates. Results of microwave

photoconductivity decay (μ -PCD) measurement indicate that high-pressure water vapor annealing (HPWVA) is effective for improving the minority carrier lifetime of the poly-Si films. The film with a thickness of 1.5 μm crystallized under a high lamp irradiance shows minority carrier lifetimes over 5 μs , indicating the high feasibility of applying the crystalline film to high-efficiency thin-film solar cells.

KEYWORDS: polycrystalline Si, flash lamp annealing, crystallization, minority carrier lifetime, high-pressure water vapor annealing

1. Introduction

Recently, the market for solar cells has been growing extensively, thus, further improvement in their efficiency is required. Most of the commercial solar cells available are currently based on bulk crystalline silicon (c-Si) and the market share for thin-film solar cells using microcrystalline silicon ($\mu\text{c-Si}$) and amorphous silicon (a-Si) prepared by deposition techniques is quite low owing to their lower conversion efficiency. The principal reason for their lower cell performance is their shorter minority carrier diffusion lengths. In the case of a-Si containing a larger number of dangling bonds than crystalline silicon, the diffusion length is usually less than 1 μm . $\mu\text{c-Si}$ also has a shorter diffusion length owing to the a-Si phase surrounding the crystal grains. However, if the a-Si phase is removed and the crystallinity is improved, oxygen (O) atoms are easily absorbed into the grain boundary and the electronic property degrades markedly. Therefore, $\mu\text{c-Si}$ with high crystallinity but with no O absorption is desired for high-efficiency thin-film solar cells.

Such $\mu\text{c-Si}$ films can be formed by the rapid thermal annealing (RTA) of a-Si films for several tens of seconds at a temperature higher than 800 $^{\circ}\text{C}$.¹⁾ This special $\mu\text{c-Si}$ film named nano-grain polycrystalline-Si (ngp-Si) consists of small dense grains with a size of approximately 50 nm from the bottom to the top of the film and shows high

crystallinity and a low O absorption levels that is lower than the detection limit of Fourier transform infrared (FT-IR) spectroscopy. A high carrier mobility of about $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ can be realized in ngp-Si films. The technical issue of the desorption of hydrogen atoms during RTA and the resulting increase in defect density up to $1 \times 10^{18} \text{ cm}^{-3}$ can be resolved by posttreatment using high-pressure water vapor annealing (HPWVA).²⁾ The defect density can be decreased down to a value less than $10^{17} / \text{cm}^3$. However, there is another issue, namely, that of thermal damage to the glass substrates. When annealing time is several tens of seconds, glass substrates are also wholly heated at the same temperature as the Si film owing to the sufficient thermal diffusion length of glass. Therefore, cheap glass substrates such as sodalime glass with poor thermal resistance are unsuitable for normal RTA. If annealing time is decreased down to the order of nanoseconds, which can be realized by excimer laser annealing, the thermal diffusion length of c-Si and a-Si is less than $1 \text{ }\mu\text{m}$, which is not appropriate for solar cells demanding the crystallization of a-Si films with a thickness on the order of micrometers for sufficient optical absorption. Thus, we focus on millisecond treatment, which is sufficient for enabling thermal diffusion in c-Si and a-Si with a thickness of several μm but can prevent the total heating of the substrate. One method of realizing millisecond annealing is plasma jet crystallization (PJC).³⁻⁹⁾ Flash lamp annealing

(FLA) can also realize millisecond pulses and has a sufficiently high power to crystallize a-Si films with a film thickness over 1 μm . Although there have been several reports on the crystallization of a-Si with a thickness of several hundred nm by FLA,¹⁰⁻¹²⁾ the feasibility of crystallizing μm -order a-Si for application in solar cells and the properties of such crystallized films have not been clarified.

In this study, we have investigated the crystallization of a-Si films deposited on quartz substrates by FLA and the fundamental properties of such crystallized films. The effect of HPWVA on the c-Si films formed by FLA has also been investigated, and the minority carrier lifetime of the crystallized films has been evaluated.

2. Experimental Methods

Precursor a-Si films with thicknesses from 100 to 1500 nm were deposited by catalytic chemical vapor deposition (Cat-CVD) on $20 \times 20 \text{ mm}^2$ quartz substrates. Cat-CVD, often called Hot-Wire CVD, is a method of preparing device-quality thin films at low substrate temperatures utilizing the catalytic cracking reaction between source gases and a heated catalyzer. The a-Si films prepared by Cat-CVD have low hydrogen contents of about 3%, thus, the thermal desorption of hydrogen during annealing and the resulting structural damage to the film can be suppressed. Another

advantage of Cat-CVD is that a-Si films with a thickness of several μm can be easily deposited without peeling because of their low film stress. A tungsten catalyzer was heated at 1750 °C during deposition to decompose the source gases of SiH_4 and H_2 with flow rates of 50 and 10 sccm, respectively. The substrate temperature during deposition was about 320 °C and the deposition rate of a-Si films was about 2 nm/s.

Flash lamp annealing was performed with a duration of less than 10 ms. Lamp irradiance was systematically changed to determine the proper condition for crystallizing a-Si films. Although the lamp irradiance is supposed to be several tens of J/cm^2 , we represent it as relative lamp irradiance since the lamp irradiance cannot be measured exactly. Some of the lamp-annealed films were treated by HPWVA under a pressure of 3.0 MPa at 350 °C for 1 h.

The crystallinity of the films before and after FLA was characterized by micro-Raman spectroscopy using a He-Ne laser with a wavelength of 632.8 nm, which corresponds to a penetration depth of c-Si of about 3 μm and a penetration depth of a-Si of about 0.1 μm , with focusing to 10- μm -size spot. The peak wavenumber and full width at half maximum (FWHM) of c-Si Raman signal can be estimated by fitting the experimental data to the Lorentzian function. The crystallinity of the films was determined using $(I_c + I_{\mu c}) / (I_c + I_{\mu c} + I_a)$, where I_c , $I_{\mu c}$, and I_a represent the integration

of Raman signals related to c-Si, μ c-Si, and a-Si, respectively. The typical wavenumbers of Raman shifts are 480 cm^{-1} for a-Si, 500 cm^{-1} for μ c-Si, and 520 cm^{-1} for c-Si. The grain size in the crystallized films was estimated from the FWHM of X-ray diffraction peaks using Scherrer's equation. Minority carrier lifetime was measured by microwave photoconductivity decay (μ -PCD) measurement with a pulse laser wavelength of 770 nm focused onto a 2-mm-size spot. In the μ -PCD measurement, sample surface was passivated with an iodine/ethanol solution to eliminate the effect of surface recombination.

3. Results

Figure 1 shows the Raman spectra of the Si films with different thicknesses after FLA under the same irradiance. No c-Si phase can be observed, and the broad signals centered at 480 cm^{-1} related to the a-Si phase are dominant in the spectra of the films with a film thickness less than 300 nm. On the other hand, in the case of thicker films, the c-Si phase can clearly be seen. These results indicate that thick a-Si films can be crystallized under a low lamp irradiance compared with thin films. This mechanism will be discussed later.

Figure 2(a) shows the lamp irradiance dependence of the Raman spectra of the

lamp-annealed films with a thickness of 1.5 μm measured at the center of the samples. In the case of a relative lamp irradiance of 1, only signals originating from a-Si can be observed. On the contrary, sharp peaks located around 520 cm^{-1} dominate the spectra at higher irradiances, indicating the formation of polycrystalline Si (poly-Si) films. Such crystallization does not occur in the case of a-Si deposited by PECVD owing to the peeling of a-Si films that occurs under lamp irradiance lower than that needed for crystallization, which may be because of the higher hydrogen content of about 10% in a-Si films. Figure 2(b) shows the Raman spectra of the Si films on Si substrates after FLA with various irradiances. No marked change in the spectra occurs even after FLA with irradiance sufficiently high for crystallization in the case of the quartz substrate, indicating the strong dependence of the crystallization of a-Si on the substrate.

Figure 3(a) shows the crystallinity of the lamp-annealed films with a thickness of 1.5 μm as a function of relative lamp irradiance. Film crystallinity exceeds 0.9 in the case of high lamp irradiance over 1.17. Figures 3(b) and 3(c) show the FWHM and wavenumber of the c-Si peaks as a function of relative irradiance from the Raman spectra measured at the center and edge of the films. At the center of the film, the wavenumber and FWHM of the c-Si peaks are about 517 and 7 cm^{-1} , respectively, almost independent of lamp irradiance. These values are inferior to those of the

reference monocrystalline Si of 520 and 4 cm^{-1} , respectively. This indicates that the poly-Si films consist of small grains. The grain sizes estimated from the XRD curves are less than 60 nm. Therefore, ngp-Si films consisting of grains of several tens of nm in size with high crystallinity are formed by FLA. On the other hand, the FWHM measured at the edge of the sample decreases with increasing lamp irradiance. The peak wavenumber increases and reaches 519.5 cm^{-1} . The Raman spectra measured at the center and edge of the poly-Si film irradiated under a relative lamp irradiance of 1.36 are summarized in Fig. 4. The differences in the crystallinities and peak wavenumbers can clearly be seen. This difference may be due to the inhomogeneous thermal condition in the lateral direction. FLA is a nonthermal equilibrium treatment and Si films generally have a higher temperature than the substrates during FLA. The generated heat close to the edge of the Si film does not diffuse into the substrate as easy as that generated around the center of the sample because there is less substrate material to pass the heat, resulting in higher temperature treatment in the edge region.

Figure 5 shows the microwave decay curve of 1.5- μm -thick silicon films crystallized under a relative lamp irradiance of 1.36 before and after HPWVA. Before HPWVA, no significant signal can be seen, whereas a decay curve corresponding to a minority carrier lifetime of 8.6 μs evaluated from the fitting of the microwave decay

curve to the exponential function appears after HPWVA. Although such a long carrier lifetime of post-crystallized Si films has also been reported in poly-Si films formed through metal-induced crystallization¹³⁾, such crystallization requires at least several hours. The importance of the result in this study is in the fact that such high-quality poly-Si films can be formed through highly mass-productive millisecond treatment by which thermal damage to the glass substrate can be prevented.

Table I shows the carrier lifetimes of the 1.5- μm -thick silicon films annealed under several lamp irradiances. Without surface chemical passivation using the iodine/ethanol solution, no decay curves can be obtained even when HPWVA is carried out on the lamp-annealed films, which indicates a large surface recombination velocity. No significant lifetime can be obtained in any of the silicon films without HPWVA. This means that a large number of dangling bonds acting as recombination centers are present in the crystallized films and that the defect termination process is necessary to realize high-performance films. In the case of the lamp irradiance lower than 1.27, no decay curves cannot be observed even if the films show high crystallinity close to 1. Figure 6 shows the carrier lifetime of the poly-Si film formed under a relative irradiance of 1.34 as a function of measured position. The highest lifetime is obtained not at the center of the sample but 2.5 mm away from the center. As shown in Fig. 3, better film

properties such as FWHM and the peak wavenumber of c-Si Raman signals are obtained close to the edge of the film in the case of poly-Si films annealed under a high lamp irradiance, which probably affects the results of carrier lifetime.

Figure 7 shows the Raman spectra of the Si films of 1.5 μm thickness before and after FLA with a relative irradiance of 1.27 with and without HPWVA. A clear peak around 2000 cm^{-1} corresponding to Si-H bonds is seen before FLA, whereas no peaks are observed after FLA, indicating the desorption of H atoms. No Si-H signals are detected after HPWVA. This indicates that the mechanism of HPWVA may not depend on the termination of dangling bonds caused by H atoms but rather on another effect. Further investigation is required for understanding the mechanism.

4. Discussion

4.1 *Thickness dependence of crystallization*

Since the nucleation rate for crystallization strongly depends on temperature, the maximum temperature of the films during FLA is important. The thermal diffusivities (a) of a-Si and quartz (SiO_2) are 4.0×10^{-3} and $8.6 \times 10^{-3}\text{ cm}^2/\text{s}$, respectively, as estimated from the equation of $a = K/\rho c$, where K is the conductivity, ρ is the density, and c is the specific heat capacity. The parameters used for this estimation are

summarized in Table 2. Therefore, using a diffusion time (t) of 1 ms, the thermal diffusion lengths (\sqrt{at}) in a-Si and quartz can be estimated to be about 20 and 29 μm , respectively, indicating that the generated heat in the a-Si film during FLA with a millisecond duration almost homogeneously diffuses through entire Si film and also into the quartz surface with a length of at least several tens of μm . Therefore, the thickness dependence of the crystallization under the same lamp irradiance can be understood as a result of differences in the total generated heat in a-Si films caused by optical absorption and in the thermal diffusion length of the generated heat. Since flash lamp light has a broad spectrum, mainly in visible range, the total generated heat in thick a-Si films is larger than that in thin a-Si films. Furthermore, the total thermal diffusion length from the surface is relatively small in case of thick a-Si because of the lower thermal diffusivity of a-Si, as shown schematically in Fig. 8. Since the generated heat diffuses almost homogeneously through the a-Si film and also into a portion of the quartz substrates in each case, the thick film can hold more heat per unit thickness, resulting in crystallization at lower lamp irradiance. In the case of the Si substrate showing no crystallization, the thermal diffusion length of c-Si is estimated to be about as long as 100 μm , indicating that generated heat is distributed in a depth three times longer or more than in the quartz substrate. Although the total generated heat is expected to be

larger because of optical absorption in Si substrate, this contribution must be relatively small owing to the effective optical absorption in a-Si. Consequently, the remaining heat per unit film thickness of a-Si on Si substrates becomes smaller than that on glass substrates.

The film thickness dependence seen in the FLA of a-Si on a glass substrate is unlikely in the case of PJC with the same millisecond duration, showing no thickness dependence for crystallization.⁵⁾ This difference derives from the mechanism of heat generation. In FLA, heat is generated through the optical absorption of flash lamp light mainly consisting of the visible broad spectrum. On the other hand, only the surface of a-Si is heated in PJC, so that the total amount of heat is independent of a-Si film thickness. Since there is no critical difference in thermal diffusivity between a-Si and quartz substrate, as shown above, thin and thick a-Si are attained at almost the same temperature, thus, poly-crystallization starts to occur under the same treatment condition.

4.2 *Minority carrier lifetime*

As mentioned above, only poly-Si films after HPWVA and relative irradiance over 1.34 show long carrier lifetimes over 5 μ s. The crystallinity of the film with relative

irradiance of 1.17 and 1.27 is over 0.97 and seems to be sufficiently high. Therefore, another film property affects whether poly-Si films with a long carrier lifetime are formed. One possible reason for this is the difference in the crystallization mechanism. In low irradiance cases, solid-phase crystallization (SPC) probably occurs throughout the film judging from the FWHM of the Raman peak. On the contrary, the FWHM of the c-Si peak in the Raman spectrum of the edge of the film formed under a relative irradiance of 1.36 is about 5 cm^{-1} , close to the FWHM of monocrystalline Si of 4 cm^{-1} , which is probably an indication of melting growth. However, the FWHM of the Raman peak of c-Si measured at the center of the film showing a long carrier lifetime is more than 7 cm^{-1} , indicating the existence of small grains. This might be because the center of the film consists of a mixture of c-Si formed by SPC and melting growth, thus, a long carrier lifetime can be obtained from the part of melting-grown Si. According to this discussion, the positional dependence of carrier lifetime shown in Fig. 6 seems to be quite reasonable.

The minority carrier lifetime of over $5 \mu\text{s}$ corresponds to a carrier diffusion length of over $10 \mu\text{m}$, assuming a minority carrier mobility of $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ from the equations of $L = (D\tau)^{1/2}$ and $D/\mu = kT/q$, where L , D , τ , and μ represent the minority carrier diffusion length, diffusion coefficient, lifetime, and mobility, respectively. At the

present time, the carrier mobility of this film, not only the minority carrier but majority carrier mobility, has not been precisely measured. Since the resistivity of intrinsic ngp-Si is so high, the mobility measurement carried out using the Van der Pauw method, for instance, is not so easy. When the sample is heated up to 200 °C, the resistivity decreases to ease the measurement because of thermally generated carriers. Then, we could detect some indication of the mobility of approximately $50 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This value is very crude and should not be considered so seriously. However, this indicates that the mobility is not so small. On the other hand, in the case of ngp-Si with high crystallinity formed by RTA with a duration of several tens of seconds, the majority carrier mobility for boron- and phosphorus-doped ngp-Si is around $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Since poly-Si films formed by FLA show high crystallinity, similar majority carrier mobilities are expected. Although minority carrier mobility is generally different from majority carrier mobility and is strongly affected by defect density, there must be small amount of defects in this lamp-annealed film because of the long minority carrier lifetime. Therefore, the assumed minority carrier mobility and resulting diffusion length are probably reasonable.

5. Conclusions

In this study, we demonstrated that $\mu\text{c-Si}$ films with high crystallinity can be formed on quartz substrates by FLA of precursor a-Si films with a thickness of over 1 μm deposited by Cat-CVD. It has been clarified that thicker films can be crystallized with lower lamp irradiance and the mechanism has been qualitatively discussed. Some of the crystalline Si films formed by FLA with limited lamp irradiation conditions show long minority carrier lifetimes of over 5 μs after HPWVA, indicating their high potential for application in high-efficiency thin-film solar cells.

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Figure captions

Figure 1 Raman spectra of Si films with various thicknesses after FLA with relative lamp irradiance of 1.04.

Figure 2 Raman spectra of Si films on (a) quartz and (b) Si substrates with thickness of 1.5 μm annealed under various lamp irradiances. The weak c-Si peaks at 520 cm^{-1} shown in Fig. 2(b) are from the Si substrates.

Figure 3 (a) Crystallinity, (b) FWHM, and (c) peak wavenumber of Raman signals related to c-Si as function of relative lamp irradiance.

Figure 4 Raman spectra measured at center and edge of poly-Si film annealed under relative lamp irradiance of 1.36.

Figure 5 Time dependence of microwave decay of poly-Si film annealed under relative lamp irradiance of 1.36.

Figure 6 Carrier lifetimes of poly-Si film annealed under relative lamp irradiance of 1.34 as function of measured position. The inset shows a photograph of the sample surface.

Figure 7 Raman spectra of 1.5- μm -thick Si films before and after FLA with relative irradiance of 1.36. The spectrum from poly-Si after HPWVA is also shown.

Figure 8 Schematic diagrams of thermal diffusion in cases of thick and thin a-Si films.

Table I Carrier lifetimes of poly-Si films annealed under various lamp irradiances measured under several conditions.

Relative lamp irradiance		1.17	1.27	1.34	1.36
w/o CP		×	×	×	×
with CP	w/o HPWVA	×	×	×	×
	with HPWVA	×	×	7.5 μ s	8.6 μ s

Table II Parameters of a-Si, SiO₂ and Si used for calculation of thermal diffusion length.

	K (Wcm ⁻¹ K ⁻¹)	ρ (g/cm ³)	c (Jg ⁻¹ K ⁻¹)
a-Si	0.007	2.30	0.77
SiO ₂	0.014	2.20	0.74
Si	0.26	2.30	0.95

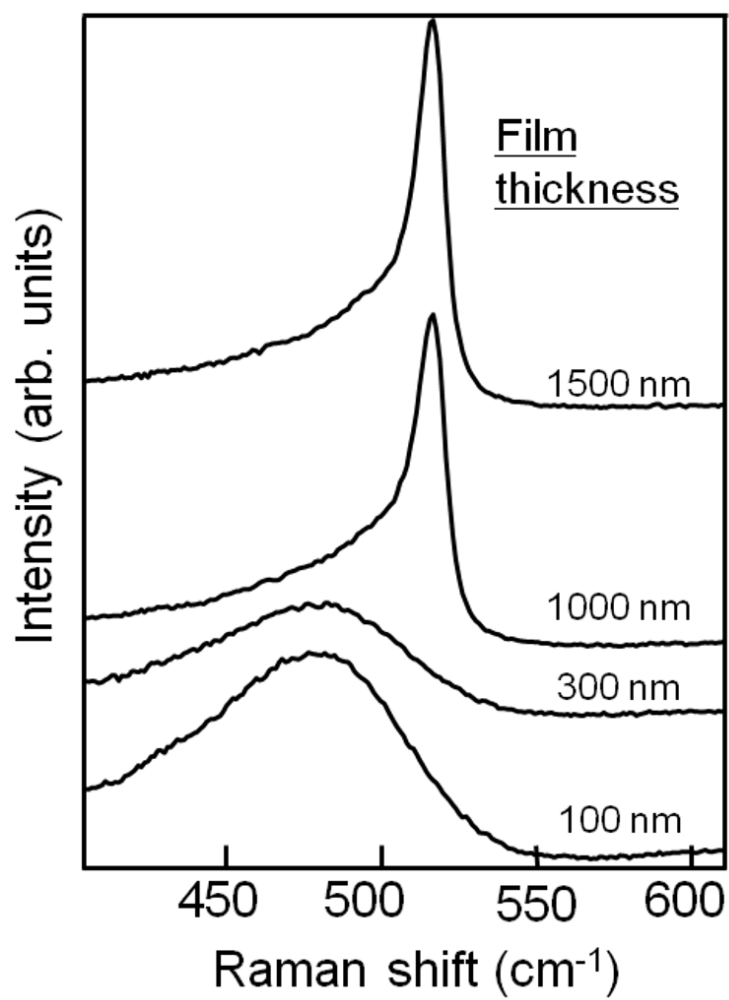


Figure 1 Ohdaira *et al.*,

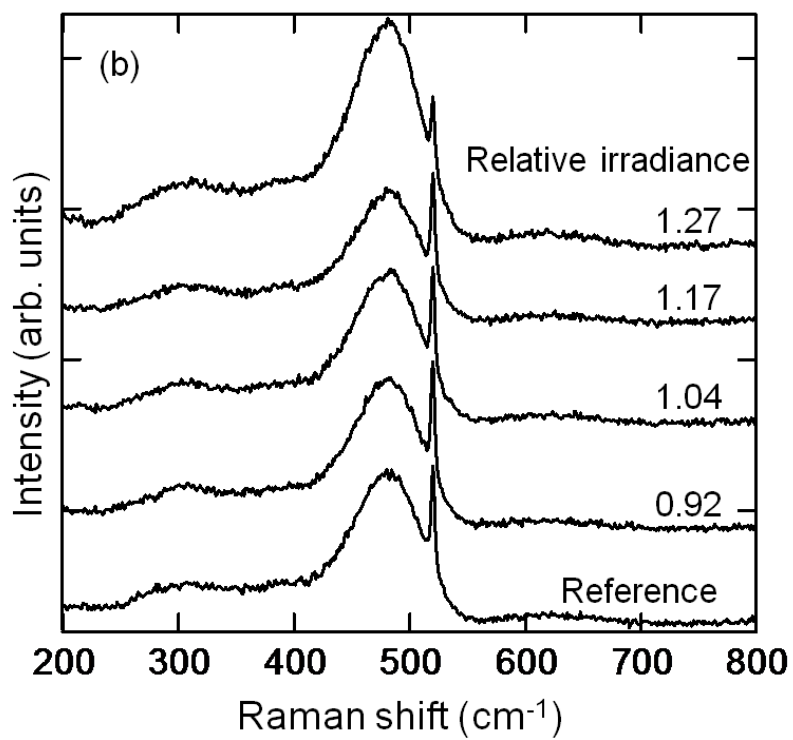
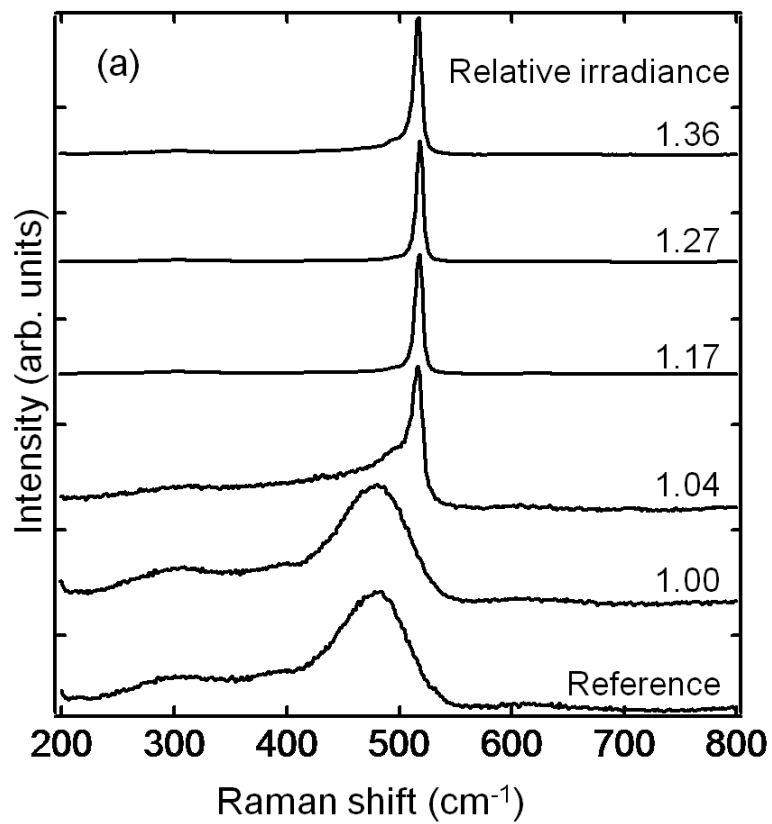


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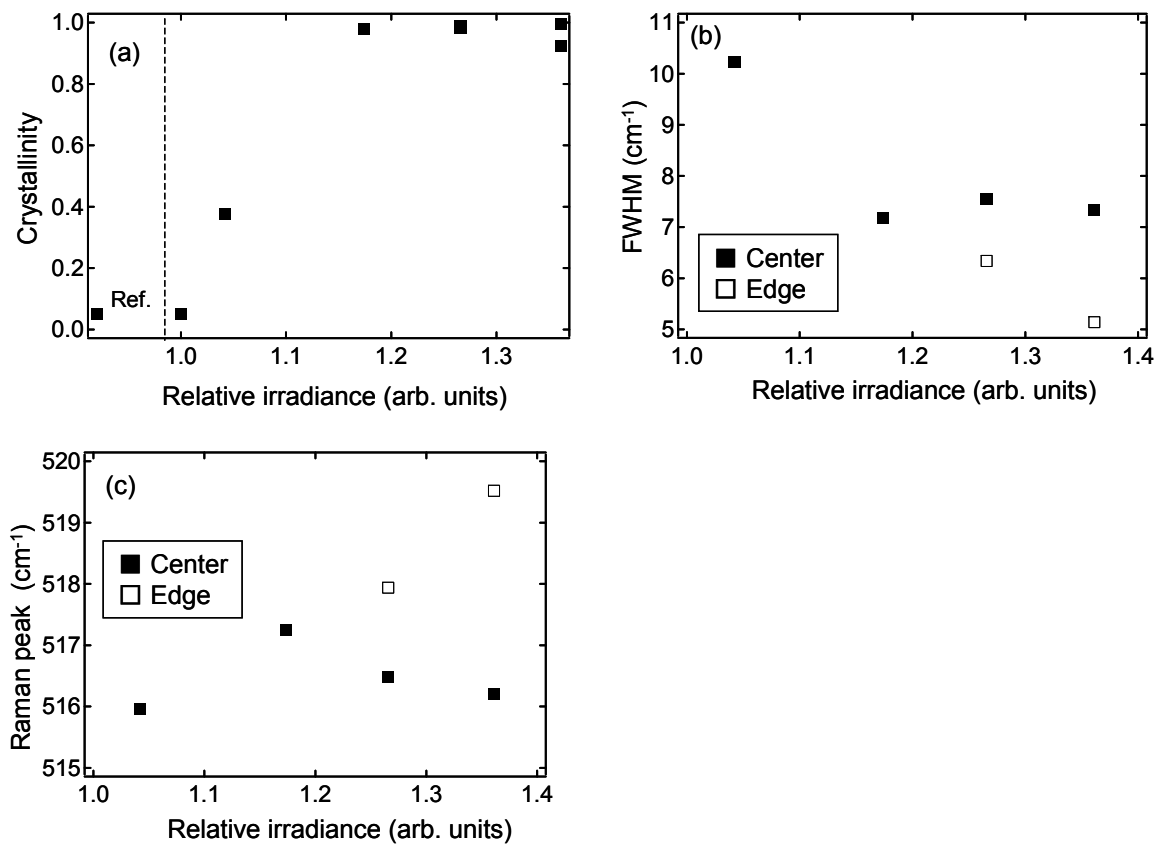


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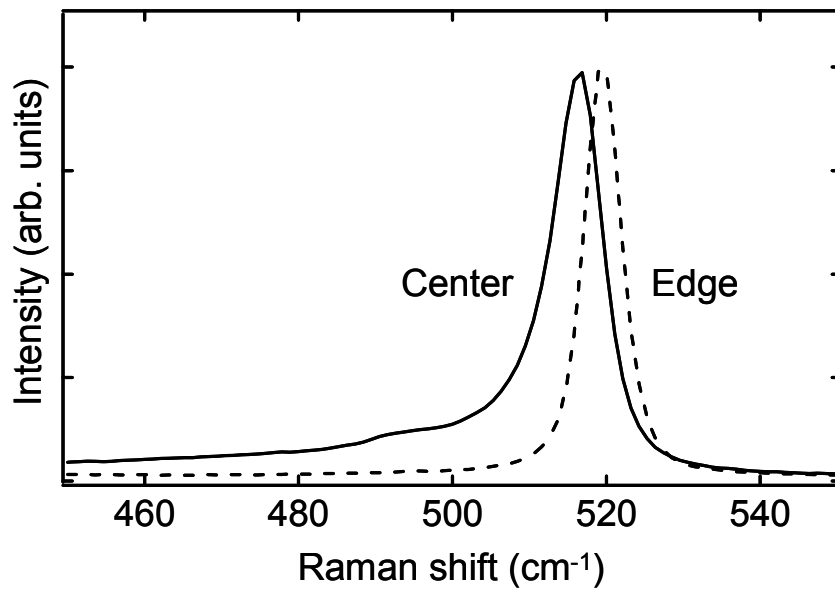


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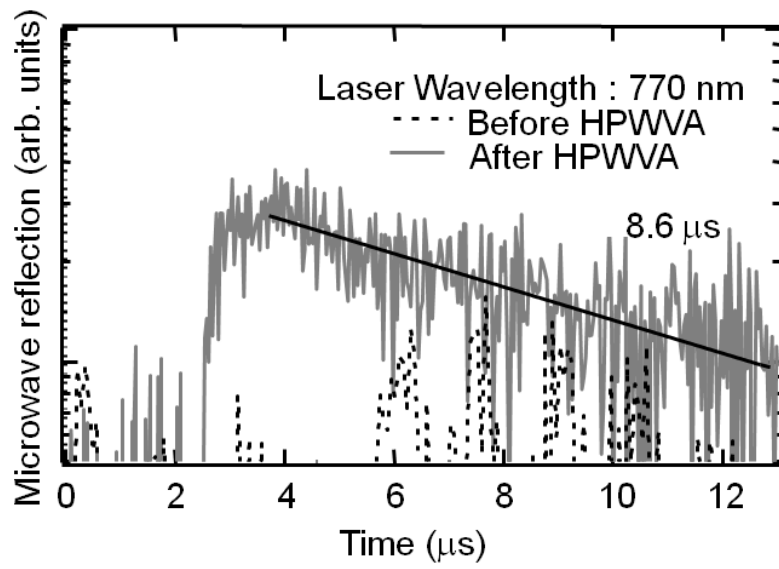


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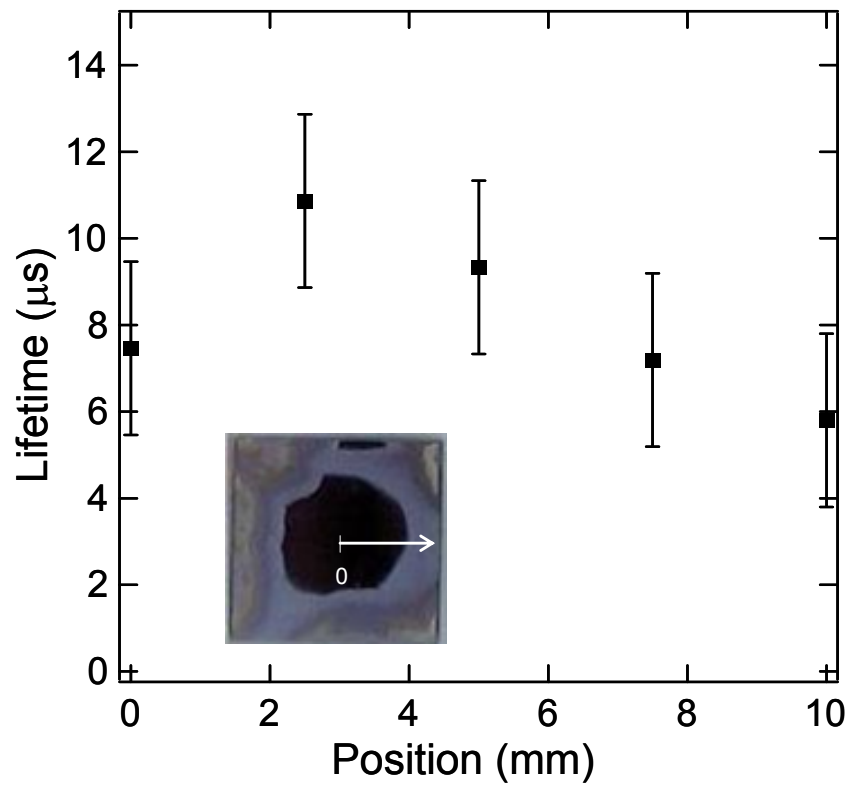


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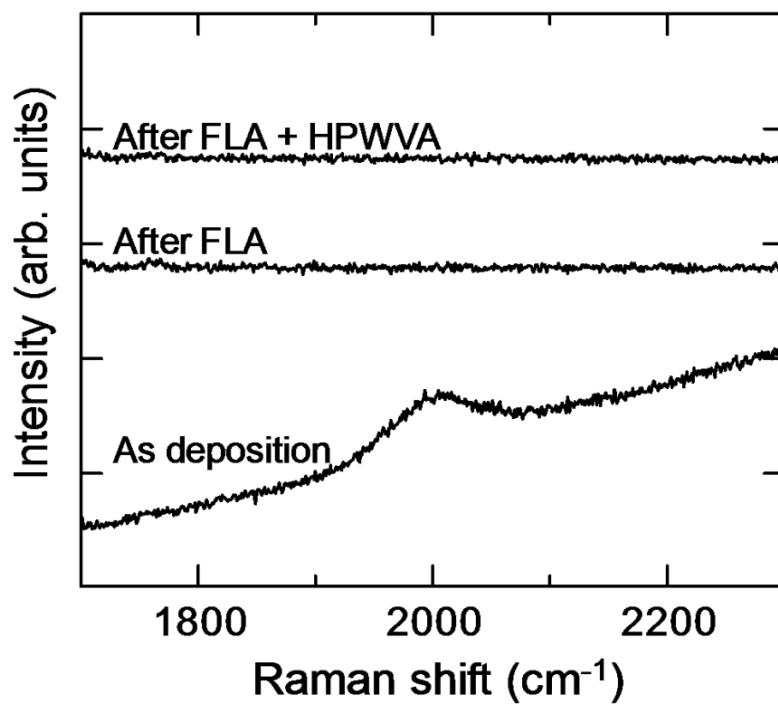


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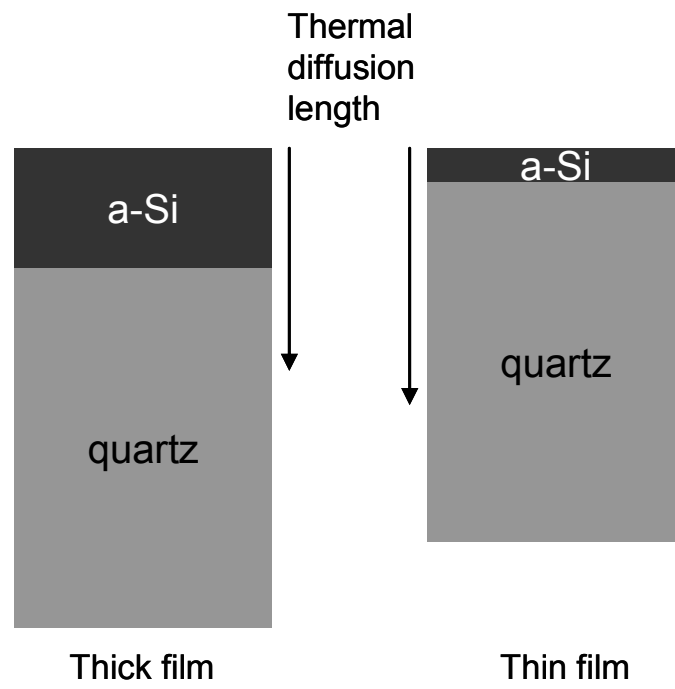


Figure 8 Ohdaira *et al.*,