

Available online at www.sciencedirect.com



SURFACE SCIENCE

Surface Science 601 (2007) 1429-1436

www.elsevier.com/locate/susc

Roles of SiH_4 and SiF_4 in growth and structural changes of poly-Si films

A. Haddad-Adel *, T. Inokuma, Y. Kurata, S. Hasegawa

Department of Electrical and Electronic Engineering, Faculty of Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

Received 5 September 2005; accepted for publication 18 April 2006 Available online 19 December 2006

Abstract

The structural properties of polycrystalline silicon films, prepared by plasma enhanced chemical vapor deposition system, with different flow rates of SiH₄/SiF₄ mixtures at 300 °C were investigated. This study indicates that the low hydrogen coverage on the growing surface, under optimum fluorine radicals, will be leaded to an improvement of crystallized area as compared with case of high hydrogen coverage surface. Moreover, the studies of the role of SiH₄ and SiF₄ radicals show that the SiH₄ radicals are important in the nucleation and growth of grains. However, SiF₄ radicals are effective in the structural change of grain boundaries regions and by this way, in the present system, establish the growth of grains under the dominant $\langle 110 \rangle$ direction. The stress investigation indicates that addition of high flow rate of SiF₄ in amorphous film, results in the nearly stress free films. Finally, we found that the changes in *g*-value reflect the changes in the intrinsic compressive and tensile stress in the both polycrystalline and amorphous silicon films. © 2006 Published by Elsevier B.V.

Keywords: Plasma-enhanced chemical vapor deposition; Polycrystalline thin films; Preferential orientation; Low-angle/high-angle grain boundary; Hydrogen coverage; Crystallization; g-Value of electron spin resonance; Stress

1. Introduction

Polycrystalline silicon films (poly-Si) have attracted intensive interest because of the potential to prepare high performance and large area semiconductor devices such as solar cells [1,2] and thin film transistor (TFT) in flat panel displays [3–5]. The direct deposition of poly-Si films at a temperature below the strain point on the glass substrates is an attractive and economical technology for producing silicon displays. For this purpose, recent main research subjects are low-temperature deposition of poly-Si films, which can be widely used in the active-matrix liquid–crystal displays that are now typically found in computer technologies and an increasing number of monitors.

In the poly-Si films, the charge carrier mobility as an important parameter in the electrical properties is mainly determined by polycrystalline structure. Polycrystalline

silicon materials are typically heterogeneous and anisotropic consisting of crystalline grains and amorphous-like silicon tissue in grain boundaries (GBs). The GBs and intregranular defects can act as electrical potential barriers and scattering sites, which decrease the carrier transport mobility and also serve as midgap states working to increase the leakage currents [6]. A reduction in the GBs effects is a key to enhance the TFTs performance. Some methods for this purpose are as follows. The low oxygen content that avoids extrinsic GB activation [7,8] and high hydrogen incorporation that results in passivation of the Si dangling bonds in the GBs, which decreases the density of GBs states in the film [9,10]. The reduction in the GBs regions by an increase in the grain size is another method to reduce the GBs effects and laser crystallization is a well-known method for this purpose [11]. However, high cost and poor film uniformity reduce some of the advantages of this technique. Beside the above-mentioned methods that cause a reduction in the effects of GBs, the formation of lowangle GBs that is responsible for a preferential oriented

Corresponding author. Tel.: +81 76 234 4882; fax: +81 76 234 4870. *E-mail address:* azadadel@yahoo.com (A. Haddad-Adel).

structure, also may enhance the transistor characteristics [12]. The low-angle GBs are those GBs that the angle between the two grains is small ($<10^\circ$). The low-angle boundaries can be represented as an array of dislocations that the regions of the two grains placing in between the dislocations are in good match with each other. In such GBs, cores of dislocation are regions of poor fit with highly distorted crystal. However, when the angle between two grains is above $10-15^\circ$, a high-angle boundary is formed and has amorphous-like structure. In high-angle boundaries, the dislocation spacing is so small that cores of individual dislocations can no longer be physically identified. The differences between low-angle and high-angle GBs can be summarized as follows:

- High-angle boundaries contain large areas of poor fit while low-angle boundaries contain large areas of good fit separated by misfit dislocations.
- High-angle boundaries have an open structure with lots of free volume while low-angle boundaries have little free volume.
- In case of high-angle boundaries, the interatomic bonds are either broken or highly distorted at the boundary while in case of low-angle boundaries the interatomic bonds are only slightly distorted.

Moreover, in the previous article [13], we reported that the high degree preferentially oriented poly-Si films, prevents the oxygen contamination owing to establishment of the low-angle GBs regions in such films. These properties for the low-angle GBs indicate that the growth of poly-Si films with a preferentially orientation seems to be a key to enhance the TFTs performance by reducing of defects and oxidation rate in the GBs regions. In that work [13], the poly-Si films with $\langle 110 \rangle$ texture were deposited by plasma enhanced chemical vapor deposition (PECVD) method using a SiH₄/SiF₄ system. In the present work, in order to enhance the degree of the $\langle 110 \rangle$ preferential orientation and to reduce the defects, such as stress in these films, we investigate mechanism of addition of SiH₄ and SiF₄ on the enhancement of crystallization and preferentially orientation of poly-Si films by using different flow rate of SiH_4 , $[SiH_4]$, and flow rate of SiF_4 , $[SiF_4]$.

2. Experimental details

Polycrystalline Si films were deposited by PECVD system at a temperature of 300 °C using SiH₄/SiF₄ mixtures in a hot wall type fused quartz reactor, employing the inductive coupling of rf power at 13.56 MHz. This deposition system has been presented elsewhere [14]. In this work, a diluted gas of SiF₄ with He gas (SiF₄: 5%, He: 95%) was used. Therefore, the net flow rate of SiF₄ was changed between 0 and 0.5 sccm under five different conditions of [SiH₄] = 0.2, 0.5, 1, 2, and 5 sccm. The film thickness was kept at 0.5–0.6 µm by varying the deposi-

tion time. The rf power and gas pressure during film deposition were maintained at 20 W and 33.3 Pa, respectively. The unique feature in the preparation process of the samples before deposition of the poly-Si films is that the substrate were sequentially exposed to the hydrogen and nitrogen plasma for 20 min to make their surface clean. The plasma exposure also causes the change in the surface roughness [15], beside the above-mentioned surface cleaning effects. In a previous paper [15], we have reported that the presence of a proper degree of the surface roughness improves the crystallinity and increases the grain size [15].

Polycrystalline Si films were deposited on glass (corning 7059) substrate for measurements of X-ray diffraction (XRD), Raman scattering and stress. The single (111)crystal Si substrate with a resistivity higher than $10^3 \Omega$ cm was used for infrared (IR) absorption measurement and electron spin resonance (ESR). For the ESR measurement the fused quartz substrate was also used to investigate effects for the use of the different substrates in addition to the above crystal Si substrates with a proper oxidized layer. As a result, we did not find significant difference between the ESR spectra for the samples on both substrates. The morphology was investigated by XRD measurement. The degree of preferential orientation in $\langle hkl \rangle$ texture was represented by X-ray relative intensity, $I_{XRD}(\langle hkl \rangle)$, for a given texture, which was normalized by the corresponding X-ray intensity for Si powder with a roughly completely random texture. The different film thickness in each sample was also corrected using the absorption coefficient of X-ray for Si. The details for the results of the I_{XRD} were presented in a previous paper [13]. The grain size, δ , in a given depth direction was estimated from the half-width value of the corresponding X-ray spectra by means of the Scherrer formula.

The crystallization ratio (volume fraction of crystalline phase), ρ , was estimated from the intensity of the Raman spectra using the procedure proposed by Tsu et al. [16]. The Raman spectra was decomposed into two components with narrow and broad line shapes corresponding to a crystalline Si phase (c-phase) at around 520 cm^{-1} and an amorphous Si phase (a-phase) at around 480 cm^{-1} . The third component between 480 and 520 cm^{-1} , due to very small crystallites, was relatively weak; therefore, we ignored the contribution of it to the values of ρ . Then the ρ values were estimated from the intensity ratio of both the a- and c-phase components [16]. Therefore, the real ρ values may be somewhat different from the values shown in the diagram. The g factor was measured using an X-band ESR spectrometer with magnetic-field modulation frequency of 100 kHz, and the measurements were carried out at room temperature. The infrared vibrational absorptions were measured using a Fourier-transform spectroscope at a normal light incidence.

The film stress was estimated from changes in the curvature of the substrate/film system with a rectangular shape (the length L being sufficiently longer than the width), using Stoney's formula [17] as:

$$\sigma = \frac{1}{3} (Y_{\rm S}/(1-v_{\rm S})) \left(\frac{b^2 \delta}{dL^2}\right)$$

here, $Y_{\rm S}$ is Young's modulus and $v_{\rm S}$ the Poisson ratio for the substrate. The parameters *b* and *d* are the thicknesses of the substrate and film, respectively. The displacement is represented by δ from before and after the film deposition of one edge of the substrate in the longitudinal direction, which respect to another edge. Values of $Y_{\rm S} =$ 7.7×10^{10} N/m² and $v_{\rm S} = 0.28$ were used for the corning glass substrate.

3. Results

Fig. 1 shows (a) deposition rate, and (b) ρ values of poly-Si films as a function of [SiF₄] for films prepared with different [SiH₄]. As seen in Fig. 1, changes in the [SiH₄] are more effective than the [SiF₄] in the changes of both deposition rate and ρ . This result means that the main precursors for film growth in this system arise from SiH₄. As shown in Fig. 1(b), a completely amorphous phase is obtained in the films having [SiH₄] = 5 sccm, while the ρ values in the samples having [SiH₄] < 5 sccm can be increased with decreasing [SiH₄] to 0.5 sccm and reaches to 90% under the high [SiF₄].

Fig. 2 shows the XRD spectra for the poly-Si films deposited at $[SiF_4] = 0.5$ sccm under different $[SiH_4]$ values as a parameter. In these diagrams an amorphous structure has been obtained for the film with $[SiH_4] = 5$ sccm, which is consistent with the Raman results seen in Fig. 1(b). A reduction in $[SiH_4]$ causes crystallized films with the random structure at $[SiH_4] = 2$ sccm and with a further decrease in $[SiH_4]$ in the range of $[SiH_4] \leq 1$ sccm, a



Fig. 1. (a) Deposition rate and (b) the crystalline volume fraction, ρ , for poly-Si films with varying [SiF₄] from 0 to 0.5 sccm with [SiH₄] = 0.2, 0.5, 1, 2, and 5 sccm at a fixed temperature of 300 °C.



Fig. 2. XRD spectra for poly-Si films with a fixed value of $[SiF_4] = 0.5$ sccm with different $[SiH_4]$ values of 0.2, 0.5, 1, 2 and 5 sccm at a fixed temperature of 300 °C.

dominant $\langle 110 \rangle$ texture can be obtained. However, all the other crystallized films with $[SiF_4] = 0$ sccm exhibit random textures. Thus, formation of a preferred oriented structure in $\langle 110 \rangle$ direction should start at $[SiH_4] = 1$ sccm in films with $[SiF_4] > 0$ sccm. These results mean that SiF_4 plays an important role in creation of dominant $\langle 110 \rangle$ texture, though the degree of these preferred textures is likely to be controlled by the ratio of SiH_4 to SiF_4 .

In Fig. 3(a) $I_{\text{XRD}}(\langle 110 \rangle)$ and (b) $\delta(\langle 110 \rangle)$ values are plotted as a function of [SiH₄] with different [SiF₄] values as a parameter. Both the $I_{XRD}(\langle 110 \rangle)$ and $\delta(\langle 110 \rangle)$ values for films with $[SiF_4] = 0$ sccm monotonically decrease with an increase in the [SiH₄], different from the behaviors of films with other [SiF₄] values. According to Fig. 3, the $I_{\rm XRD}(\langle 110 \rangle)$ values for films with $[SiF_4] \ge 0.3$ sccm have maximum at $[SiH_4] = 0.5$ sccm, while $\delta(\langle 110 \rangle)$ for these films have maximum at $[SiH_4] = 1$ sccm, which means that in the films with [SiH₄] < 1, with a reduction in the $\delta(\langle 110 \rangle)$ the $I_{\text{XRD}}(\langle 110 \rangle)$ increases. An increase in the intensity with a reduction in the grain size can take place when the number of grains increases. In other words, the $\langle 110 \rangle$ nucleation rate increases during the growth of poly-Si films with $[SiH_4] < 1$ sccm. Furthermore, Fig. 3 shows that the $I_{\rm XRD}$ and δ values for $[SiH_4] \leq 1$ sccm monotonically increase with increasing [SiF₄] that acts as etchant.



Fig. 3. (a) XRD intensity and (b) grain size, δ , of the $\langle 110 \rangle$ texture as a function of [SiH₄], with open symbols, for films with different [SiF₄] values of 0, 0.3, 0.4 and 0.5 sccm at a fixed temperature of 300 °C.



Fig. 4. Absorption intensity of Si–H₂ bonds at 2100 cm^{-1} measured by FT–IR as a function of [SiF₄], for films with different [SiH₄] values of 0.2, 0.5, 1, 2 and 5 sccm and at a fixed temperature of 300 °C.

Fig. 4 shows the absorption intensity at 2100 cm^{-1} as a function of [SiF₄] with different [SiH₄] values as a parameter. It is well known that the 2000 and 2100 cm^{-1} peaks arise from the structure involving Si-H and Si-H₂ bonds, respectively. The Si-H bonds usually exist in the amorphous region [18] and the Si-H₂ bonds depend on the structure of Si films can appear on GBs regions of poly-Si films or on internal surfaces of amorphous silicon films [19]. If the oscillator strength is fixed, the Si-H₂ absorption intensity in Fig. 4 would be proportional to the density of incorporated H-related bonds. In the present work, all films consist of Si-H₂ bonds while the Si-H bonds are observed only in the films with higher $[SiH_4]$ values of 1, 2 and 5 sccm in which more than 30% of the films area are amorphous, as shown in Fig. 1(b). The absorption intensity of Si-H bonds in those films (not presented here) increases with increasing $[SiH_4]$ values independently of the $[SiF_4]$ values.

The presented results in Fig. 4 shows that in the deposited poly-Si films, addition of SiF₄ to SiH₄ in the feed gases results in the both reduction and increase in the H density in the films with $[SiH_4] \leq 1$ sccm and $[SiH_4] = 2$ sccm, respectively. This different behavior may be interpreted by the presented results in Figs. 2 and 4, which indicate that the spectral profiles for hydrogen in the GB regions may change between the films with random structure and preferentially oriented films. As mentioned before the preferentially oriented poly-Si film has a low-angle GBs, while a high-angle GBs is formed in a randomly oriented poly-Si film. According to the changes in the absorption intensity of Si-H₂ bonds in the GBs regions, two assumptions are possible for these films; (1) interaction between silicon and hydrogen in a low-angle and high-angle GBs is different, and/or (2) extraction of hydrogen by fluorine in lowangle GBs is more practicable than in a high-angle GBs, which means that the behavior of F radicals in the high-angle GBs and low angle GBs is different.

Fig. 5(a) and (b) shows stress, respectively, as a function of $[SiF_4]$ and $[SiH_4]$ with different $[SiH_4]$ and $[SiF_4]$ values as their respective parameters. In these diagrams, the stress as a function of $[SiF_4]$ are shown by closed symbols, and as a function of $[SiH_4]$ are represented by open symbols. The



Fig. 5. Stress in the poly-Si films as a function of (a) $[SiF_4]$ (closed symbols) and (b) $[SiH_4]$ (open symbols). In these diagrams, positive and negative values of stress denote tensile and compressive stress, respectively.

tensile stress, which shows shrinkage of the film in reference to substrate, is shown by positive value. On the contrary, negative values of stress denote compressive stress, which means a stretch in film in reference to substrate. The measured stress, σ , is composed of two different types of stresses: one is the intrinsic stress, σ_i , depending on the growth process of the film, and another is due to thermal expansion mismatch between the film and the substrate, σ_t . The σ_t values can be given by

$$\sigma_t = (\alpha_{\rm F} - \alpha_{\rm S})\Delta T Y_{\rm F} / (1 - v_{\rm F})$$

where α_F and α_S are the thermal expansion coefficient for the deposited film and the substrate, respectively. We used the value of $\alpha_{\rm S} = 5 \times 10^{-6}/{\rm K}$ for the corning 7059 glass substrates, which was cited from a catalog. The thermal expansion coefficient for c-Si, $(\alpha_{\rm F})$, is 3×10^{-6} /K [20], but that for a-Si will be considerably smaller than this value. The ΔT value is assumed as the difference between the deposition temperature and room temperature at which the stress was measured. The $Y_{\rm F}$ and $v_{\rm F}$ are Young's modulus and the Poisson ratio for the deposited films, respectively. The total values of $Y_{\rm F}/(1 - v_{\rm F})$ for c-Si and a-Si films were assumed to be 1.8×10^{11} and 4.2×10^{11} N/m² [21], respectively. Using these values, we expect occurrence of a compressive stress, especially, the absolute magnitude of this value will become large in films with poor crystallization ratio. However, the presented results show an opposite behavior, which means that the observed stress was due to some intrinsic stress, different from thermal expansion mismatch.

As shown in Fig. 5(a), changes in the stress are rather complex. In films with $[SiF_4] \ge 0.3$ sccm, with an increase in $[SiH_4]$ the stress values are likely to change from compressive to tensile stress and again from tensile to compressive stress. Thus, the tensile stress is likely to take a maximal at around $[SiH_4] = 1$ sccm. In other words, the minimal compressive stress is obtained in $[SiH_4] = 1$ sccm. Changes in the stress results can be summarized as follows. For those crystallized films which exhibit compressive stress ($[SiH_4] = 0.2$ and 0.5 sccm), an increase in $[SiF_4]$ causes an increase in the absolute value of compressive stress. However, in amorphous films with $[SiH_4] = 5 \text{ sccm}$, addition of SiF₄ results in a reduction of compressive stress and finally under high $[SiF_4]$, nearly stress free amorphous film can be obtained. Also in those films that were randomly oriented at $[SiH_4] = 2 \text{ sccm}$ and exhibiting tensile stress, the film becomes a nearly stress free film under high $[SiF_4]$. In films with $[SiH_4] = 1 \text{ sccm}$, an increase in the $[SiF_4]$ from 0 to 0.3 sccm acts to convert their stress from compressive to tensile. However, for $[SiF_4]$ higher than 0.3 sccm, the tensile stress slightly decreases with an increase in $[SiF_4]$.

As shown in Fig. 5(b), for $[SiH_4] \leq 0.5$ sccm and $[SiH_4] = 5$ sccm, all films have a compressive stress, while under the intermediate values of $[SiH_4] = 1$ to 2 sccm, it changes to a tensile stress. The maximum tensile stress for films with $[SiF_4] \neq 0$ sccm occurs at around $[SiH_4] =$ 1 sccm, which is similar to the δ behavior in these films as seen in Fig. 3(b). Kitahara et al. [22] has reported that in large grains ($\delta > 500$ nm), the tensile stress is accumulated in the grains and will be relaxed at GBs. The similarity between the behavior of the stress and δ in the grains with $\delta > 50$ nm, indicates that the model proposed for the stress of poly-Si by Kitahara et al. [22] can be also applied for the poly-Si films with $\delta > 50$ nm. Furthermore, the accumulated stress in individual grains may change from a tensile stress to a compressive stress, with a reduction in δ ($\delta < 50$ nm).

The physical origins of intrinsic stress can vary with different factors such as deposition rate, amount of bonded hydrogen, and the structure of the grains and GBs regions, which cause the compressive or tensile stress and consequently the relative proportion of these two types of stress determines the total film stress. It has been reported that a reduction in bonded hydrogen content causes shrinkage in the film and consequently tensile stress develops in these films [23], which means that the compressive stress in these films reduces [23]. In amorphous films, the inherent nature of the amorphous silicon network causes a compressive stress. Moreover, Miura et al. [24] reports that in the initial stage of crystallization of an amorphous silicon film, the sign of stress changes from compressive to tensile stress as observed in films with $[SiH_4] = 2$ sccm in the presented results. Reduction in the stress of films with $[SiH_4] = 2$ and 5 sccm with increasing [SiF₄] may be explained in terms of changes in their hydrogen contents (Fig. 4) according to the above mentioned mechanism for the changes in the tensile stress. However, for films with lower [SiH₄], changes in the stress cannot be explained by this mechanism. Therefore, the changes in their stress may be caused by the changes in the grain size and structure of GBs regions in these films.

In films with $[SiH_4] = 1$ sccm, observation of a reduction in the tensile stress at $[SiF_4] \ge 3$ sccm with a reduction in the hydrogen content in these films (Fig. 4) may be explained as follow. In the poly-Si films, the $\langle 110 \rangle$ texture is associated with columnar grains [5]. According to the proposed model of $\langle 110 \rangle$ grain growth by Kamiya et al. [25], growth of large columnar grains results in a greater distribution of GBs in the lower portion of the film. As a result, with a reduction in the hydrogen content, which causes a decrease in the volume of GBs regions, the volume of the lower portions of the films decrease and finally a small compressive stress occurs in these films, which results in a reduction in the total value of their tensile stress.

More reduction in the [SiH₄] causes the development of crystallization (Fig. 1(b)) and a reduction in the grain size with an increase in the number of grains (Fig. 3). In these films, which are more than 80% crystallized, addition of SiF₄ to the feed gases causes the preferentially orientation of $\langle 110 \rangle$ grains and hence fabrication of low angle GBs. In these films may be due to low interaction of hydrogen with silicon or high etching rate of hydrogen by F radicals (as discussed under Fig. 4), the hydrogen content in the GBs regions is low. In such GBs regions that have a low angle and low hydrogen content, the Si atoms should bond to each other instead of additional hydrogen atoms that are usually available in the high-angle GBs regions. These Si-Si bonds may have longer bond length or larger bond angle in comparison with normal Si-Si bonds. Formation of such bonds in the GBs regions around the grains should cause the stretch of the crystallized Si-Si bonds inside the grains (Fig. 5(b)). Presence of such stretched Si–Si bonds in the GBs regions and grains area cause a compressive force from the substrate to relax these stretched bonds. With a reduction in the number of grains in the films with $[SiH_4] = 0.2$ sccm when compared with the films with $[SiH_4] = 0.5$ sccm (Fig. 3), we expect that the length or angle of Si-Si bonds in these GBs regions increase more and subsequently the compressive stress in these films improves.

In the poly-Si films, the ESR signal mainly arises from the Si dangling bonds within GBs and amorphous regions and the value of g reflects the local structure around the Si dangling bonds through spin-orbit interaction. In this work, the obtained ESR signal for poly-Si films has a rather symmetric shape, which indicates that the most of dangling bonds in these films will arise from GBs regions. Fig. 6 shows the changes in g values with varying [SiF₄] with different [SiH₄] as a parameter. As revealed in Figs. 5(a) and 6, in the films with $[SiH_4] = 5$ sccm, which are completely amorphous, with increasing $[SiF_4]$ both the absolute values of compressive stress and g values monotonically decrease. However, those for other films show a complex behavior. At $[SiF_4] \ge 0.3$ sccm, with an increase in [SiH₄] the g-values at first decrease and then increase again. Thus, the g-values is likely to take a minimal at around $[SiH_4] = 1$ sccm, which resembles the minimal compressive stress in these films, as shown in Fig. 5(a). Moreover, changes in the g-value as a function of [SiF₄] also show same behavior with the changes in the compressive stress in these films. This result suggests that there is a close relationship between occurrence of stress and the type of



Fig. 6. The value of g factor, obtained by ESR measurement, for films with varying [SiF₄] from 0 to 0.5 sccm with different [SiH₄] values of 0.2, 0.5, 1, 2 and 5 sccm at a fixed temperature of $300 \text{ }^{\circ}\text{C}$.

defects. Ishii et al. [26] have reported that the changes in the bond length and specially in the bond angle are effective on the changes of g-values. In that paper [26], through a calculation using an extended Hückel theory, they found that when a trivalent Si atom bearing the dangling bond moves vertically toward the plane formed by three backbonded Si atoms, the g-value decreases. This result states a reduction in the g-value with an increase in the intrinsic tensile stress or the same behavior between the changes in the g-value and compressive stress. As shown in the poly-Si and amorphous Si films in Figs. 5(a) and 6, the resultant stress and the g-values show same behavior with that reported by Ishii et al. [26] with an increase in $[SiF_4]$. The obtained results in stress and ESR measurements demonstrate that the resultant stresses should be due to the changes in the local structure within the GBs regions. These results also indicate that the investigation of the changes in g is a suitable substitute for studying the changes in the intrinsic compressive and tensile stress in the both poly-Si and amorphous films. In these films, independent on the dominant stress, the changes in the g-values reflect, respectively, same behavior and inverse behavior with changes of intrinsic compressive stress and tensile stress. According to these results in amorphous films, with a reduction in the compressive stress, the g-value also decreases from 2.0055 to 2.0047 in the nearly stress free films.

4. Discussion

In the presented work, the physics of PECVD poly-Si films using the SiH₄/SiF₄ system was investigated. With a decrease in [SiH₄], the deposition rate reduces, while the ρ values, which were obtained from a change in the Raman spectral intensity, increase. A reduction in [SiH₄] from 5 sccm to 1 sccm, causes an increase in both the δ and XRD intensity in $\langle 110 \rangle$ direction. A further decrease in [SiH₄] below 1 sccm leads to a reduction in δ , however the decrease in the XRD intensity starts at [SiH₄] = 0.5 sccm (Fig. 3).

To explain the above-mentioned discrepancy in the peak position of the XRD intensity and δ in the $\langle 110 \rangle$ direction,

we should at first have a short over view on the growth mechanism of poly-Si films. The plasma diagnosis investigations show that the major growth precursors in a $SiH_4/$ SiF₄ system are SiH_nF_m $(n + m \leq 3)$ [27,28]. The precursor formation may be enhanced as the deposition rate increases with increasing [SiH₄] values, (Fig. 1(a)). After arrival of the precursors on to the growth surface, they must diffuse on the surface (surface migration). Since the adsorbed atoms diffuse, they can desorb or re-evaporate, as they are only weakly bonded to the surface, or they can encounter another diffused atom to form an adsorbed atom pair. This atom pair because of its larger mass, is less likely to desorb than an individual adsorbed atom. Due to the diffusion on surface and consequently encountering with other atoms, a larger and more stable cluster can be formed. The cluster may finally reach a final critical size, beyond the condition that it is unlikely to desorb, forming a stable nucleus and further creating a stable Si-Si network. During these processes, the effective etching of weakly adsorbed bonds by hydrogen and fluorine atoms can establish the crystalline structure. In other words, the crystalline silicon network can be constructed by the processes of adsorption, surface diffusion and desorption of volatile products. Under such an assumption for growth of crystallized Si, an amorphous structure will result when the reaction time for producing volatile products by etchants is longer than the effective adsorption time of precursors; i.e., by increasing the arrival rate of silicon atoms under an excess $[SiH_4]$ flux, the structure will tend to be amorphous structure (Fig. 1). Furthermore, Nakahata et al. [27] shows that under excess [SiH₄], the proportion of fluorine-related deposition precursors are reduced and the major deposition precursors change from SiH_nF_m to SiH_n , which indicates that the fluorine-related species are effective for growing crystalline silicon.

Those deposition conditions, such as low deposition rate, which allow adsorbed silicon atoms to diffuse farther on the surface before being immobilized by subsequently arriving silicon atoms, would lead to larger grains. Therefore, an increase in δ values due to a reduction in [SiH₄] from 5 sccm to 1 sccm (Fig. 3(b)) should be caused by a decrease in the deposition rates with a decrease in the $[SiH_4]$ in these films (Fig. 1(a)). In the SiH_4/SiF_4 system, in which hydrogen atoms are obtained from the decomposition of SiH₄ radicals, a further decrease in [SiH₄] may result in lower hydrogen content in the plasma region. Consequently, we expect this phenomenon to lead a reduction in the H coverage over the growing surface. Thus, the diffusion length reduces and adsorbed silicon will easily find a suitable position to form atomic layers, leading to an increase in the nucleation rate in these films [29]. According to the following equation

$$\delta \approx \frac{1}{\sqrt{N_n}}$$

the grain size, δ , is related to the initial density of nuclei, N_n [5]. This equation shows that with an increase in the nucle-

ation rate, δ decreases [30], as was observed in films with [SiH₄] < 1 sccm.

These findings indicate that in poly-Si films, high H coverage over the growing surface would enhance the surface migration of adsorbates and leads to an increase in δ , while low H coverage cause an increase in nucleation rate and a decrease in δ . However, the Raman results demonstrate that in as deposited poly-Si films prepared with the PECVD system which have a limitation in the magnitude of grains, films consist of higher number of small grains are more crystallized than films with low number of large grains. In other words, an increase in the nucleation rate under optimum condition should be more important than an increase in the grain size in the enhancement of the crystallization ratio of the deposited poly-Si films in PECVD system, as shown in Figs. 1(b) and 3 [31].

As discussed before, it is well known that in a such system the concentration of F radicals that reach the growing surface of the film and etch the undesirable atoms and weak Si-Si bonds is an important factor in the crystal growth. The binding energies related to film growth with A-B bonds can be obtained as E(A-B) as follows: E(H-F) = 5.8 eV, E(Si-F) = 5.6 eV, E(Si-H) = 3.1 eV and E(Si-Si) = 1.8 eV [32]. Formation of H–F bonds as the more favorable bond in the plasma regions is an effective parameter for the control of the density of F atoms arriving on the growing surface. Therefore, in the films with the same $[SiH_4]$, an increase in the $[SiF_4]$ should cause an enhancement in the etching effect by F and consequently both the $I_{\text{XRD}}(\langle 110 \rangle)$ and $\delta(\langle 110 \rangle)$ values can be increased as seen in Fig. 3. According to the presented binding energies, after the H–F bond, formation of Si–F bond has the highest possibility. In some conditions such as very low density of H radicals, formation of H-F bonds as a volatile product decreases and consequently in the absence of H-F bonds, formation of Si-F bonds increases. Thus, in films with $[SiH_4] = 0.2$ sccm with the high probability of Si-F bond formation, desorption of Si-F bonds as a volatile gas results in a reduction in the desirable Si atoms for the nucleation. In turn, in these films with a small δ and lower number of grains, the XRD intensities will also decrease. Our unsuccessful experience in the achievement of poly-Si film with our desired thickness under the condition of low $[SiH_4] = 0.1$ sccm and high $[SiF_4] = 0.5$ sccm, may confirm this assumption.

The above-mentioned results indicate that although the F radicals are an etchant with higher ability when compared with the H etchant, the amount of H in the plasma region and its reaction on the growing surface is much more important factor in the crystallization processes in the SiH₄/SiF₄ system. This investigation show that the amount of [SiH₄], which determine the arrival rate of main precursors on the growing surface, can be considered as a main factor in the change of structure from amorphous to highly crystallized film. However, addition of SiF₄ is also necessary for changing structure from random to preferentially growth of grains in the $\langle 110 \rangle$ direction, which results

in the low GBs regions with low H content. According to the presented results by Raman, XRD, FT–IR, stress and ESR measurements, in the poly-Si films addition of SiH₄ is more effective in the growth and crystallization of Si films, while addition of SiF₄ may cause changes in the GBs regions. Enhancement in the preferentially orientation of grains by increasing in [SiF₄], which changes GBs regions, demonstrates that the structure of GBs regions should be effective in the growth direction of grains.

5. Conclusion

The structural properties of the PECVD poly-Si films deposited with different [SiH₄] and [SiF₄] were investigated. The high degree orientation of the grains in the $\langle 110 \rangle$ direction were observed in film with [SiH₄]/[SiF₄] = 0.5 sccm/0.5 sccm, while the largest grain size (120 nm) was obtained for film under [SiH₄]/[SiF₄] = 1 sccm/0.5 sccm. The high flow rate of [SiH₄] = 5 sccm, resulted in an amorphous Si film and no film with the desired thickness was obtained at [SiH₄]/[SiF₄] = 0.1 sccm/0.5 sccm. According to these structural changes in the deposited poly-Si films using a SiH₄/SiF₄ mixture, the following results were obtained.

The H coverage, which depends on the flux of both H and F radicals in the plasma region, can affect the grain size and number of grains. This study demonstrates that although a high hydrogen coverage over the growing surface is necessary to obtain a large grain, but a low H coverage on the growing surface and under optimum condition could be more effective in increasing the crystallized region and the degree of preferential orientation of poly-Si films. Moreover, further investigation shows that the change in $[SiH_4]$ is effective in the nucleation, crystallization and size of grains, while $[SiF_4]$ is effective in the changes of GBs regions. The studies on the intrinsic stress indicate that in amorphous and high-angle grain boundary regions, addition of high $[SiF_4]$ results in the nearly stress free films.

Acknowledgements

The authors wish to thank Professors M. Kumeda and A. Morimoto for use of the X-ray diffractometer and Raman spectrometer. This work was partially supported by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Sports, Culture, Science and Technology in the Japanese Government.

References

- J. Meier, S. Dubail, J. Cuperus, U. Kroll, R. Platz, P. Torres, J.A. Anna Selvan, P. Pernet, N. Beck, N.P. Vaucher, Ch. Hof, D. Fischer, H. Keppner, A. Shah, J. Non-Cryst. Solids 227–230 (1998) 1250.
- [2] K. Yamamoto, T. Suzuki, M. Yoshimi, A. Nakajima, Jpn. J. Appl. Phys. 36 (1997) L569.
- [3] P. Migliorato, D.B. Meakin, Appl. Surf. Sci. 30 (1987) 353.
- [4] D. Pribat, Mat. Sci. Forum 455-456 (2004) 56.

- [5] T. Kamins, Polycrystalline Silicon for Integrated Circuits and Displays, second ed., Kluwer, Boston, 1998.
- [6] Y. Morimoto, Y. Jinno, K. Hirai, H. Ogata, T. Yamada, K. Yoneda, J. Electrochem. Soc. 144 (1997) 2495.
- [7] J.-L. Maurice, in: Polycrystalline Semiconductors II, in: J.H. Werner, H.P. Strunk (Eds.), Springer Proceedings in Physics, Vol. 54, Springer, Berlin, 1992, p. 166.
- [8] T. Kamiya, Z.A.K. Durrani, H. Ahmed, Appl. Phys. Lett. 81 (2002) 2388.
- [9] T.I. Kamins, P.J. Marcoux, IEEE Electron Device Lett. 1 (1980) 159.
- [10] I.-W. Wu, T.-Y. Huang, W.B. Jackson, A.G. Lewis, A. Chiang, IEEE Electron Device Lett. 12 (1991) 181.
- [11] F. Petinot, F. Plais, D. Mencaraglia, P. Legagneux, C. Reita, O. Huet, D. Pribat, J. Non-Cryst. Solids 227–230 (1998) 1207.
- [12] E.W. Maby, M.W. Geis, Y.L. LeCoz, D.J. Silversmith, R.W. Mountain, D.A. Antoniadis, IEEE Electron Device Lett. EDL-2 (1981) 241.
- [13] A. Haddad-Adel, K. Kurata, T. Inokuma, S. Hasegawa, J. Non-Cryst. Solids 351 (2005) 2107.
- [14] S. Hasegawa, S. Narikawa, Y. Kurata, Philos. Mag. B 48 (1983) 431.
- [15] S. Hasegawa, N. Uchida, S. Takenaka, T. Inokuma, Y. Kurata, Jpn. J. Appl. Phys. 37 (1998) 4711.
- [16] T. Tsu, G. Gonzales-Hernandez, S.S. Chao, S.C. Lee, K. Tanaka, Appl. Phys. Lett. 40 (1982) 534.
- [17] G.G. Stoney, Proc. R. Soc. London 82 (Ser. A) (1909) 172.

- [18] E. Garcia-Caurel, C. Niikura, S.Y. Kim, B. Drévillon, J.E. Bourée, J. Non-Cryst. Solids 299–302 (2002) 215.
- [19] A.A. Langford, A.H. Mahan, M.L. Fleet, J. Bende, Phys. Rev. B 41 (1990) 8359.
- [20] P.J. Burkhardt, R.F. Marvel, J. Electrochem. Soc. 116 (1969) 864.
- [21] S. Hasegawa, Y. Amano, T. Inokuma, Y. Kurata, J. Appl. Phys. 72 (1992) 5676.
- [22] K. Kitahara, A. Moritani, A. Hara, M. Okabe, Jpn. J. Appl. Phys. 38 (1999) L1312.
- [23] M.P. Hughey, R.F. Cook, Appl. Phys. Lett. 85 (2004) 404.
- [24] H. Miura, H. Ohta, N. Okamoto, T. Kaga, Appl. Phys. Lett. 60 (1992) 2746.
- [25] T. Kamiya, K. Nakahata, A. Miida, C.M. Fortmann, I. Shimizu, Thin Solid Films 337 (1999) 18.
- [26] N. Ishii, M. Kumeda, T. Shimizu, Jpn. J. appl. Phys. 20 (1981) L673.
- [27] K. Nakahata, K. Ro, A. Suemasu, T. Kamiya, C.M. Fortmann, I. Shimizu, Jpn. J. Appl. Phys. 39 (2000) 3294.
- [28] B. Lee, L.J. Quinn, P.T. Baine, S.J.N. Mitchell, B.M. Armstrong, H.S. Gamble, Thin Solid Films 337 (1999) 55.
- [29] M. Jana, D. Das, A.K. Barua, J. Appl. Phys. 91 (2002) 5442.
- [30] H.J. Lim, B.Y. Ryu, J.I. Ryu, J. Jang, Thin Solid Films 289 (1996) 227.
- [31] S.K. Kim, K.C. Park, J. Jang, J. Appl. Phys. 77 (1995) 5115.
- [32] L. Pauling, The Nature of the Chemical Bonds, Cornell University Press, New York, 1960.