

ROLES OF H RADICALS IN THE LOW TEMPERATURE GROWTH OF POLY-SI FILMS BY PLASMA CVD USING $\text{SiF}_4/\text{SiH}_4/\text{H}_2$

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Abstract

Effects of H radical treatment were investigated on the films deposited with SiH_4/H_2 and $\text{SiF}_4/\text{SiH}_4/\text{H}_2$ plasmas. For both cases, almost pure etching occurred on the thin films less than 60\AA . In the case of thick films more than 600\AA , crystallized layer remained beneath the roughened layer. This results indicates that H radicals have roles of both etching and crystallization, and that the crystallization effect reaches more deep layer in comparison to the etching effect.

1. Introduction

In the low temperature growth of poly-Si growth on glass substrates, the volumetric fraction of c-Si, a-Si and voids in the films has been known to change with thickness [1]. The layer deposited just on a glass substrate is mostly a-Si, and c-Si fraction gradually increases with thickness. In our previous work, we have studied the effects of SiF_4 addition, and shown that F radicals mostly worked in preferential etching of a-Si tissue [2]. In this work, we have aimed at H radicals which are known to have the roles of surface passivation [3], crystallization [4] and etching [5]. As the structure of deposited layer just on glass substrate is different from that formed on the pre-deposited film, it is suggested that the effects of H radicals change with film thickness. Therefore, we have investigated the thickness dependence using *in situ* ellipsometric monitoring of the film surface during H radical treatment.

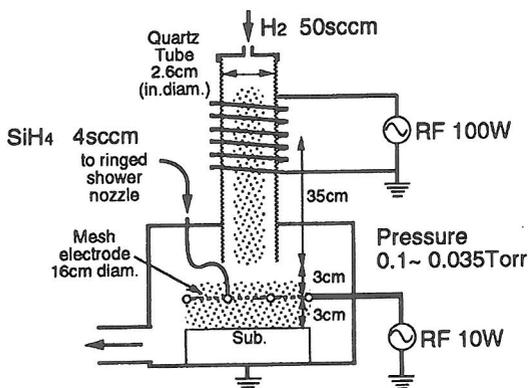


Fig.1 Experimental setup for film deposition and H radical treatment

2. Experimental

Figure 1 shows the experimental setup for film deposition and H radical treatment. The film deposition was carried out on Corning 7059 glass substrate by using a capacitively coupled RF plasma CVD method with SiH_4/H_2 gas mixtures. The H radical treatment was done by an inductively coupled RF plasma generator, namely, an H radical source. Details of the H radical source were reported elsewhere [6]. In order to lead H radicals on to the substrate through the powered electrode, a mesh was used as in the figure.

Surface monitoring was carried out with monochromatic ellipsometry (ME) at a wavelength of 380nm during film deposition and H radical treatment, and with spectroscopic ellipsometry (SE) in the range of 350-380nm for the film before and after the deposition without discharge. Angle of incidence was set at 73.8° .

Trajectory of $\tan\Psi$ and $\cos\Delta$ obtained by ME during the deposition and H radical treatment sequences was analyzed through comparison to theoretically calculated trajectory using a three layer model [1]. As the components of deposited films, we considered a-Si, c-Si and void fractions. Dielectric functions for these components at 300°C were determined as described previously[1]. We assumed that parameters of thickness and volumetric fractions of the components for each layer changed linearly from initial state to final one during the deposition and H radical treatment. We deduced the parameters for initial and final states on the basis of following SE measurement results. Spectra of ellipsometric parameters of $\tan\Psi$ and $\cos\Delta$ obtained by SE measurement after the deposition and H radical treatment were translated into the film composition using the static three layer model.

3. Results and Discussions

3.1 Effect of H_2 dilution to SiH_4 and $\text{SiF}_4/\text{SiH}_4$ plasmas

Figure 2(a), 2(b) and 2(c) show thickness dependence of the volumetric fraction of c-Si in the films deposited with and without SiF_4 for the H_2 dilution rate of 80, 96 and 99%. RF power, pressure, total flow rate and substrate temperature was 100W, 0.1Torr, 100sccm and 300°C , respectively. Flow ratio of $\text{SiF}_4/\text{SiH}_4$ was 1/1. As can be seen in the

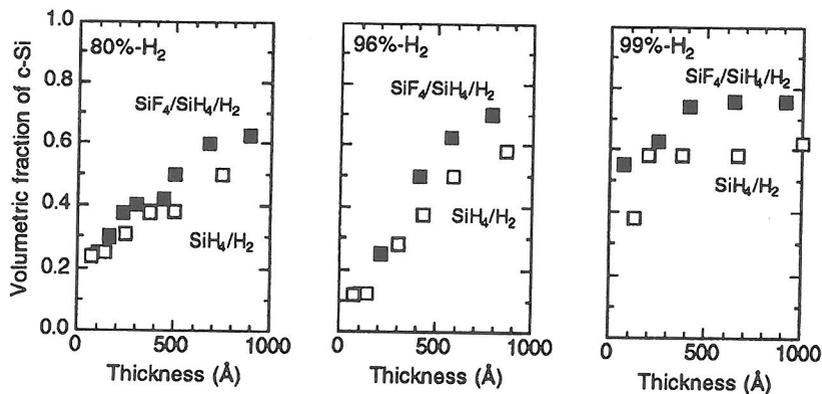


Fig.2 Volumetric fraction of c-Si in deposited films as a function of film thickness

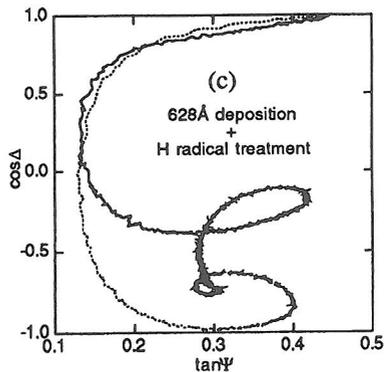
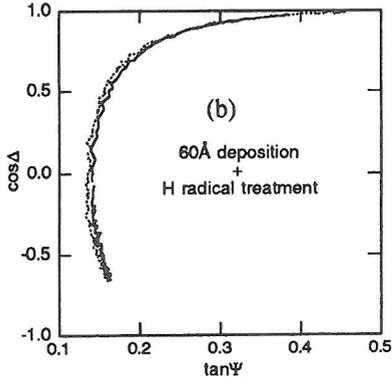
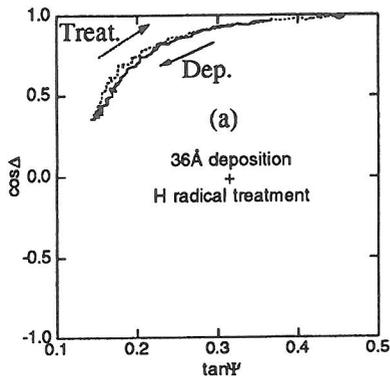


Fig.3 Trajectories during film deposition and H radical treatment for different film thickness of (a) 36Å, (b) 60Å and (c) 628Å.

figure, the initial increasing rate of the volumetric fraction of c-Si is improved by SiF_4 addition, and especially with increasing H_2 dilution rate. These results indicate that H_2 molecules and/or H radicals should affect on growing film surface to promote increase of crystalline phase. H_2 molecules are regarded to work mainly as a terminator of reactive species, such as Si, SiH, SiH_2 in gas phase, and not to work on growing film surface directly. Therefore, we have aimed at the H radicals impinging onto the growing film surface. As the film structure deposited with and without SiF_4 must be different, we examined H radical treatment on the films deposited with SiH_4/H_2 and $\text{SiF}_4/\text{SiH}_4/\text{H}_2$ plasmas. In order to investigate the film-thickness dependence of the H radical treatment, we examined the treatment for three kinds of the thickness of approximately 40, 60 and over 600Å.

3.2 Effect of H radical treatment on the films deposited with SiH_4/H_2 plasma

Figures 3(a), 3(b) and 3(c) show the trajectories during film deposition and H radical treatment for the film thickness of 36, 60 and 628Å, respectively. Solid and dotted lines correspond to the trajectories for the film deposition and H radical treatment. As can be seen in Figs.3(a) and 3(b), the trajectory during the H radical treatment retracts almost the same one obtained during the deposition sequence. This means that the effect of the H radical treatment is mostly etching of the films for the thickness less than 60Å.

On the contrary, the trajectory during the H radical treatment on the more thick film of 628Å is fairly different from that during the deposition. Difference appears especially at initial stage of the H radical treatment. Therefore, another model is required for describing the initial stage. After passing through the region of $\cos\Delta=0$, tendency of

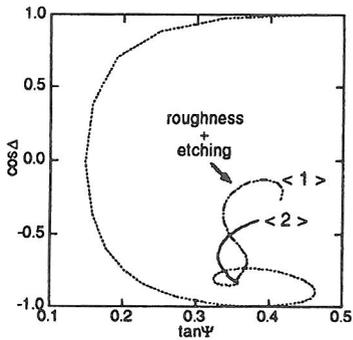


Fig.4 Calculated trajectories according to the model s in Fig.5.

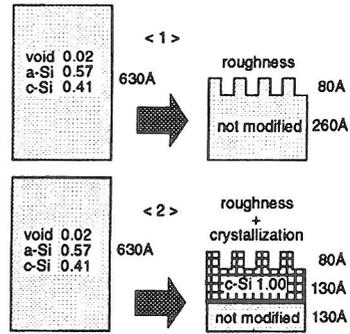


Fig. 5 Surface modification models corresponding to Fig.4.

trajectory becomes almost the same to the results on thin films, because thickness of the film becomes similar level for Figs.3(a) and 3(b).

As the value of $\cos\Delta$ at the converged point in the trajectory increases with surface roughness, we have calculated trajectories according to the model including surface roughness formation. Figure 4 shows trajectories for two models of <1> pure etching and roughness formation and <2> pure etching, roughness formation and surface crystallization. Schematics for these models are shown in Fig.5. As can be seen in the figure, the model <1> does not match to the experimental result. On the other hand, the model <2> successfully explains tendency of the experimental result.

Summarizing above results, we can conclude that the H radicals work in both etching and crystallization. As the crystallized layer remains on the surface after etching, the crystallization effect reaches more deep layer in comparison to the etching effect. Almost pure etching effect for the case of the thin films is considered to be due to lack of thickness margin to remain crystallized layer, and due to that films are formed with weak Si-Si bonds easy to be removed. Roughness formation for the thick film is considered to be due to increase of Si-Si bond strength, and due to partial removal of Si atoms by destructing relatively weaker bonding.

3.3 Effect of H radical treatment on the films deposited with $\text{SiF}_4/\text{SiH}_4/\text{H}_2$ plasma

The films deposited with F-containing source gases contain Si-F bonds in the films, although concentration of Si-F bonds is lower than that of Si-H by approximately one order of magnitude. Shimizu et al. suggested surface crystallization though the chemical annealing by H radicals, and its effects on F containing surface is stronger than only H containing one, because reactivity of H and F is higher than that of H and H. Therefore, effects of H radical treatment are expected to be different. As the decomposition degree of SiF_4 was approximately 1/6 of SiH_4 at RF power of 10W [2], deposition of the films was carried out at 100W where the decomposition degree was 1/2 of SiH_4 . The condition for the H radical treatment was kept at the same one as in above section.

Figures 6(a) and 6(b) show the trajectories for deposition and H radical treatment on the films of 38 and 62Å. Comparing these figures to Figs.3(a) and 4(b), we can see

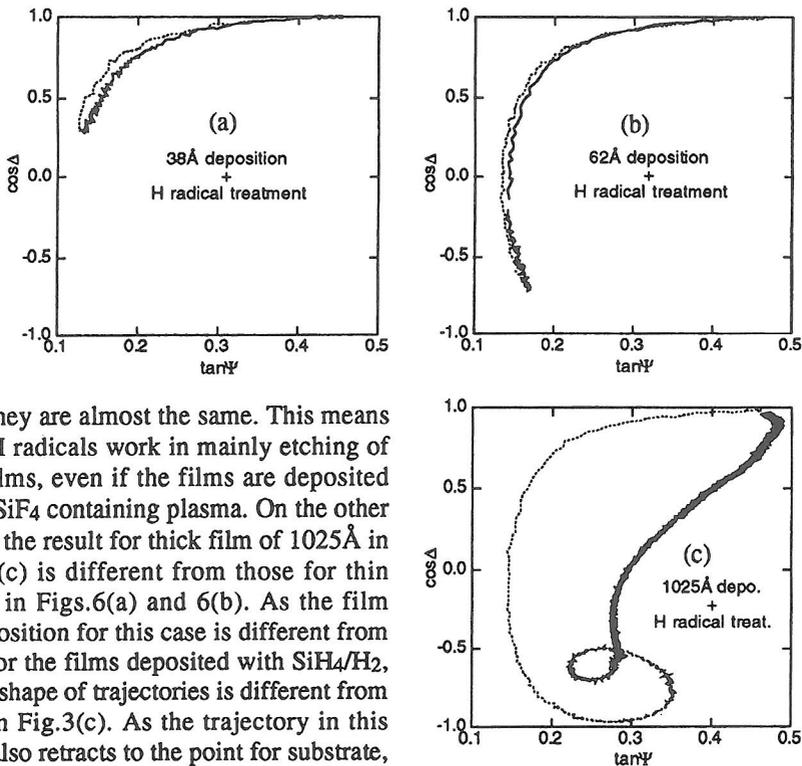


Fig. 6 Trajectories during film deposition with $\text{SiF}_4/\text{SiH}_4/\text{H}_2$ plasma and H radical treatment for different film thickness of (a) 40Å, (b) 62Å and (c) 1025Å.

that they are almost the same. This means that H radicals work in mainly etching of the films, even if the films are deposited with SiF_4 containing plasma. On the other hand, the result for thick film of 1025Å in Fig.6(c) is different from those for thin films in Figs.6(a) and 6(b). As the film composition for this case is different from that for the films deposited with SiH_4/H_2 , basic shape of trajectories is different from that in Fig.3(c). As the trajectory in this case also retracts to the point for substrate, etching surely progress. In order to explain this behavior, we have compared the experimental result to calculated one. As the value of $\cos\Delta$ increases around the starting point of the H radical treatment, we have applied similar model used for explaining the H radical effects on the film deposited with SiH_4/H_2 . Figures 7(a) and 7(b) show the trajectories calculated with the models (a) and (b), respectively. Schematics for these models are shown in Figs.8(a) and 8(b), which are corresponding to with and without crystallization, respectively. Regarding the Fig.7(a), only $\cos\Delta$ increases and $\tan\Psi$ keeps almost the same value. On the other hand, $\tan\Psi$ in the Fig.7(b) moves toward lower value once, which shows better agreement with the experimental results. These results means that there are no qualitative differences in the roles of H radicals on the film deposited with and without SiF_4 .

In order to compare qualitatively, we have investigated the ratio between the thickness of etched-out layer d_e and remaining crystallized layer d_c . We obtained $d_e=335\text{Å}$ and $d_c=132\text{Å}$ ($d_e/d_c=0.4$) for the case without SiF_4 , and $d_e=150\text{Å}$ and $d_c=50\text{Å}$ ($d_e/d_c=0.33$) for the case with SiF_4 . Although we have expected the difference in the chemical-annealing effect on the film deposited with and without SiF_4 , we cannot find out explicit difference from the results obtained in this work.

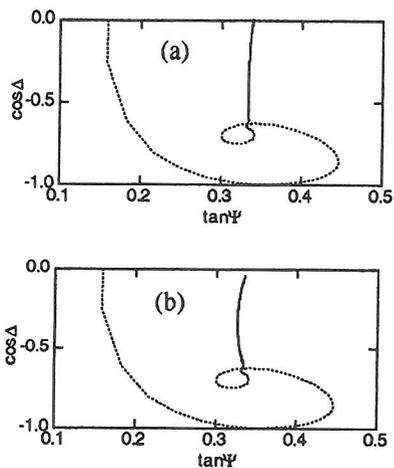


Fig. 7 Calculated trajectories under surface modification for two models shown in Fig.8.

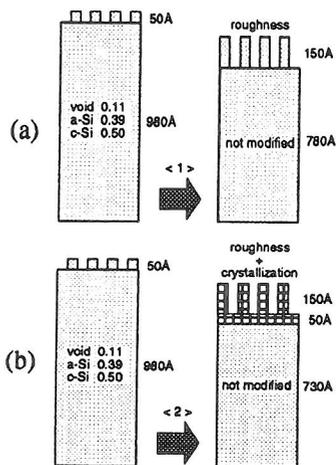


Fig. 8 Two models for surface modification.

4. Conclusion

In conclusion, we investigated thickness dependence of H radical treatment on the films deposited with SiH_4/H_2 and $\text{SiF}_4/\text{SiH}_4/\text{H}_2$ plasmas. In both cases, H radicals worked in both etching and crystallization, and qualitative differences were not found in the present experimental conditions. In the case of thin films less than 60\AA , almost pure etching occurred. In the case of thick films more than 600\AA , crystallized layer under roughened one remained after the etching. This results indicates that the crystallization effect reaches more deep layer in comparison to the etching effect.

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