Enhanced Crystallization of Si at Low Temperature by O_2 Flow during Deposition

Hyoung Gin Nam† and Kyung Hwan Koo

†Electronic Engineering Division, Sun Moon University

ABSTRACT

Effects of O_2 flow during deposition on Si crystallization at low substrate temperature were studied. Silicon thin films were prepared on SiO_2 substrates in a low-pressure chemical vapor deposition chamber using a mixture of SiH_4 and H_2. In some cases O_2 was intentionally introduced during deposition. Growth of polysilicon was observed at the substrate temperature as low as 480°C when O_2 was flowed during deposition implying that crystallization of Si was enhanced by O_2 flow. On the other hand, O_2 flow did not show any significant effects at higher substrate temperature, where deposition rate is relatively fast. Enhancement mechanism of Si crystallization by O_2 flow was suggested from these results.

Key Words : Enhanced crystallization, polysilicon thin film, O_2 flow

1. INTRODUCTION

Growth of polysilicon at low temperature has attracted much attention in areas such as flat panel display (FPD) as well as solar cell, where wide-area wafers are essential. Since glass is widely used for these applications, there has been a number of studies[1-2] to grow poly Si at temperatures lower than the glass deformation temperature. However, the technology and/or the mixture of gases used in these studies are not quite compatible with Si-based electronics industry. More recently, attempts have been made to lower the Si crystallization temperature by lateral growth adding a small amount of transition metals such as Ni[3-5]. However, these results are not practical in that various amount of metals are left within the film, indicating that carrier life time killer will be present in the active region of electronic devices such as thin film transistor (TFT). In addition, lithography steps are increased in some cases.

We made an attempt to grow polysilicon film by a simpler, more Si technology compatible method. We deposited Si thin film on SiO_2 in a low-pressure chemical vapor deposition (LPCVD) chamber with various deposition parameters. In some cases, O_2 was intentionally introduced during deposition. In this paper, we report the observation of enhanced Si crystallization by O_2 flow during deposition. We also discuss the possible mechanism responsible for the enhancement.

2. EXPERIMENT

Si thin films were prepared by LPCVD using H_2 and SiH_4. H_2 flow rate was adjusted at 75sccm, and SiH_4 flow rate was set at 25sccm. In some cases O_2 was intentionally introduced to the chamber during deposition at the flow rate of 5sccm. That is, O_2 was flowed for first 10 min (t_{ox}) of the total deposition time (t_{dep}) in Case I, whereas O_2 was flowed for the first 20min of t_{dep} in Case II. On the other hand, deposition was carried out in an O_2-free environment in Case III. The total deposition time was 50 min. The chamber and the gas lines were purged with N_2 prior to deposition for 5 min. The substrate used was 500 nm thick SiO_2 thermally grown on Si wafers. The substrate temperature was raised with a resistive heater and maintained at 480°C during deposition. The film thickness was estimated to be about 12 nm by cross-section transmission electron microscopy

†E-mail : hgnam@sunmoon.ac.kr

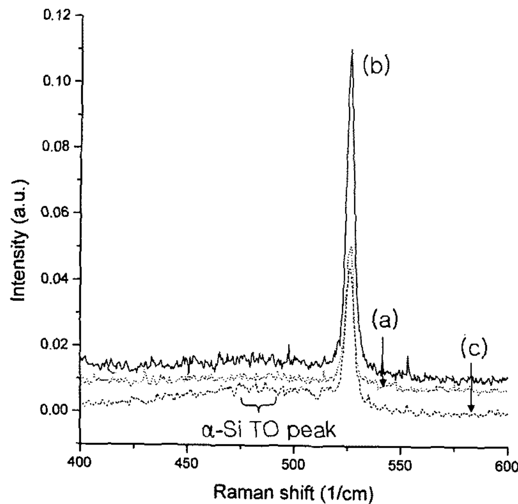

Fig. 1. Raman spectra from samples prepared at 480°C (a) t_{ox}/t_{dep}=0.2 (b) t_{ox}/t_{dep}=0.4 (c) t_{ox}/t_{dep}=0.

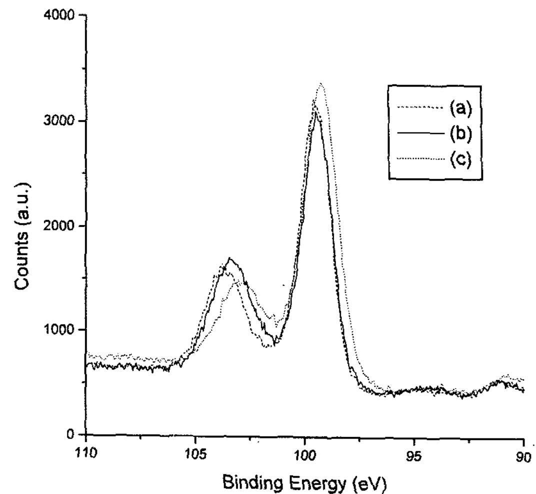

Fig. 2. XPS spectra from the surface of samples (a) t_{ox}/t_{dep}=0.2 (b) t_{ox}/t_{dep}=0.4 (c) t_{ox}/t_{dep}=0.

(XTEM).

As can be seen from Fig. 1, which shows Raman spectra, a sharp peak is located at about 520cm^{-1} with the full width half maximum (FWHM) of 4.1cm^{-1} for Case II, where t_{ox}/t_{dep} is 0.4. This peak is well known to be the crystalline silicon TO peak. As for Case I and Case III, the observed spectra are similar in the sense that the peaks are relatively less sharp compared to Case II. However, there is a significant difference between Case I and Case III. The spectrum obtained from the sample prepared with t_{ox}/t_{dep} of 0 (Case III) reveals a broad peak located at about 480cm^{-1}, which is known to be the amorphous Si TO peak. These results are clearly in agreement with the observations made with atomic force microscopy (AFM) in Fig. 4 and apparently indicate that better crystallinity is obtained when considerable O_2 is introduced to the deposition chamber.

X-ray photon spectroscopy (XPS) analyses were performed to investigate the amount O_2 incorporated within Si film. Fig. 2 shows XPS results obtained from the surface of the samples. The spectra have two peaks, namely Si-Si peak located near 98-99 eV, and Si-O peak centered at about 103 eV, indicating the presence of the native SiO_2 at the surface. As the samples are etched by sputtering, the magnitude of the Si-O peaks significantly decreases.

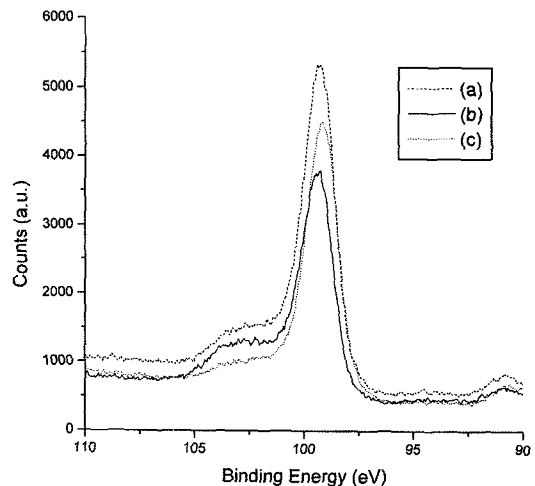

Fig. 3. XPS spectra obtained after 3min sputter etch (a) t_{ox}/t_{dep}=0.2 (b) t_{ox}/t_{dep}=0.4 (c) t_{ox}/t_{dep}=0.

Fig. 3 shows XPS results obtained after sputter etch of the films for 3min. It is clearly shown that the film prepared without O_2 flow does not show the Si-O peak. On the other hand, it is shown that the films prepared with O_2 flow contain small amount of O_2 within the films. It is noteworthy that O_2 was introduced for the first 10 and 20 min during 50 min long deposition for Case I and Case II, respectively. In other words, the latter portion of the films were deposited in an O_2 free ambient. As a consequence,

Si-O bonds are expected to locate near the Si/SiO_2 substrate interface. On the contrary, however, XPS results indicate that less Si-O bonds are present as the film was sputter etched. Noting that O_2 is known to diffuse into Si films, the results imply that evaporation of volatile species, which contain Si-O bonds, may be involved during deposition. The most probable species in this case would be SiO[6-7].

To elaborate on this hypothesis, we prepared samples at higher deposition rate, that is, higher substrate temperature, namely 600°C. The deposition rate at this temperature was observed to be 70 times faster than that at 480°C. Fig. 4 shows the atomic force microscopy (AFM) data. It is interesting to note that no significant differences depending on O_2 flow are observed from samples prepared at 600°C, whereas samples deposited at 480°C show larger grain size as the amount of O_2 flow is increased. In addition, the grain size of the sample formed at the lower temperature with all other deposition parameters adjusted the same is larger than that of the samples prepared at the higher temperature.

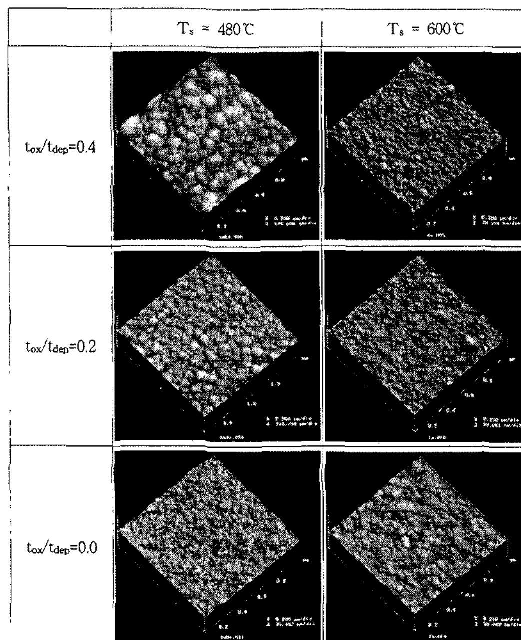

Fig. 4. AFM data from samples prepared at the substrate temperatures of 480°C and 600°C.

3. DISCUSSION

To discuss the mechanism responsible for the enhancement of Si crystallization, we note that the substrate temperatures used in this study is not high enough to result in considerable Si oxidation to form SiO_2. On the other hand, our results indicated some volatile species may evaporate during deposition. We speculate that this volatile species could be SiO. With this conjecture, then, formation and subsequent evaporation of SiO will leave behind vacancies, which act as heterogeneous nucleation sites for Si.

The observations made from the samples prepared at 600°C are in good agreement with the conjecture made above. In other words, faster deposition of Si will retard the evaporation of SiO. Hence, enhancement of crystallization through vacancy generation is negligible in this case. Instead, formation of SiO_2 may compete with that of SiO at this intermediate temperature range when relatively fast deposition rates are used. Therefore, most of O_2 is eventually consumed to form SiO_2 preferably along the grain boundary, which will hinder grain growth to result in rather small grains as observed.

As for the small amount of O_2 detected in the film, in-situ annealing at the substrate temperature used, 480°C in this case, is deemed sufficient to obtain O_2-free poly Si film. Thicker film can be grown using this thin film as the template. Furthermore, optimization of deposition parameters may well eliminate all together the necessity of the post-annealing as well as the two-step deposition, which we are currently investigating.

4. CONCLUSION

In conclusion, we studied growth of polysilicon film at low temperatures by LPCVD. It was observed that crystallization of Si is enhanced when O_2 was introduced during deposition. Poly Si film was obtained at substrate temperature as low as 480°C with O_2 flow. It was stated that the enhancement is a consequence of the formation and subsequent evaporation of SiO. That is, the vacancies generated by evaporation of SiO become heterogeneous nucleation sites. On the other hand, in cases where the films

were deposited at fast rates, enhancement of crystallization apparently did not take place. On the contrary, the observed grain size was rather small. This was suggested to be due to evaporation of SiO being significantly retarded by incoming Si atoms at fast rates.

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