The Substrate Effects on Kinetics and Mechanism of Solid-Phase Crystallization of Amorphous Silicon Thin Films

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ABSTRACT

The substrate effects on solid-phase crystallization of amorphous silicon (a-Si) films deposited by low-pressure chemical vapor deposition (LPCVD) using Si_2H_6 gas have been extensively investigated. The a-Si films were prepared on various substrates, such as thermally oxidized Si wafer (SiO_2/Si), quartz and LPCVD-oxide, and annealed at 600 °C in an N_2 ambient for crystallization. The crystallization behavior was found to be strongly dependent on the substrate even though all the silicon films were deposited in amorphous phase. It was first observed that crystallization in a-Si films deposited on the SiO_2/Si starts from the interface between the a-Si and the substrate, so called interface-induced crystallization, while random nucleation process dominates on the other substrates. The different kinetics and mechanism of solid-phase crystallization is attributed to the structural disorderness of a-Si films, which is strongly affected by the surface roughness of the substrates.

I. INTRODUCTION

Polycrystalline silicon (poly-Si) film has been a key material of thin-film transistors (TFTs) which can serve as a basic transistor of peripheral driver circuits as well as a pixel switch of active matrix liquid crystal display (AMLCD). Also, it has been widely accepted that poly-Si TFTs with staggered structure are necessary in high-density static random-access memories (SRAM) as a load transistor of the memory cells [1]. The performance of poly-Si TFTs was found to be strongly influenced by grain boundaries and intragranular traps of the poly-Si active layer. Solid-phase crystallization of amorphous silicon (a-Si) films at low temperature is a useful method for enlarging the grain size of the finally obtained poly-Si films, leading to a decrease in effective defect density per unit area of the films [1]-[3].

When a-Si film precursor was prepared by low-pressure chemical vapor deposition (LPCVD), the deposition parameters such as temperature and source gas were found to directly affect the crystallization behaviors. The use of Si_2H_6 gas instead of conventional SiH_4 enables to deposit a-Si films at low temperature as low as 430 °C, resulting in poly-Si films with large grains due to a low nucleation rate [3]. However, the a-Si films deposited by using Si_2H_6 require a prolonged annealing ($>$ 20 h below 600 °C) for the complete crystallization, which is a critical problem in device applications. Hasegawa *et al.* also reported that a-Si films deposited at low temperature using Si_2H_6 gas are crystallized throughout the films without preferred nucleation sites, so called bulk-induced crystallization process, while crystallization in a-Si films deposited at relatively high temperature ($>$ 550 °C) using SiH_4 gas starts from the interface between the substrate and the a-Si films, called interface-induced crystallization [4]-[5]. However, they have not given a clear explanation for the difference described above. The kinetics and mechanism of solid-phase crystallization of a-Si films deposited by LPCVD at a low temperature using Si_2H_6 gas has not been understood yet. In this paper, we report the substrate effects on the solid-phase crystallization of a-Si films deposited by LPCVD using Si_2H_6 gas. The crystallization behavior is found to be strongly dependent on the substrate, and the surface roughness of the substrate plays an important role in crystallization of a-Si films.

II. EXPERIMENTS

In the experiments two types of substrates, a thermally oxidized Si wafer (SiO_2/Si) and a quartz, were mainly used. The oxidation process was performed at 920 °C in a wet ambient, resulting in growth of 300-nm-thick oxide on Si wafer. Amor-

phous silicon films with a thickness of 120 nm were deposited by LPCVD using Si_2H_6 gas. The deposition temperature and pressure were 470 °C and 0.25 Torr, respectively. Before the deposition of a-Si films the substrates were boiled in a mixed solution of H_2O_2 and H_2SO_4 at 110 °C and then rinsed with deionized water. The a-Si films were isothermally annealed at 600 °C in a nitrogen ambient furnace for solid-phase crystallization.

In order to investigate the crystallization kinetics, x-ray diffraction (XRD) and Raman scattering studies were carried out for the a-Si samples as a function of annealing time. Planar and cross-sectional views of grains in the Si films were also examined by transmission electron microscopy (TEM). The surface morphology of the substrate has been observed by using atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

1. Kinetics of a-Si Crystallization and Microstructure of Crystallized Film

Fig. 1 shows the relative intensity of the (111) peak of XRD for Si films on the SiO_2/Si and the quartz substrates as a function of annealing time. The main crystalline plane of the crystallized film is (111) while (220) and (311) peaks are weakly observed from the fully annealed samples, which agrees well with the results already reported [3], [6]. From the XRD studies, we have found that crystalline nuclei are faster formed on the SiO_2/Si than on the quartz, and also grain-growth rate is higher on the SiO_2/Si substrate than on the quartz. The time needed for the complete crystallization of a-Si films on the SiO_2/Si is greatly reduced to 8 h from ~ 15 h on the quartz. The crystallization kinetics of a-Si films deposited by LPCVD on a quartz using Si_2H_6 gas has been widely studied by others [3]-[4], [6], and our results agree well with their data. However, the different crystallization behavior of a-Si films on the SiO_2/Si and the quartz was first reported in this paper.

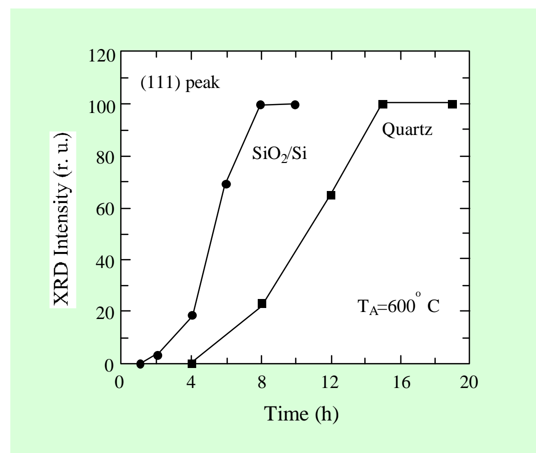

Fig. 1. XRD intensity of the (111) texture for Si films on a quartz and a thermally oxidized Si wafer as a function of annealing time.

The detailed kinetics of solid-phase crystallization of a-Si films was studied

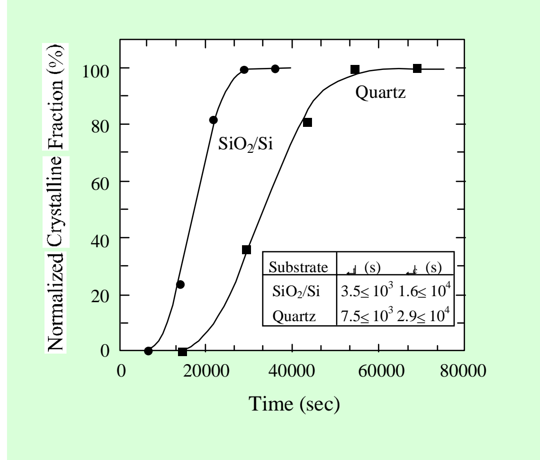

Fig. 2. Crystalline fraction measured from Raman scattering for Si films on the two substrates as a function of annealing time. The solid lines are the results of fitting the experimental data to the equation of crystallization kinetics with the effective transient time τ_t and characteristic crystallization time τ_c shown in the inset.

by using Raman scattering measurements. Fig. 2 shows the crystalline fraction that was evaluated from the Raman spectra for the Si films on the SiO_2/Si and the quartz as a function of annealing time. The crystalline fraction was calculated by the integrated Raman scattering intensity of the crystalline phase relative to that of the amorphous part, in which the scattering cross-section for crystalline and amorphous phases was taken into account [7]. The experimental data were normalized with the maximum crystalline fraction of ~ 0.9 that was obtained for both samples after full crystallization. The Raman scattering results also have confirmed that a-Si films are faster crystallized on the SiO_2/Si than on the quartz.

Overall kinetics of solid-state phase transformations are often described by an empirical equation [8]. The volume fraction transformed X is expressed as a function of time t as follows:

$$X = 1 - \exp[-(Kt)^n] \qquad (1)$$

where K is the reaction-rate constant and n is the time exponent. For solid-phase crystallization of a-Si films, the above formula can be explicitly written with the effective transient time τ_t for nucleation and the characteristic time τ_c of crystallization [9]. Assuming that the nucleation rate r_n and grain-growth velocity v_g are time independent, the crystalline fraction X as a function of annealing time is

$$X(t) = 1 - \exp[-\{(t - \tau_t)/\tau_c\}^3] \qquad (2)$$

where $\tau_c = [(\pi/3) v_g^2 \varepsilon r_n]^{-1/3}$, and ε is the film thickness. The solid lines shown in Fig. 2 are the results of fitting the experimental data to the analytical formula (2), and the inset indicates the best fitting values of τ_t and τ_c for both curves. The effective transient time and the characteristic time for crystallization of a-Si films on the SiO_2/Si substrate are shortened to $\sim$1/2 compared with that on the quartz, as shown in Fig. 2.

The microstructure of poly-Si films obtained after full annealing has been investigated using plan-view TEM observations.

Fig. 3 shows the plan-view TEM micrographs for the poly-Si films formed by annealing of a-Si films on the SiO_2/Si and quartz substrates. The a-Si films on the thermal oxide and on the quartz were annealed for 10 h and 19 h, respectively, at 600 °C. These annealing processes lead to fully crystallized poly-Si films on the two substrates. The grain size of the fully crystallized poly-Si film on the SiO_2/Si is about 2 μm, which is comparable to or slightly smaller than that on the quartz (2∼3 μm). Although the time needed for the complete crystallization of a-Si films on the SiO_2/Si is greatly reduced to 8 h, the decrease in grain size of the finally obtained poly-Si films is relatively small. Also, grains of the poly-Si films on the SiO_2/Si substrate have dendritic structure that is generally observed in the solid-phase crystallized films [10]-[11]. The electrical properties of poly-Si films are governed by the density of electrically active defects that are strongly influenced by the crystallinity (grain size and its structure) of the films. From the view point of crystallinity, the electrical properties of the poly-Si films formed on the SiO_2/Si may be identical to those on the quartz. These results imply that poly-Si films with large grains can be formed by a short annealing of a-Si deposited by LPCVD at a low temperature using Si_2H_6 gas. Therefore, the disadvantage of a prolonged annealing for complete crystallizing a-Si films deposited at a low temperature can be settled if one selects a proper substrate.

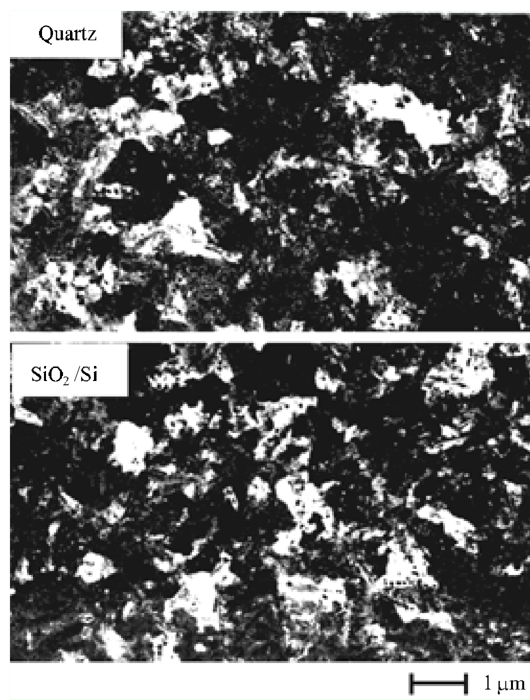

Fig. 3. Plan-view TEM micrographs of poly-Si films formed by solid-phase crystallization of a-Si deposited on the SiO_2/Si and quartz substrates.

2. Nucleation Mechanism of a-Si Crystallization

We have studied cross-sectional TEMs in order to explain the difference of crystallization kinetics of a-Si films between the SiO_2/Si and the quartz substrates. Fig. 4 shows the cross-sectional TEM micrographs of the a-Si film that was deposited on the quartz and then annealed at 600 °C for 8 h. The crystalline fraction of the film is around 30 % measured from the Raman spectrum. We could observe the grains that were generated over all regions of the a-Si

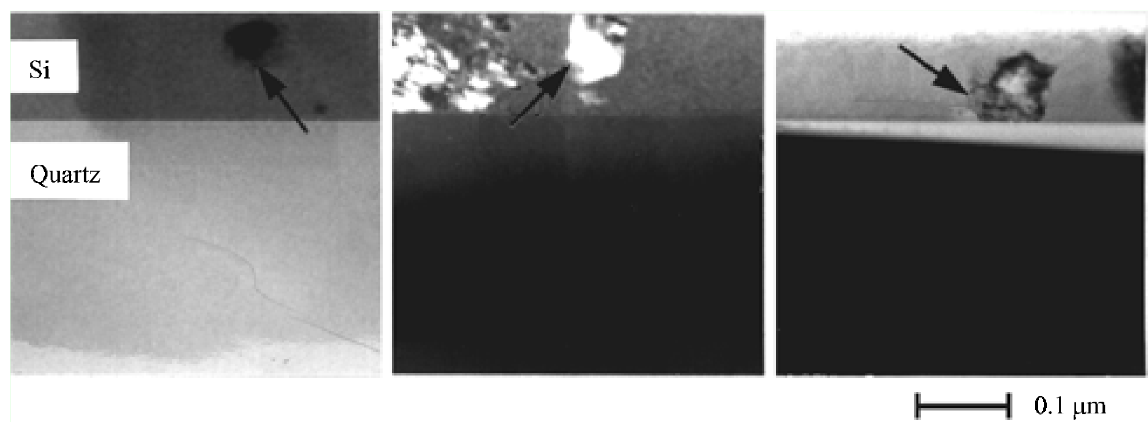

Fig. 4. Cross-sectional TEM micrographs of the a-Si deposited on the quartz and then annealed at 600 °C for 8 h, showing grains generated at center and upper (free surface) and lower (interface with the substrate) parts of the a-Si film.

film, center and upper (free surface) and lower (interface between the a-Si and the quartz) parts of the film. The result indicates that random or homogeneous nucleation process dominates in a-Si films deposited on the quartz. Our observation agrees well with the result of Hasegawa *et al.* [4]. They deduced the bulk-induced crystallization through homogeneous nucleation for a-Si films on a quartz from the fact that the signals from a crystalline phase started to appear at the same time in both XRD and Raman scattering measurements. However, we directly found the homogeneous nucleation process in crystallization of a-Si films on a quartz substrate using cross-sectional TEM.

In contrast to the quartz substrate, crystalline nuclei in a-Si films on the SiO_2/Si were only observed at the interface between the a-Si and the substrate as shown in Fig. 5. Figure 5 shows the cross-sectional TEM micrograph of the Si film deposited on the SiO_2/Si substrate. The film was annealed at 600 °C for 4 h, which results in a crystalline fraction of ~ 20 %. We could find the grains generated at the interface between the a-Si and the thermal oxide of the substrate and then grown, which is the first observation not reported yet. TEM studies show that most of nuclei in a-Si films on the SiO_2/Si substrate are generated at the interface and then grow until the film is completely crystallized. It shoud be noted here that a-Si film, consisting of a composite double layer with the mixed-phase film (crystallites embedded in an amorphous matrix), deposited on SiO_2 at a relatively high temperature using SiH_4 gas is crystallized from the inter-

face between the a-Si and the mixed-phase film [12]. The mixed-phase film acts as a seeding layer for crystallization of the a-Si regions. In our study, however, we observed interface-induced crystallization in a-Si films deposited at a low temperature using Si_2H_6 gas without any seeding layer.

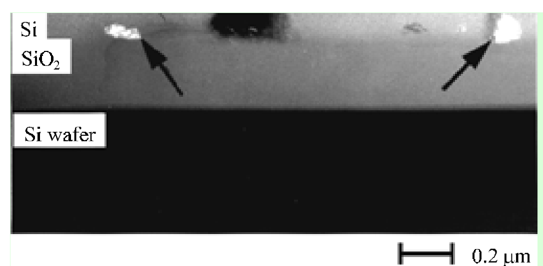

Fig. 5. Cross-sectional TEM micrograph of the a-Si film deposited on the SiO_2/Si and then annealed at 600 °C for 4 h. The arrows indicate the grains generated at the interface between the a-Si and the thermal oxide of the substrate.

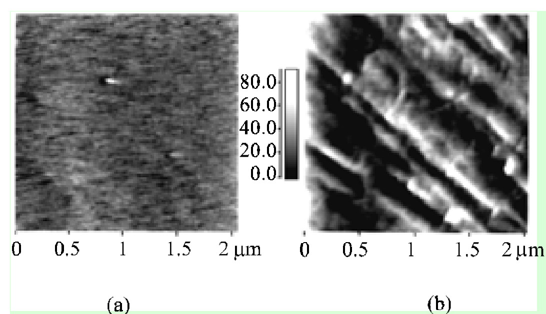

Fig. 6. Surface structure and its roughness of (a) the thermal oxide grown on Si wafer and (b) the quartz observed by AFM.

It has been confirmed from the cross-sectional TEM observations that a-Si deposited on the SiO_2/Si starts to be crystallized from the interface between the SiO_2 and the a-Si film, called interface-induced crystallization or nucleation, while random nucleation process dominates on the quartz. The different nucleation mechanism of the solid-phase crystallization of a-Si films is considered to be strongly correlated to the surface morphology of the substrates upon which a-Si films are deposited. The surface structure of the substrate was investigated by AFM before a-Si deposition, and its data are shown in Fig. 6. The surface of the thermal oxide grown upon Si wafers is very smooth with a root mean square (RMS) roughness of 4.2 Å. However, the quartz has a ditch-like surface with a large RMS roughness of 13.0 Å, which we think results from the polish process of the substrate. The very rough surface of the quartz substrate might severely decrease the surface diffusivity of Si atom, specifically, at the initial stage of the deposition process, resulting in the a-Si film with a large structural disorder. Therefore, a longer transient time and characteristic time are required for crystallization of a-Si films deposited on the quartz than the SiO_2/Si substrate, as shown in Fig. 2, and the interface between the a-Si film and the quartz substrate can be no longer a preferred site for nucleation due to the large disorder at the initial stage of the deposition process.

Based on our results, we suggest that the structural disorder of Si network nearby on the substrate plays a crucial role in

interface-induced nucleation. In general, nucleation and grain growth in solid-phase crystallization of a-Si films have been found to be directly dependent on the structural disorder of Si network. As the structural disorder is increased, the nucleation and grain growth rates are decreased [3]. It has been also reported that the crystallization behavior on a quartz is changed from interface-induced nucleation for a-Si film deposited at a relatively high temperature using SiH_4 gas to random nucleation process for that deposited at a low temperature using Si_2H_6 [4]-[5]. However, our results showed that the interface-induced crystallization was continued to the a-Si film deposited at a low temperature using Si_2H_6 gas when the thermal oxide with a very smooth surface was used, as shown in Fig. 5. The very smooth surface of the SiO_2 can remarkably relieve the increase of the structural disorder due to lowering the deposition temperature from 550 °C (SiH_4) to 470 °C (Si_2H_6). However, the use of quartz as a substrate causes the structural disorder of a-Si film, at least, nearby on the substrate to further increase due to the large surface roughness shown in Fig. 6(b). As a result, a-Si films deposited on a quartz using Si_2H_6 gas have the largest structural disorder because of the rough surface of the substrate and the low deposition temperature. Furthermore, the interface between the a-Si film and the quartz substrate has a structural disorder comparable to or larger than the bulk has, because the surface diffusivity of a Si atom is very low at the initial stage of the deposition process due to the rough surface of the substrate. Therefore, the interface between the a-Si film and the quartz can be no longer a preferred nucleation site, and the crystallization on the quartz proceeds through homogeneous bulk nucleation process.

In order to examine how other surface properties of the substrate beside surface roughness influence on crystallization of a-Si films, we have changed the oxide formation method of the SiO_2/Si substrate from the thermal oxidation to LPCVD. The LPCVD-oxide deposited on Si wafers at 720 °C has a rough surface of 9.8 Å RMS value measured by AFM. The crystallization kinetics on the LPCVD-oxide was shown to be nearly identical to that on the quartz. Although chemical properties of the surface are the same for both LPCVD- and thermally grown oxides from Si wafers, the former has an even larger surface roughness than the latter. Therefore, a-Si films prepared on the LPCVD-oxide might be crystallized through random nucleation process as on the quartz, requiring a prolonged time of $\sim$ 15 h at 600 °C for complete crystallization. This result implies that the surface roughness of the substrate, rather than its chemical properties, may determine the crystallization kinetics and mechanism of a-Si films, which supports our model for nucleation mechanism of a-Si films described

above. Our result achieved on the LPCVD-oxide agrees partially with that of Hong *et al.* [6] who have employed a CVD-oxide deposited on Si wafers as a substrate. They could not obtain a fully crystallized film from a-Si deposited below 525 °C until annealing was performed over 30 h (at 600 °C), which was two times longer than our anneal time or others' [3]-[4]. Their exceptionally long crystallization annealing may be due to a large surface roughness of the CVD-oxide deposited at a low temperature along with some additional factors increasing the structural disorder of a-Si films such as higher deposition rate. The LPCVD-oxide in our study could have a relatively smoother surface compared with others because of the high deposition temperature of 720 °C.

IV. CONCLUSION

The crystallization kinetics and mechanism of a-Si films deposited by LPCVD using Si_2H_6 gas has been investigated. The a-Si films are faster crystallized on a thermally grown oxide than on a quartz or LPCVD-oxide through interface-induced nucleation process. The surface roughness of the substrate is found to strongly affect the nucleation mechanism in solid-phase crystallization of a-Si films. Thermally grown oxides with a very smooth surface may considerably relieve the increase in the structural disorder of a-Si network due to the lowered deposition temperature of a-Si films using Si_2H_6 instead of SiH_4 gas. In this case, interface-induced crystallization dominated in a-Si film deposited at a high temperature using SiH_4 gas can continuously occur even in that deposited at low temperature using Si_2H_6 gas. However, the quartz and LPCVD-oxide with a rough surface might largely decrease the diffusivity of Si atoms at the initial stage of a-Si deposition, resulting in an additional disorder nearby on the substrate. Therefore, the interface with a quartz and CVD-oxide can be no longer preferred sites when the deposition temperature of a-Si films is decreased using Si_2H_6 instead of SiH_4 gas.

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