Crystallization of Amorphous Silicon Films with Native-Oxide Free Surfaces

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Received August 13, 1991; Accepted September 17, 1991

Crystallization of amorphous Si (a-Si) on SiO₂ layers under ultra-high vacuum (UHV) conditions was examined. In the case that the a-Si layer with a native oxide free surface was annealed in the UHV molecular-beam-epitaxy chamber, it has been found that the initial nucleation and the grain growth occur at the surface. Cross-sectional transmission electron microscopy revealed the novel mode of the grain growth which resulted in the formation of mushroom-shaped Si grains at the a-Si surface. The surface crystallization phenomenon was found to be sensitive to the oxygen partial pressure during the annealing. Reappearance of the surface crystallization was also confirmed in the air-exposed a-Si film whose surface native-oxide layer was removed by HF solution just before the UHV annealing. The crystallization mechanism of the a-Si with the clean surface was discussed.

1 INTRODUCTION

In recent Si electric device technology, polycrystalline Si (poly-Si) films are widely used for electrodes. The electrical performance of the poly-Si electrode is mostly determined by its texture, grain size, and surface morphology. Full understanding of the growth mechanism of the poly-Si is required for controlling such factors. Solid phase growth (SPG) of amorphous Si (a-Si) on a SiO₂ layer is one of the formation techniques of the poly-Si layers and has been carried out by using various methods, generally as a part of the silicon-on-insulator technology. A conventional technique of the a-Si SPG consists of two procedures; the fabrication of the a-Si layer by (low pressure: LP) chemical vapor deposition (CVD)^{1,2)}, deposition by ultra-high vacuum (UHV) evaporation³⁻⁶⁾, or self-implantation⁷⁻⁹⁾, and the annealing for crystallization of the a-Si in vacuum or an inert atmosphere, such as Ar or N₂.

It should be noticed that a surface of the a-Si is subjected to native oxidation before the annealing in the conventional methods. Up to now, there are few studies of SPG of a-Si films without native oxide layers on their surfaces, although the measurement of the crystallization time for the UHV-deposited a-Si film annealed under UHV conditions was carried out by Olson *et al.*¹⁰⁾

In this paper, we will report the experimental results of SPG of the a-Si on the SiO₂ layers under UHV conditions. In the case that a-Si layer deposition on the SiO₂ layers and annealing for crystallization were successively carried out in a UHV molecular-beam-epitaxy (MBE) chamber, we found for the first time a novel mode of crystallization which is completely different from that observed previously. It consists of the nucleation at the surface of the a-Si and the formation of mushroom-shaped Si grains, suggesting high mobility of atoms on the a-Si clean surface¹¹⁾. We also investigated the effect of the O₂ partial pressure during the annealing on the growth mode. Furthermore, crystallization of the air-exposed a-Si film whose surface native

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Key Words: Amorphous Silicon, Crystallization, Native Oxide Layer, Surface, Nucleation, HF Treatment, O₂ Partial Pressure

oxide layer was removed by HF solution, was examined under the UHV condition.

2 EXPERIMENTAL

The a-Si deposition and the annealing for crystallization were performed by using MBE equipment (base pressure: 1×10^{-10} Torr) which allows O_2 and N_2 gases to be introduced. The a-Si layers of 500~1000 Å thicknesses were formed on thermal oxide layers on Si (001) wafers by Si molecular beam deposition at room temperature at a rate of 7 Å/sec. The silicon source was an electron beam evaporator (6 kV). The annealing temperature was varied from 500 to 700°C. Heating rates of the samples were also varied in the range 1~10°C/sec. The variation of a-Si surface crystallinity during the annealing was monitored, *in situ*, by reflection high energy electron diffraction (RHEED) observation, in which the RHEED halo pattern of the amorphous layers turned into a polycrystalline ring one. Surface morphology of the crystallized a-Si was observed by scanning electron microscopy (SEM). Detail structures were examined by transmission electron microscopy (TEM). Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) were also employed.

3 RESULTS

3.1 Structure of crystallized a-Si in UHV

Figure 1(a) and (b) are typical surface SEM images of the a-Si film, which were subsequently annealed in UHV just after the deposition at 600°C for 5 and 10 min, respectively. Many protrusions can be seen on a flat surface in Fig. 1(a) and the density of the protrusion increases for a longer annealing time so that the uneven surface, as shown in Fig. 1(b), is formed. Figure 2 is a cross-sectional high-resolution (HR) TEM image of the sample shown in Fig. 1(a). The protrusion is revealed to the Si grain, in which {111} lattice fringes are mainly observed. However, the region marked A shows a mottled contrast indicating an amorphous state in the layer. These results confirm that the initial nucleation for crystallization does not occur at the

Fig. 1 SEM images showing surface morphology of a-Si film surfaces annealed at 600°C for (a) 5 min and (b) 15 min.

Fig. 2 A cross-sectional TEM micrograph showing the vicinity of the Si grain. A region shows the amorphous state under the Si grain. B regions indicate the depletions of the a-Si layer. The arrow shows the original position of the a-Si surface.

a-Si/SiO₂ interface but in the vicinity of the a-Si surface. It is also notable in Fig. 2 that the preferential depletion of the a-Si around the Si grain can be seen in the region marked B. Furthermore, the top of the Si grain is located above the original position of the a-Si surface indicated

by an arrow and thus the whole feature resembles a mushroom shape. These results clearly show that mass transfer has occurred from the a-Si layer to the Si grain during annealing.

Further observations were carried out for various types of samples, which were annealed at different temperatures and time, and which had different thicknesses of a-Si and SiO₂ layers. Samples having other types of SiO₂ layers were also observed; a SiO_x ($x \sim 2$) layer formed using an oxygen molecular beam¹²⁾ and a SiO₂ layer formed using ECR oxygen plasma. All results showed that the nucleation always occurred at the a-Si surface and the mushroom-shaped grains were formed. Thus the phenomenon of the surface nucleation and the grain growth on the a-Si surface is found to be independent of annealing conditions, structure of deposited layers, and the SiO₂ layer underneath the a-Si.

Next, in order to examine the influence of the surface cleanliness on the nucleation site and the grain growth, samples whose surfaces were covered with native oxide layers were investigated. After the a-Si deposition on the SiO₂ layer, the sample was removed from the MBE chamber and exposed to air for several days. With this procedure, it was expected that the Si atoms in the surface region of several angstroms would be passivated by the native oxide layer. The sample was then loaded into the MBE chamber again and annealed in UHV. For the samples prepared under various annealing conditions, no pattern changes in the RHEED observation were seen, i.e., the amorphous halo pattern persisted during the annealing. Therefore, in this case, the initial crystallization at the a-Si surface was not detected by the RHEED observation. Figure 3 is a cross-sectional TEM image of the sample annealed at about 600°C for 60 min, showing the Si grains embedded in the a-Si layer. No mushroom-shaped Si grains can be observed and the surface morphology is rather flat. The nucleation appeared to occur in the vicinity of the a-Si/SiO₂ interface. These results demonstrate that the surface nucleation occurs only for the a-Si layer with a clean surface.

Fig. 3 A cross-sectional TEM micrograph of the sample, whose surface was exposed to air just before the UHV annealing.

3.2 Effect of O₂ on surface crystallization

Next we investigate the effect of O₂ partial pressure on the surface crystallization of a-Si films. After the deposition of a-Si, a 99.9999% O₂ gas was introduced into the MBE chamber to the designated pressure and then the wafer was annealed at 650°C for 5 min. Figure 4(a) and (b) show SEM images of the surface morphology and the corresponding AES profiles of the crystallized a-Si surface, respectively, at respective O₂ partial pressures. Under the partial pressure of 2×10^{-6} Torr, uneven surface morphology and the only Si peak in AES profile are observed. On the other hand, flat surfaces and oxygen peaks can be seen in the samples annealed under the O₂ partial pressures of 2×10^{-5} and 2×10^{-4} Torr. The chemical shift of the Si peak to SiO₂ are also observed in the both samples. These results show that the oxide layer are formed on the a-Si surface during the annealing under higher O₂ partial pressures. As a consequence, no surface crystallization has occurred leading to the formation of the flat surface morphology. Furthermore, we have confirmed that the introduction of a N₂ gas into the MBE chamber during the annealing has no influences on the surface crystallization.

3.3 Effect of HF-treatment on surface crystallization

The above results clearly indicate that the oxide layer formed on the a-Si surface inhibited the surface crystallization. Thus we tested the HF-treatment, which is conventionally used to remove thin oxide layers from the wafer surface by HF solution (HF:H₂O=1:30), for the native oxide-covered a-Si film. After exposure of a wafer with a UHV-deposited a-Si film into air, the wafer was dipped into the HF solution for 1 min. Then it was loaded into the MBE chamber again and annealed at 650°C for 5 min. Figure 5(a) is a

SEM image showing the surface morphology. The observed protrusions prove that the surface crystallization *did* occur in the sample. However, the region of the flat surface can be also seen in spite of the sufficient annealing temperature and time to crystallize all a-Si region. As shown in Fig. 5(b), a cross-sectional TEM image reveals that this sample consists of polycrystalline regions with flat surfaces and protrusive grains. It is also notable that a wedge-shaped concavity, as indicated by an arrow, is observed around the grain.

In the same way, we also applied the HF-treatment to the air exposed a-Si films fabricated by LPCVD. Surface morphology of the LPCVD sample, which was annealed in UHV after the HF-treatment, is shown in Fig. 6. In this case, the protrusive Si grains are observed on the whole surface, forming uneven surface morphology which is similar to that in Fig. 1(b). To verify the substantial differences in the crystallization modes between the a-Si films formed by MBE (MBE a-Si) and by LPCVD (LPCVD a-Si), distribution of impurities (H, O, C, N) was analyzed

Fig. 4 Dependence of surface morphology (a) and surface AES profiles (b) upon O_2 partial pressures of 2×10^{-6} , 2×10^{-5} , and 2×10^{-4} Torr.

Fig. 5 (a) A surface SEM image of the MBE a-Si film annealed at 650°C for 5 min, whose native oxide layer was removed by HF solution before the UHV-annealing.
(b) A cross-sectional TEM micrograph of the vicinity of the protrusion shown in (a).

Fig. 6 A surface SEM image of the LPCVD a-Si film annealed at 650°C for 5 min, whose native oxide layer was removed by HF solution before the UHV-annealing.

by SIMS. Figure 7 shows the concentration profiles of respective impurities in the samples which were dipped into HF solution. Note that the concentration of H, O, and N in MBE a-Si are higher than that in LPCVD a-Si. Especially, the profiles of H and O in MBE a-Si suggest the percolation of H_2O molecule into the film.

4 DISCUSSION

We can now deduce a mechanism of SPG of a-Si under the UHV condition. In case of the conventional SPG, it is believed that the nucleation at the a-Si/ SiO_2 interface is due to the release of the stress induced by the thermal expansion difference between Si and SiO_2 ^{2,6)} and/or of that which is attributed to the porosity of the a-Si, especially that deposited by vacuum-evaporation at room temperature¹³⁾. However, such a stress relaxation mechanism can not explain the surface nucleation phenomenon as in the present case. Thus we require another mechanism. First, compared to the crystallization time of the native oxide covered a-Si, that of the a-Si with clean surfaces is shorter by a factor of 10. This result suggests high mobility of Si atoms in a-Si, which contribute to crystallization. Second, the preferential depletions of the a-Si around the Si grains shown in Fig. 2 directly indicate the migration of Si atoms around the nucleus. Third, such phenomenon is very sensitive to the surface cleanliness of a-Si. Therefore, we can propose one possible mechanism of SPG of a-Si under the UHV condition as follows (see Fig. 8). It is deduced that the mobility of Si atoms on the clean a-Si surface is high enough to contribute to the nucleation and the grain growth at the surface (Fig. 8(a)). If the surface atoms could migrate with high mobility near the temperature of the a-Si crystallization, the migrating atoms would collide with high frequency and then nucleate at the a-Si surface (Fig. 8(b)). The nucleation rate at the surface may be higher than that at the interface, at least in the temperature range of the experiment. The grain growth can proceed in two ways. One is a conventional solid phase growth from the nucleus downward into the a-Si. The

Fig. 7 SIMS analyses of H, O, N, and C in the MBE (a) and LPCVD (b) a-Si films just after the HF treatment.

Fig. 8 Model of crystallization of the a-Si film with a clean surface.

other is a novel mode in which the migrating atoms with high mobility climb up the surface of the nucleus (Fig. 8(c)). The nucleus virtually acts a sink of such surface migrating atoms and grows into the Si grain (Fig. 8(d)).

It was previously reported that the electron evaporated a-Si film was easily subjected to the gas absorption¹⁴⁾. The gas species, such as O and

H₂O in this case, are considered to inhibit the atom migration partially on the a-Si surface during the annealing. This means that the supply of Si atoms which will be crystallized is also restricted to the region where surface crystallization can occur. This idea well explains the structure of the wedge shaped concavity around the protrusive grain observed in Fig. 5(b).

Recently, it has been reported by Watanabe *et al.* that poly-Si layers, which have uneven surface morphology composed of hemispherical grains, are grown by LPCVD in specific growth conditions¹⁵⁾. The poly-Si was successfully applied to storage electrodes of stacked capacitors of dynamic-random-access-memories. Since the structures of the poly-Si layers are quite similar to our case, it is suggested that the crystallization with the above mentioned mechanism can also occur in the LPCVD process. Furthermore, reappearance of the surface crystallization was also confirmed in the air-exposed LPCVD a-Si film whose surface native-oxide layer was removed by HF solution just before the UHV annealing. Therefore, the surface crystallization phenomenon is substantially dependent on cleanliness of the surface and independent of the fabrication method of the a-Si film. It is important to suppress the oxygen partial pressure during the a-Si fabrication and the subsequent annealing in order to accomplish the present type of crystallization.

5 CONCLUSION

Crystallization of the a-Si films was performed under the UHV condition. The experimental results showed the novel crystallization mode suggesting high mobility of surface atoms of a-Si, which led to the formation of uneven surface morphology. It is pointed out that this phenomenon belongs to the category of the crystallization of a-Si films which have clean surfaces.

The authors would like to thank H. Watanabe and N. Ikarashi for their useful discussions.

Thanks are also due to Y. Matsumoto, M. Nakamae, M. Ogawa, H. Watanabe, and F. Saito for their encouragement.

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