Electron backscattered diffraction study of poly-Si by Ni-mediated crystallization of amorphous silicon using a SiO$_2$ nanocap

Y. J. Chang, J. H. Oh, K. H. Kim, and Jin Jang
Advanced Display Research Center and Department of Physics, Kyung Hee University, Seoul 130-701, Korea

D. I. Kim and K. H. Oh
School of Materials Science and Engineering, Seoul National University, Kwanak-ku, Seoul 151-744, Korea

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Low-temperature polycrystalline silicon (poly-Si) is of increasing interest for the display on glass. Among several techniques for the low-temperature poly-Si the Ni-mediated crystallization of amorphous silicon (a-Si) is promising one. We studied the crystalline orientation of the disk-shaped grains in the poly-Si formed by Ni-mediated crystallization of a-Si using a SiO$_2$ nanocap by electron backscattered diffraction measurements. A SiO$_2$ nanocap layer was formed by O$_2$ plasma treatment on a-Si and an ultrathin Ni layer was deposited on the nanocap. It was heated in a UV scan system for crystallization. The Ni atoms in a-Si diffused through the nanocap and formed NiSi$_2$ crystallites. Disk-shaped grains were then grown from these nuclei. The size of disk-shaped grains in poly-Si increases from ~6 to ~20 μm when the thickness of nanocap on a-Si changes from 2.4 to 3.2 nm. On the other hand, without the nanocap layer, its size is ~3.5 μm. The crystalline quality of poly-Si is improved by introducing a nanocap layer, which is due mainly to the increase of the grain size. © 2004 American Vacuum Society. [DOI: 10.1116/1.1714886]

I. INTRODUCTION

Polycrystalline silicon (poly-Si) on glass is of increasing interest because of its application to large-area electronics such as active-matrix liquid crystal displays and active-matrix organic light-emitting diodes. Metal-induced crystallization (MIC) was found to be a good candidate for device-quality poly-Si with a relatively low thermal budget. Of the various approaches available, silicide-mediated crystallization (SMC) of a-Si is a promising technique for large-scale manufacturing of high performance poly-Si thin-film transistors on glass. SMC is one of MIC methods using NiSi$_2$ crystallites which have the cubic lattice structure with a very small mismatch of 0.4% with Si. Thus the NiSi$_2$ crystallites that are able to be formed at 400 °C can be the seeds for crystallization of a-Si. The NiSi$_2$ crystallites act as nucleation sites for crystallization. The crystallization of a-Si proceeds as a result of NiSi$_2$ migration throughout the a-Si network.

Recently, high-quality poly-Si on insulator by metal-induced lateral crystallization (MILC) has been demonstrated. However, the metal layer for the conventional MIC, and/or MILC poly-Si, was deposited at least on a portion of the surface on the a-Si. In this case, the metal-contacted region on the a-Si for MIC is necessary. It is well known that crystallization temperature of a-Si can be lowered by the addition of Ni atoms in a-Si, and the amount of Ni atoms should be minimized to have good material property.

In previous work, to reduce metal contamination and to have uniform grain size with clean and smooth surface, we studied Ni-induced crystallization of a-Si using a thin Ni layer on SiN$_x$/a-Si:H, in which the capping layer (SiN$_x$) was a filter against metal contamination for SMC of a-Si. Ni could be diffused through the SiN cap layer into the a-Si layer and the Ni atoms in the a-Si form NiSi$_2$ precipitates, which can be nucleation sites for crystallization. This method could give the advantages such as the nondirect contact of metal to a-Si and the reduction of metal impurities. However, the capping layer should be removed for device fabrication.

In this work, we proposed a SiO$_2$ nanocap layer between a-Si:H and an ultrathin Ni layer. Low-temperature poly-Si (LTPS) formed by Ni-silicide-mediated crystallization of a-Si by an UV annealing technique was studied. The crystalline properties of the disk-shaped grains in poly-Si have been investigated by electron backscattered diffraction (EBSD). The grain texture and microstructural mapping can be seen simultaneously and the characteristics of the grain boundary can be analyzed through EBSD measurement.

II. EXPERIMENT

Figure 1 shows the crystallization process for LTPS. The SiO$_2$ buffer layer and a-Si layer were sequentially deposited on Corning 1737 glass by low-pressure chemical vapor deposition at a substrate temperature of 450 °C. The nanocap (SiO$_2$) layer was formed by O$_2$ plasma treatment on the a-Si in the plasma-enhanced chemical vapor deposition system. The thickness of the nanocap was varied by O$_2$ plasma treatment from 0 to 480 s. The thicknesses of a-Si and SiO$_2$ nanocap layers, measured by spectroscopic ellipsometry, were 50 and 2.4–4.1 nm, respectively. Next, Ni area density

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$^a$Mobile Product Engineering Group, AMLCD Division, Samsung Electronics, Kiheung, Korea.

$^b$Electronic mail: jjang@khu.ac.kr
of $1.02 \times 10^{14}$ cm$^{-2}$ was deposited on the sample. Heat treatment of samples was carried out at 580 °C for 10 min in an UV annealing system.

The Ni area density was obtained from the integration of the Ni depth profile for the crystallized Si layer measured by secondary ion mass spectroscopy. The crystallographic properties of the poly Si films were examined by EBSD technique. A JEOL 6500F Schottky-type field-emission gun scanning electron microscope equipped with a Oxford INCA Crystal EBSD system was used for EBSD analysis. EBSD experiments were carried out at an accelerating voltage of 15 KV and a prove current of 4 nA. Pseudo-Kikuchi patterns were integrated for 90 ms and the orientation mapping condition was $128 \times 128$ pixels scanned with about a 0.8 μm step in each analysis point. The backscattered electrons form a Kikuchi pattern that can be indexed to yield a unique description of the local orientation in a crystalline region.\[11\]

III. RESULTS AND DISCUSSION

Figure 2 shows the relationship between the average grain size calculated from EBSD data and the thickness of nanocap according to O$_2$ plasma treatment time. In order to calculate the grain size by EBSD, the number of data points or pixels in one grain is calculated. Using the known pixel step size and numbers, the grain area is calculated statistically and the criterion for the grain identification was determined by 7.5° misorientation which indicates the boundaries between the grains. The grain size distribution and its shape calculated from EBSD appear later in this article. The thickness of nanocap layer increases from 2.4 to 3.2 nm when the O$_2$ plasma treatment time increases from 15 to 120 s. There is a native SiO$_2$ of 1.8 nm that corresponds to zero plasma treatment time. The grain size increases with the plasma treatment time. This is due to the reduction in the Ni density in the a-Si because the grain size increases with decreasing the Ni area density.

Figure 3 shows the X-ray photoelectron spectrum (XPS) of SiO$_2$ binding energy in SiO$_2$ nanocap according to O$_2$ plasma treatment time. The SiO$_2$ peak intensity increases with increasing O$_2$ plasma treatment time, indicating that the SiO$_2$ binding becomes stronger as the treatment time is increased.

From the formation of silicon oxide and suboxides in the Ni/Si system, it is shown that neither Ni oxide nor mixed compounds such as Ni$_2$SiO$_4$ is involved in the barrier formation.\[12\] It demonstrates that the silicon suboxides (Si$_2$O$_3$, Si$_2$O, and SiO) are formed as the advancing Ni/Ni$_3$Si interface encounters oxygen in the Ni films. As more oxygen is encountered, Si takes on a full coordination of oxygen, forming SiO$_2$. When a sufficient layer of SiO$_2$, around 10 nm, has formed, Ni is no longer able to diffuse through the cap layer for Ni-mediated crystallization.\[12\] The increase of thickness and formation of dense SiO$_2$ nanocap...
upon increasing the \( \text{O}_2 \) plasma treatment time are responsible for the more effective barrier against Ni diffusion.

Figure 4 shows the crystalline orientation mapping images for the surface normal direction to the poly-Si films. The color coordinate, from which the orientation of a grain can be decided. The color of the mapping image corresponds to a particular crystalline orientation and the standard triangle shows a prominent three-dimensional texture. Actually, the “grain” is defined as the regions with the same crystallographic orientations and same phases,\(^\text{13}\) it is therefore quite reasonable to define the grains from EBSD analysis. Each disk-shaped grain has almost the same crystalline orientation even though it has low-angle misorientations less than 7.5° inside of one grain. Note that the misorientation angles inside a grain is less than 7.5°. The grain size reaches to several tens of micrometers, but the neighboring grains do not have the same color, indicating that the grain orientation depends on the grain itself. The disk-shaped grain can be formed during crystallization; the circular crystallization from the seeds and eventually collides with neighboring grains, leading to grain boundaries. The average grain size increases from 6.0 to 19.4 \( \mu \text{m} \) with increasing \( \text{O}_2 \) plasma time; that is, nanocap thickness. As a result, even though the same amount of Ni area density is used for crystallization, the grain size increases remarkably with increasing plasma treatment time.

The grain size is controlled by nucleation and grain growth rates in solid-phase crystallization. To obtain a large grain, it is needed to decrease the nucleation rate and to increase the grain growth rate.\(^\text{14}\) In the case of metal (Ni)-induced lateral crystallization of a-Si, it is found that oxygen existence in the Ni films has little effect on the growth rate of poly-Si.\(^\text{15}\)

Figure 5 shows the inverse pole figures for the mapping...
images of crystalline orientation for the normal direction to the surface according to O$_2$ plasma treatment time. An inverse pole figure maps show the distribution of orientations for the poly-Si. This indicates that there is no preferred orientation. A random distribution of crystalline orientations can be seen over the whole sample.

Figure 6 shows the pattern quality histograms by EBSD analysis of the SMC poly-Si films according to O$_2$ plasma treatment time. Pattern quality is an integer of the range from 0 (black) to 255 (white), which indicates the crystallinity within diffracted layer which is around 20 nm. Pattern quality indicates the crystalline properties within the incident electron beam, and we adapted it as the criterion for short-range crystallinity of poly-Si. The maximum frequency appears at 50 for SMC poly-Si film with O$_2$ plasma treated for 60 s. On the other hand, it appears at 25 for SMC poly-Si film with O$_2$ plasma treated 120 or 0 s (no nanocap). As a result, the crystalline quality of poly-Si can be improved by using a SiO$_2$ nanocap on the a-Si. However, in case of the plasma treatment time of either zero or exceeding 60 s, the pattern quality of the poly-Si is less than that of the other samples. Note that the pattern quality is 200 for a single-crystalline Si.

Figure 7 shows the EBSD misorientation mapping images and its distributions of the SMC poly-Si films according to O$_2$ plasma treatment time. Normally the grain boundary energy is proportional to the misorientation angle, and it is saturated at $\sim$15°. We defined 15° as the reference angle between low- and high-angle grain boundaries.$^{16,17}$ The grain boundary between adjacent grains is distinguished by high-angle (over than 15°) misorientation.

The grain starts from one nucleation site that is assumed to be at the center of a grain. The nuclei are formed from the aggregation of NiSi$_2$ crystallites, but it needs to be a critical size. The lateral grain growth from the seeds proceeds until collision with neighboring grains; high-angle grain boundaries then appear. Upon increasing the O$_2$ plasma treatment time, the fraction of low-angle boundary is higher and the fraction of high-angle boundary is lower because of the increase of the grain size. The amount of Ni atoms diffused into the a-Si depends on the SiO$_2$ thickness because a lot of Ni atoms reside in the SiO$_2$. The density of Ni in the a-Si decreases upon increasing the SiO$_2$ thickness; therefore, the
grain size increases with the plasma oxidation time. The field-effect mobility of the poly-Si TFTs studied in this work increases with increasing the plasma treatment time because of the increase of the grain size. These results will be published as a separated paper.

IV. CONCLUSION

We investigated the crystalline orientation of the disk-shaped grain and grain boundary characteristics in the poly-Si which was formed by SMC of a-Si using a SiO$_2$ nanocap layer and compared it without the cap layer. The nanocap was formed by the O$_2$ plasma treatment on the a-Si. Upon increasing O$_2$ plasma treatment time, the fraction of high-angle boundary is reduced and the grain size of the poly-Si increases from 6 to $\sim 20 \mu m$. The crystalline quality is improved with increasing the O$_2$ plasma exposure time, which is due to the less diffusion of Ni through the nanocap upon increasing its thickness. The SiO$_2$ nanocap layer can be a filter for the Ni diffusion to the a-Si.

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References: