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A Novel Vapor-Induced Crystallization of Amorphous Si Using the Transport of Al/Ni Chloride

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Al/Ni chloride vapor has been employed for the first time to enhance the crystallization of amorphous Si (a-Si) films. a-Si films under the vapor at 480°C were completely crystallized in 5 h. At the initial stage of the vapor induced crystallization (VIC), the seed grains were nucleated evenly throughout the film and their grain size was uniform. The final grain size was larger than 10 μm, depending on the process conditions. The poly-Si films showed a very smooth surface with a roughness of 4.26 Å due to the double surface-oxide layer formed during the VIC process.
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The solid phase crystallization (SPC) of amorphous Si (a-Si) films results in large grains compared to direct deposition of poly-Si films. To reduce the crystallization temperature and improve the crystallinity of poly-Si in the SPC process, many methods such as metal induced crystallization (MIC),[1,2] metal induced lateral crystallization (MILC),[3] field-aided lateral crystallization (FALC),[4,5] microwave-enhanced crystallization,[6] and metal induced crystallization through a cap (MICC)[7] have been developed.

In Al-induced crystallization (AIC), no intermediate-compound exists between a-Si and crystallized Si.[8] Instead, a solid solution interlayer exists between them. In AIC, the grains grow in all directions, resulting in larger grains compared to the needle-shaped grains grown by Ni-induced crystallization. AIC can significantly relieve metal contamination, compared to Ni metal induced crystallization. Al exists as a shallow acceptor with an ionization energy of 0.067 eV in single crystal Si. The incorporation of Al during the crystallization yields p-type poly-Si.[9] The disadvantage of the AIC process is that the poly-Si film has a rough surface and contains many voids.[10] By utilizing $AlCl_3$ vapor for AIC, instead of Al metal film, the surface roughness of the poly-Si film can be as smooth as that of the intrinsic poly-Si film.[11] Crystallization is enhanced with the effect of $AlCl_3$ vapor such that crystallization can be completed in 5 h at 540°C. The crystallization of a-Si using $AlCl_3$ vapor has some problems, however, such as nonuniform crystallization, poor reproducibility, and much higher crystallization temperature compared to other MIC processes with a metal layer.

In this study, we report a new VIC process that employs Al/Ni chloride vapor. The crystallization temperature was reduced to as low as 470°C and the grain size was as large as 20 μm.

a-Si films (100 nm thick) were deposited on oxidized Si wafers by low-pressure chemical vapor deposition (LPCVD) at 550°C using SiH_4 and they were crystallized by the VIC process using the vapor transport of Al/Ni chloride. In the VIC process, two heating systems are required: one for source evaporation, the other for sample annealing.

Figure 1 shows a schematic diagram of the annealing system for the VIC process. The source temperature was 200°C and the sample annealing temperature was varied from 450 to 600°C. The source was composed of $AlCl_3:NiCl_2 = 10:1$ and was transported from the source zone to the annealing zone as a vapor phase by Ar flow. Ar was continuously supplied before and during the annealing with a flow rate of 0.5L/min. The crystallinity was investigated by X-ray diffraction (XRD) and a scanning electron microscope (SEM). The grain morphology and film structure of the poly-Si were observed by SEM and a transmission electron microscope (TEM). The surface roughness of crystallized poly-Si film was investigated by atomic force microscopy (AFM).

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Figure 2 shows the crystallized fraction of the a-Si films after annealing at various temperatures for 5 h. The crystallized fraction was calculated from the XRD (111) intensities and SEM observations. Crystallization noticeably occurs at a temperature as low as 470°C. The minimum temperature for complete crystallization in 5 h was 480°C. The crystallization was remarkably retarded below 460°C. Considering that the crystallization of a-Si film with only $AlCl_3$ vapor occurs at about 540°C,[11] the crystallization with Al/Ni chloride was greatly enhanced.

Figure 3 shows an SEM image of fully crystallized poly-Si film annealed at 480°C for 10 h. The grains are impinged together and display various octagonal disk shapes. The grain size is about 15 μm and is very uniform. Also note that no voids are observed in the film. In the conventional AIC process, many voids have been observed. The grain boundaries were delineated by Secco etching with a $CrO_3:49\%\,HF:H_2O = 0.75M:1:100$ solution. In Ni-induced lateral crystallization, needle-shaped grains are grown and the width and length of the grains are about 50 nm and about 8 μm, respectively.[12] The grain size by the VIC process is much larger than that by Ni-induced lateral crystallization.

Figure 4 shows an SEM image of poly-Si grains grown on a-Si film after annealing at 480°C for 1 h in an Al/Ni chloride atmosphere. The grains were observed after removing the non-crystallized a-Si region by Secco etching. Figure 4a shows that the poly-Si grains are evenly distributed at the initial stage of crystallization and their size is very uniform. At higher magnification (Fig. 4b), the core of the grains shows a dense and smooth surface. No significant inherent structural defects were observed.

Generally, needle-shaped grains grow by Ni-silicide mediated crystallization (Ni-SMC)[12] process and round-shaped grains grow by AIC process.[8] Our early TEM observation found that, at the

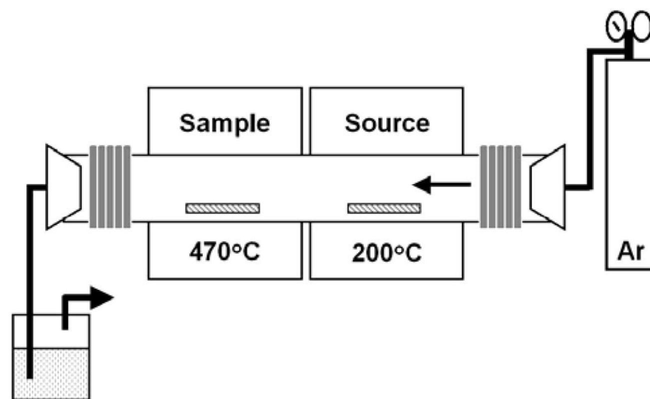

Figure 1. Schematic diagram of the annealing system for the VIC (vapor induced crystallization) process.

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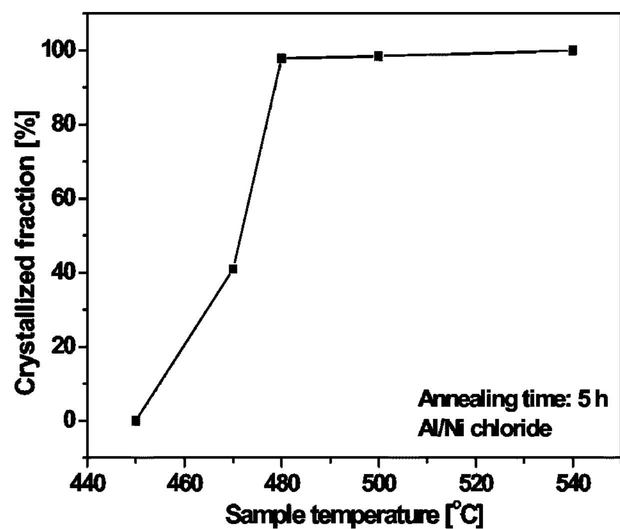


Figure 2. Crystallized fraction as a function of annealing temperature.

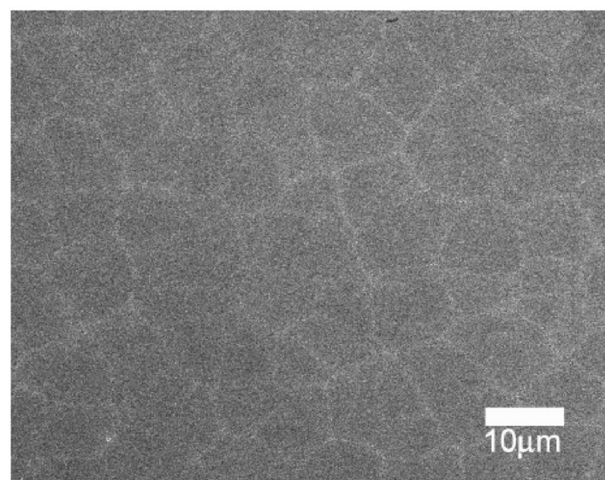


Figure 3. SEM image of fully crystallized poly-Si film annealed at 480°C for 10 h using Al/Ni chloride vapor.

growth front of those seed grains shown in Fig. 4a, needle-shaped grains grew by the SMC process and later merged themselves by the AIC process, resulting in large grains. The detailed growth mechanism in our VIC process will be reported soon.

Figure 5a is a TEM image of the cross-section of the a-Si film at the initial stage of crystallization. Note that a surface layer with a

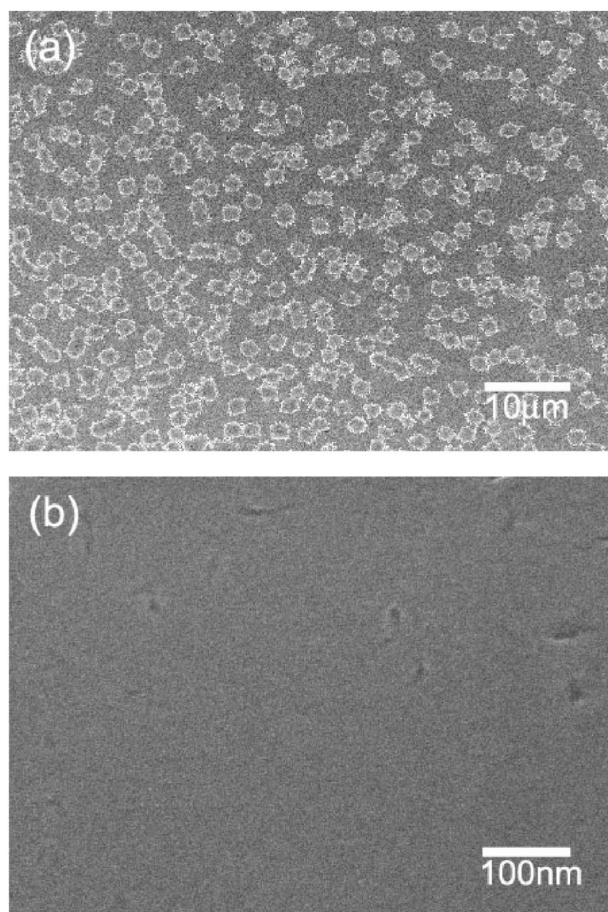
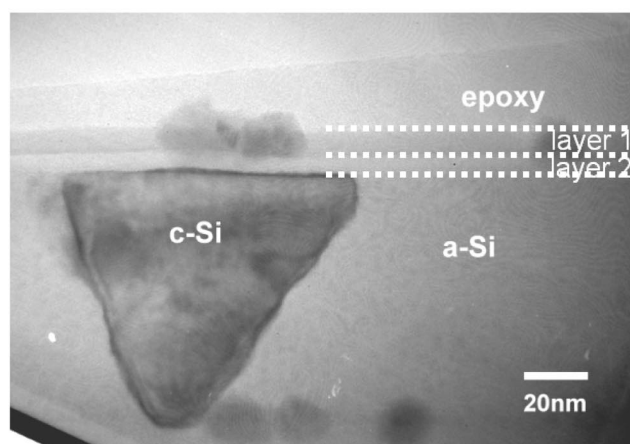
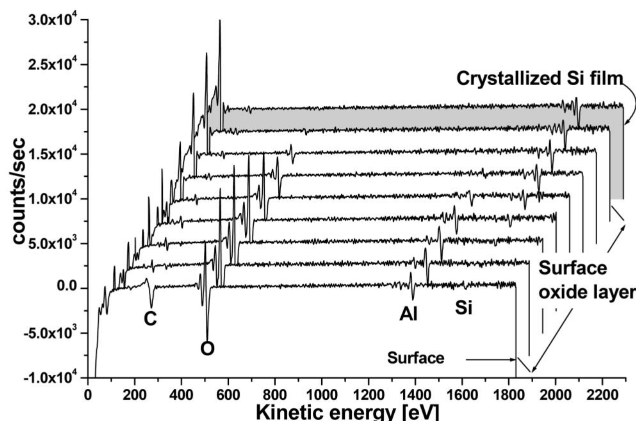


Figure 4. SEM image of poly-Si annealed at 480°C for 1 h using Al/Ni chloride vapor: (a) grain distribution and (b) microstructure in grain core.



(a)



(b)

Figure 5. (a) Cross-sectional TEM image of Si film after annealing at 480°C for 1 h using Al/Ni chloride vapor and (b) AES depth profile of the Si films annealed at 480°C for 10 h by using Al/Ni chloride vapor.

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thickness of about 20 nm was formed on the a-Si film during the VIC process. From the AES depth analysis of the poly-Si film fully crystallized using the VIC process, as shown in Fig. 5b, the surface layer was found to be composed of a top layer with Al and O components and a bottom layer with Si and O components, indicating that the surface layer is an Al_2O_3/SiO_2 double layer. The thicknesses of the Al_2O_3 and SiO_2 layers are about 10 nm each. The surface roughness of the poly-Si films crystallized by the VIC process, measured by AFM, was 4.26 Å, while that of the intrinsic poly-Si film was 6.33 Å in rms value. It is considered that the surface oxide layer limits the growth direction of poly-Si grains, resulting in a very smooth poly-Si surface. It is believed that the oxide layers are formed by the existence of oxygen even in Ar atmosphere. The double layer is formed due to the supply of Al from $AlCl_3$ gas on the a-Si film. More detailed study on the metal diffusion and contamination through the oxide layer will be reported later.

In conclusion, a VIC method that utilizes Al/Ni chloride has been introduced for the first time. It was found that the VIC process using Al/Ni chloride greatly enhanced the crystallization of a-Si and the minimum crystallization temperature was as low as 470°C. In the VIC process, seed grains were grown evenly throughout the Si film and their grain size was uniform. The grain size of fully crystallized poly-Si annealed at 480°C for 10 h was larger than 10 μm and the grains showed a dense and smooth surface. An Al_2O_3/SiO_2 layer was formed on the Si film during the VIC process, enabling a smooth poly-Si surface.

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