Microstructural improvement in polycrystalline Si films by crystallizing with vapor transport of Al/Ni chlorides

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Abstract

We developed a vapor induced crystallization (VIC) process for the first time to obtain high quality polycrystalline Si films by sublimating the mixture of $AlCl_3$ and $NiCl_2$.

The VIC process enhanced the crystallization of amorphous silicon thin films. The LPCVD amorphous silicon thin films were completely crystallized after 5 hours at 480℃. It is known that needle-like grains with very small width grow in the Ni-metal induced lateral crystallization. In our new method, the width of grains is larger because the grain can also grow perpendicular to the needle growth direction. Also the interface between the merging grain boundaries was coherent. As the results, a polycrystalline film with superior microstructure has been obtained.

1. Introduction

Demands of high-quality polycrystalline silicon thin films are increasing for the application to fabrication of electronic devices such as thin film transistors (TFTs) for OLED, solar cells, SRAM, EEPROM and image sensors. Polycrystalline Si thin films are generally fabricated by crystallizion of amorphous silicon (a-Si) thin films because it can render larger grains compared to directly deposited poly-Si films. But it generally takes tens of hours to crystallized a-Si films even at 600℃, which is an extremely high temperature for large area glass substrates.

Metal induced lateral crystallization (MILC) [1] is considered as one of the most effective and superior methods in solid phase crystallization. It controlled the direction of needle-shaped poly-Si grains and made a bundle of needle-shaped grains in the same direction. But the bundle of needle-shaped grains, (quasi-grains) had many low-angle grain boundaries. The crystallized poly-Si by MILC contained metal silicide residue. So many low-angle grain boundary and residue of metal silicide degrade device performance for example, lowering field effect mobility and increasing leakage current in TFTs.

Aluminum makes simple eutectic system with silicon. When using aluminum metal film, that made rough film surface and many voids in the poly-Si film [2,3]. The shape of grains by the AIC (aluminum induced crystallization) is more is more spherical. And aluminum exists as a shallow acceptor with the ionization energy of 0.067eV in single crystal Si. The incorporation of aluminum during the crystallization makes the poly-Si p-type. The existence of Al can significantly relieve the contamination, compared to Ni.

In this study, we investigated the vapor induced crystallization of a-Si using vapor transport of the mixture of Al/Ni chlorides and found that the microstructure of the poly-Si film was greatly improved compared to the MILC process.

2. Experimental

100-nm-thick a-Si films were deposited on the oxidized Si wafers by low-pressure chemical vapor deposition at 550°C using SiH_4. The annealing process was conducted in metal chloride atmospheres using conventional furnace. We made the metal chloride atmosphere by sublimating the mixture of $AlCl_3$ and $NiCl_2$. Ar was continuously supplied before and during the annealing with a flow rate of 0.5l/min. The sample temperature was varied and the metal chloride source temperature was fixed at 200℃.

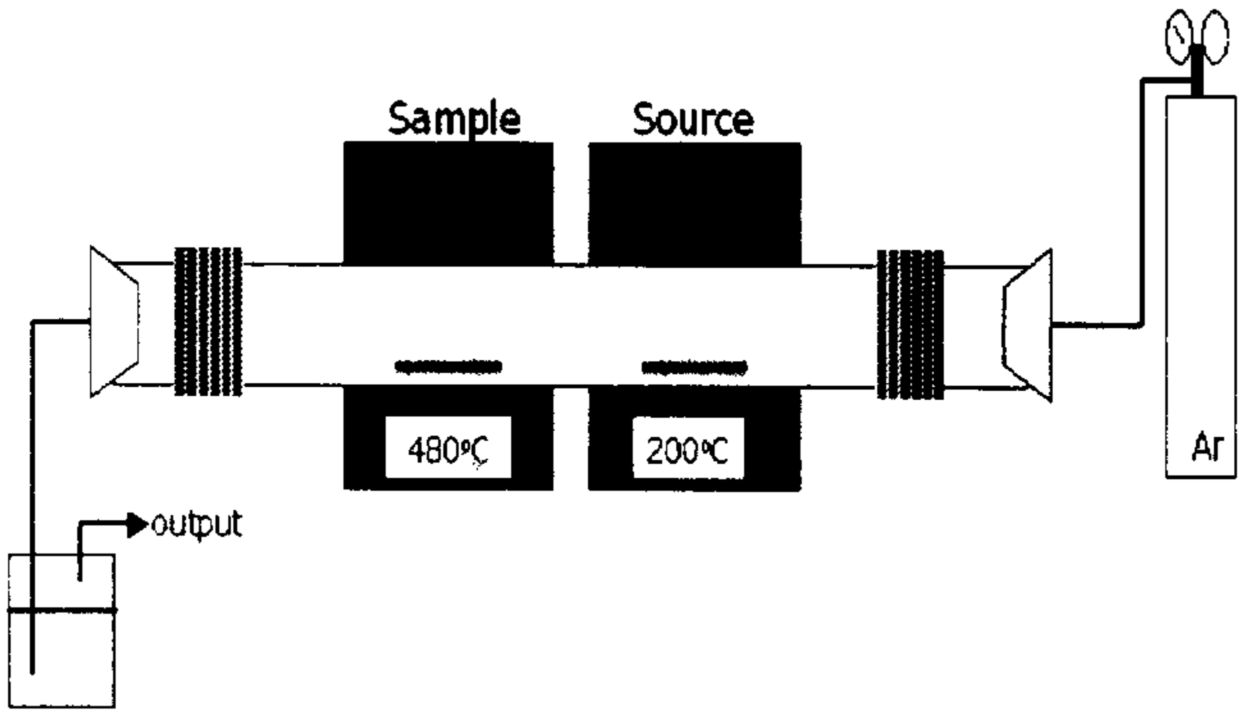


Figure 1. Schematic diagram of the furnace used for VIC (vapor induced crystallization) process.

3. Results and discussion

We reported the utilization of $AlCl_3$ vapor for AIC, instead of Al metal film [4]. Al was supplied in the form of vapor from the $AlCl_3$ located in the vicinity of the a-Si films. Crystallization was enhanced in the effect of $AlCl_3$ vapor the crystallization was completed in 5h at 540°C, while it took about 30h at 600°C for intrinsic a-Si without Al supply. The surface roughness of the poly-Si film was as smooth as that of the intrinsic poly-Si film. The grain grows circular shape (Fig. 2(a)). Al was not detected in AES depth profile in the crystallized Si film..

Using only $AlCl_3$ vapor, crystallization of a-Si had some problems for example, non-uniform crystallization, reproducibility and much higher crystallization temperature than that of other metal layer. To improve that problem, we add small amount of $NiCl_2$. This lowered the crystallization temperature (crystallization was completed at 480°C for 5 hours), made uniform crystallization and improved reproducibility.

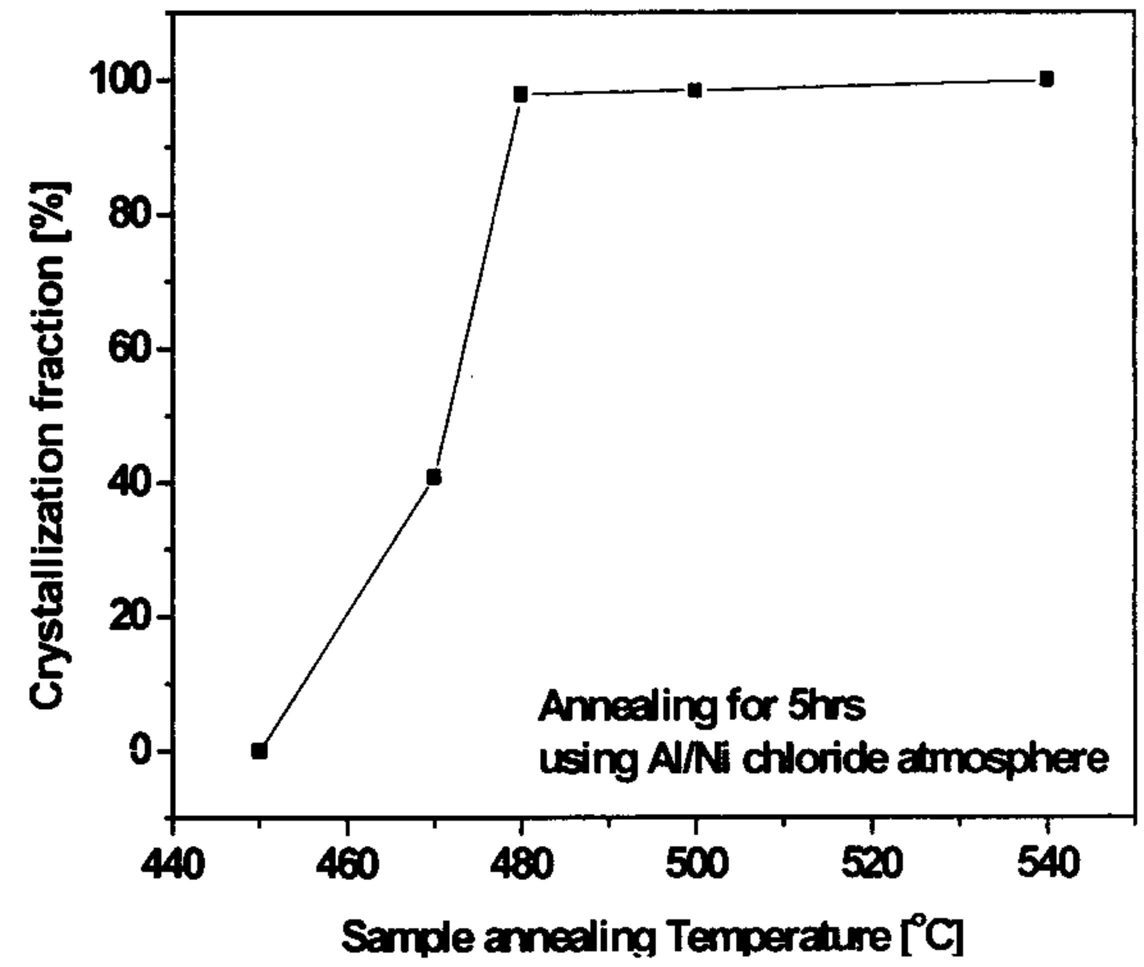
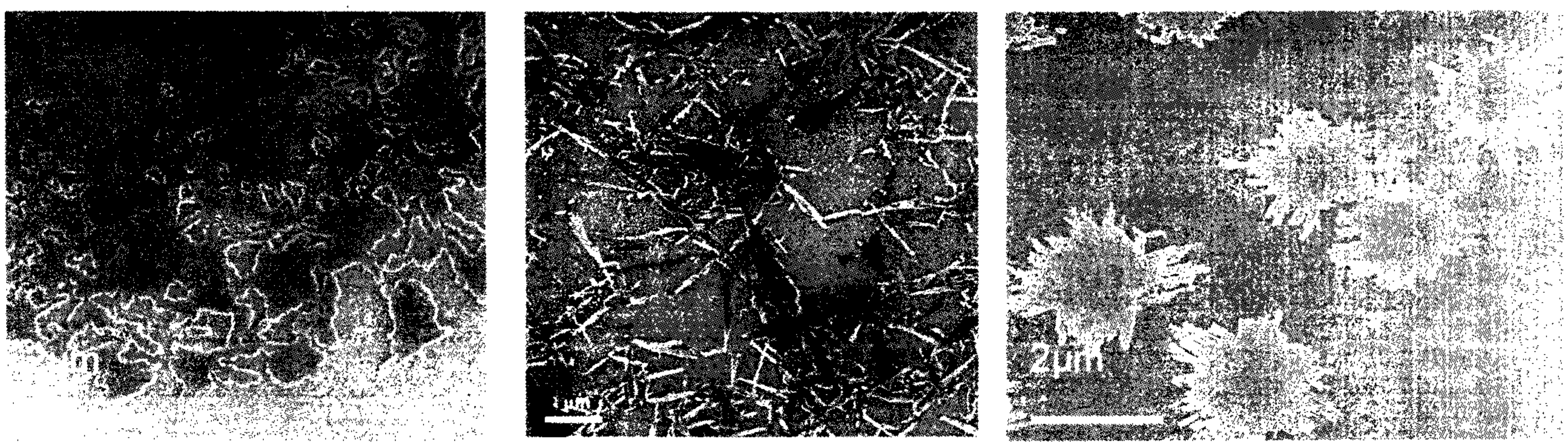


Figure 3. Crystallization fraction as a function of annealing temperature.

Figure 4 is cross sectional HRTEM image at the initial crystallization stage that shows the lateral growth from needle shape grain made by silicide moving direction. Using $AlCl_3$+$NiCl_2$ vapor phase, poly-Si grain growth can also grow perpendicular to the direction of needle growth. Nickel from $NiCl_2$ induced crystallization made the needle-shaped grain and Al from $AlCl_3$ contained in a-Si enhanced the lateral growth from needle shape grain.



(a) (b) (c)

Figure 2. Initial stage of crystallization (a) using only $AlCl_3$ atmosphere (annealing at 550℃ for 5h) (b) using Nickel solution (annealing at 500℃ for 1.5h) (c) using $AlCl_3$+$NiCl_2$ atmosphere (annealing at 480℃ for 1h).

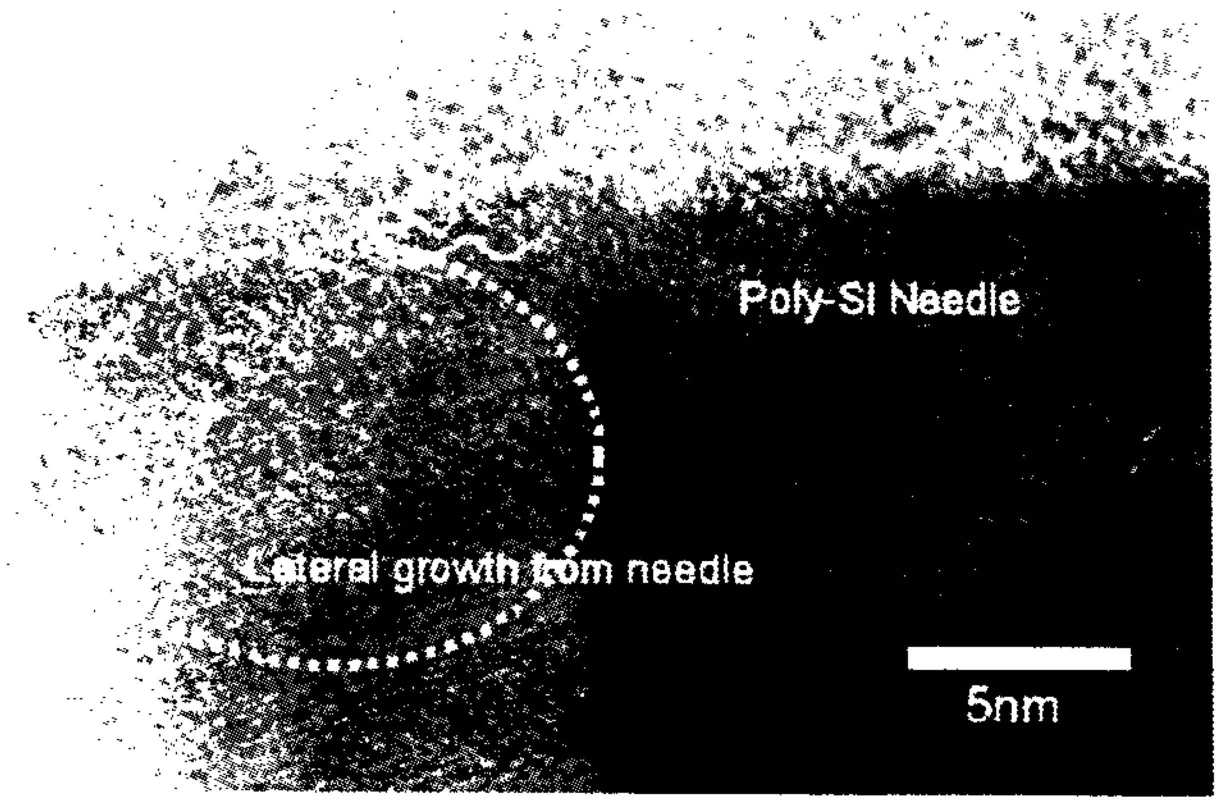


Figure 4. Cross sectional HRTEM image of poly-Si annealed at 480℃ for 1h by $AlCl_3$+$NiCl_2$

Figure 5 is the top view HRTEM image of poly-Si film crystallized by VIC. That shows a grain boundary between the merging grains. The needle-shaped grains grow defect freely and the grains merge coherently. As the results, a polycrystalline Si film with superior microstructure can be obtained.

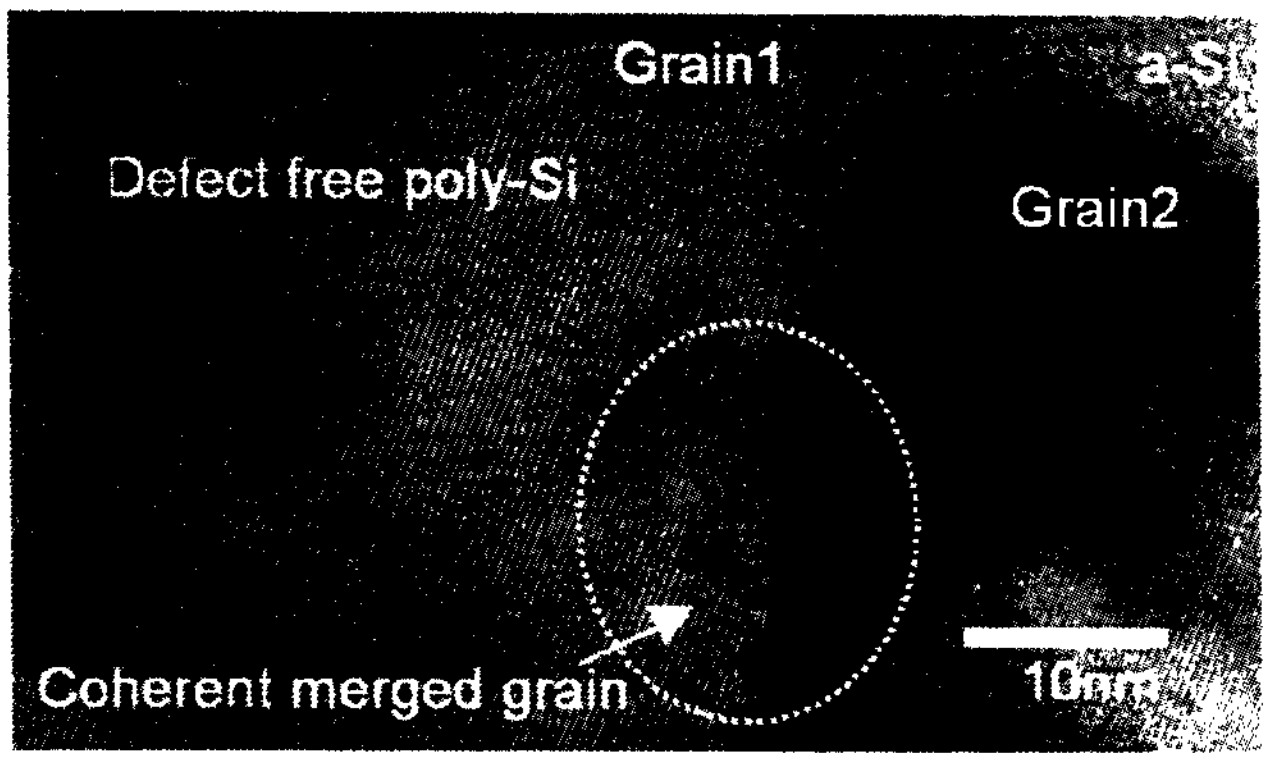


Figure 5. Plane view HRTEM image of poly-Si annealed at 480℃ for 1h by $AlCl_3$+$NiCl_2$

Figure 6 is the cross sectional TEM image at the initial crystallization stage. Surface oxide layers are shown. In AES analysis, the 1st surface layer was composed of Al and O and the 2nd surface layer was composed of Al, Si and O. It is considered that the metals are supplied through surface oxide double layer in the VIC process. That can reduce the metal contamination in crystallized Si films and provide a smoother surface. The surface roughness of the poly-Si films crystallized by the VIC process measured by AFM, was 4.26Å while that of the intrinsic poly-Si film was 6.33Å in rms value.

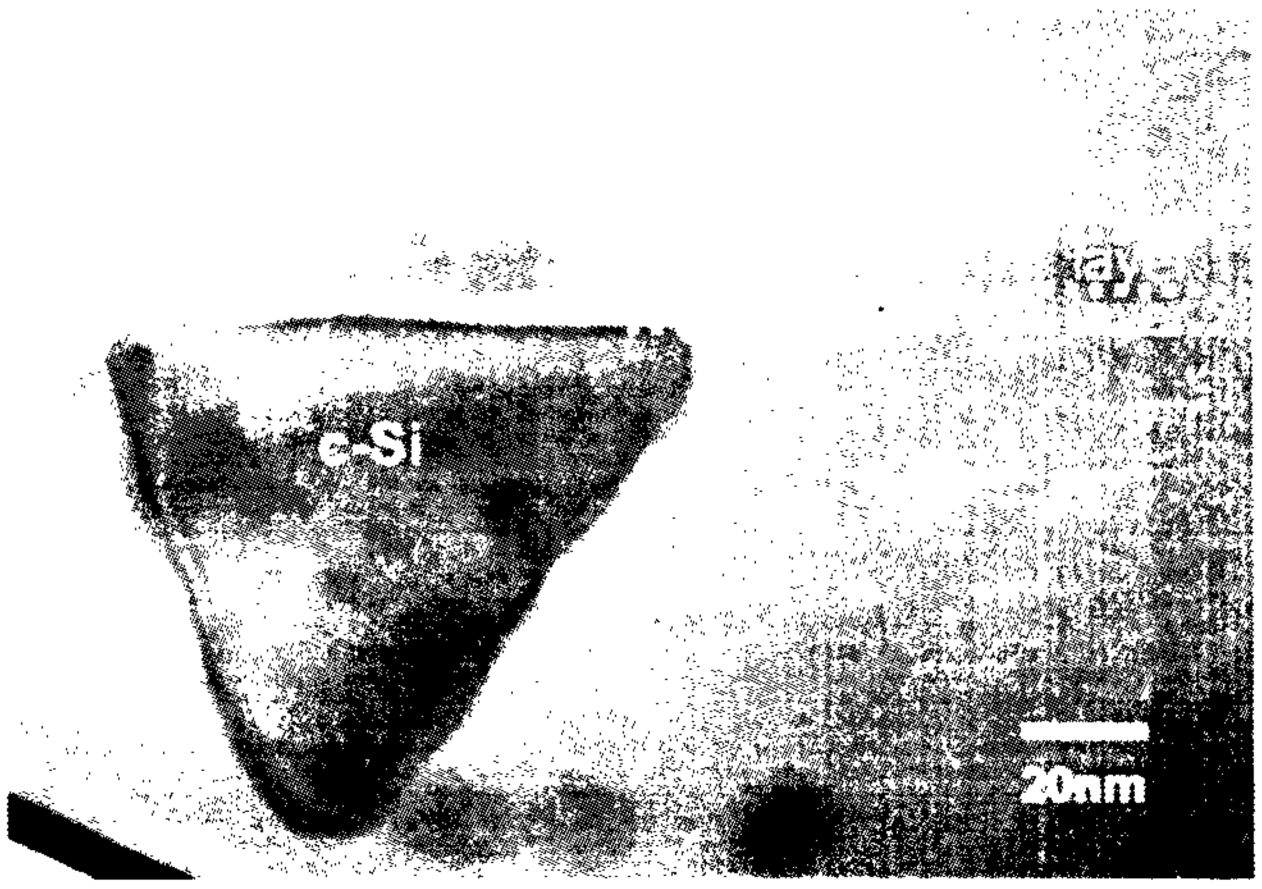


Figure 6. Cross sectional TEM image of poly-Si annealed at 480℃ for 1h by $AlCl_3$+$NiCl_2$

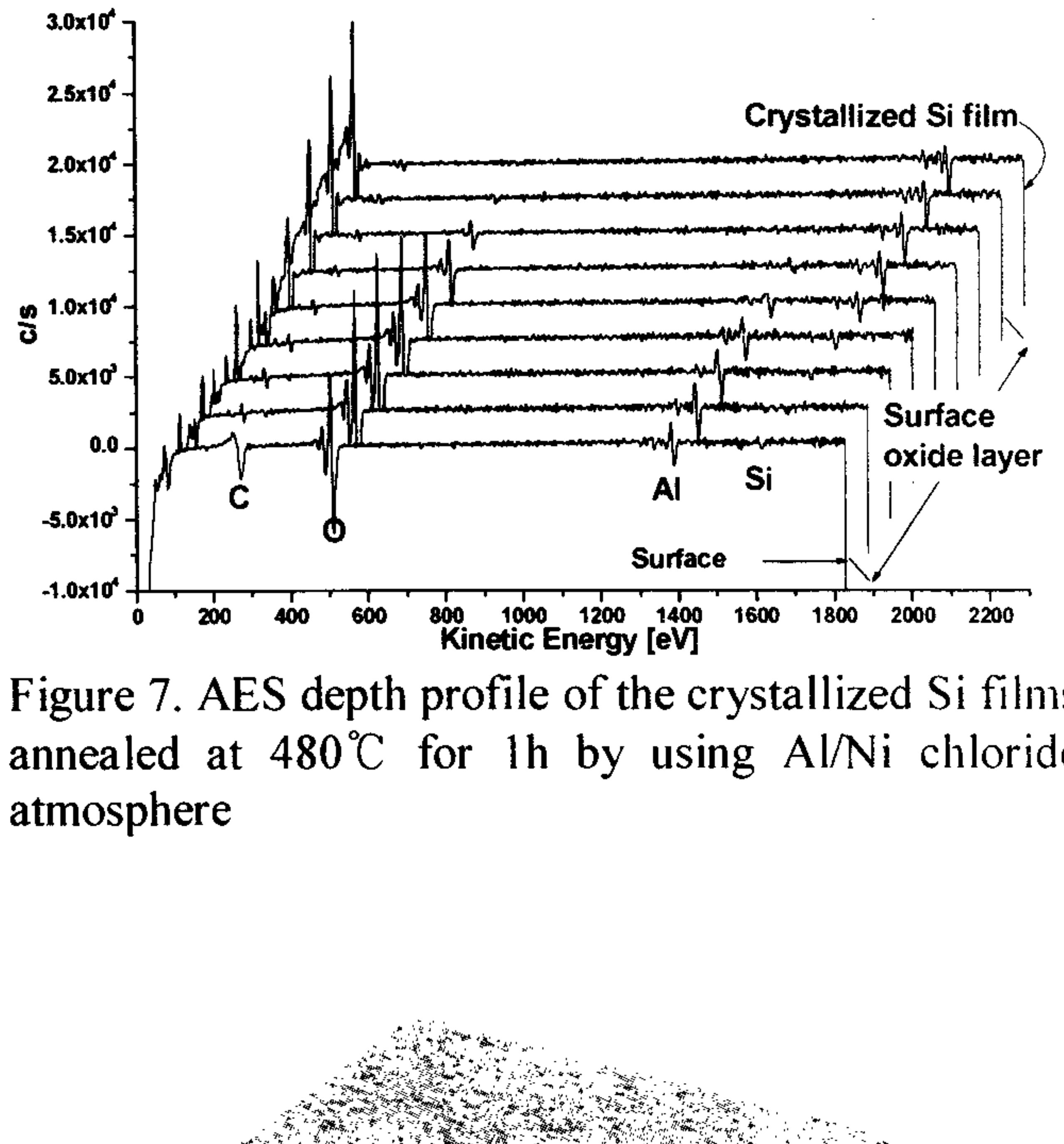


Figure 7. AES depth profile of the crystallized Si films annealed at 480℃ for 1h by using Al/Ni chloride atmosphere

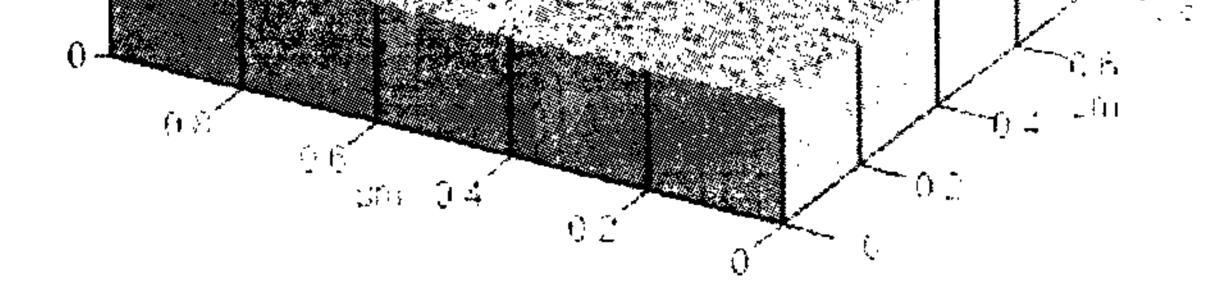


Figure 8. AFM image of poly-Si annealed at 480℃ for 5h by $AlCl_3$+$NiCl_2$ (RMS roughness = 4.26Å)

4. ConclusionWe developed a new VIC process by using Al/Ni chloride vapor. The mixture of $AlCl_3$ and $NiCl_2$ atmosphere enhanced the crystallization of amorphous silicon thin films and improved microstructure of crystallized Si film.

The LPCVD amorphous silicon films were completely crystallized after 5 hours at 480℃ using VIC process. In our new method, the width of needle-shaped grains is larger than MILC process. Because the grain can also grow perpendicular to the needle-shaped grain growth direction. In MILC process needle-shaped grain boundaries made low angle grain boundaries. But our VIC process, the interface between the needle-shaped grain boundaries was merging coherently. As the results, the polycrystalline Si films have superior microstructure. The metals supplied through surface oxide double layer in the VIC process. That can reduce metal contamination and make smooth surface, 4.26Å rms roughness by AFM. We fabricated n-channel poly-Si TFTs using polycrystalline silicon films crystallized by the VIC process. The maximum field-effect mobility is $61.3 cm^2/V\,s$ at drain voltage V_d=0.1V.

5. References

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