## Microstructural study of polycrystalline films prepared by Ni vapor induced crystallization

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#### **Abstract**

NiCl<sub>2</sub> vapor was introduced into conventional furnace to conduct vapor-induced crystallization (VIC) process. We made the metal chloride atmosphere by sublimating the NiCl<sub>2</sub> compound. The NiCl<sub>2</sub> atmosphere enhanced the crystallization of amorphous silicon thin films. As the result, polycrystalline Si film with large grain size and low metal contamination has been obtained.

#### 1. Introduction

Demands of high-quality polycrystalline silicon (poly-Si) thin films are increasing for the application to fabrication of electronic devices such as thin film transistors (TFTs), solar cells, SRAM, EEPROM and image sensors. Poly-Si thin films are generally fabricated by recrystallizion of amorphous silicon (a-Si) thin films because lager grains and smoother surfaces can be attained compare to direct deposition of poly-Si films. But it generally takes tens of hours to crystallized a-Si films even at 600°C, which is an extremely high temperature for large area glass substrates.

Metal induced crystallization (MIC)<sup>1,2</sup> is considered one of the most effective and superior methods in solid phase crystallization. By using metals, crystallization temperature and time drastically lowered. There are some effective metals such as Au, Ag, Cu, Ni, Al. But crystallized poly-Si film contained residual metal contamination. So many of residual metal induced decline of device performance for example, lowering field effect mobility and large leakage current in thin film transistor (TFT) application.<sup>3</sup>

In our previous work, we reported the utilization of AlCl<sub>3</sub> vapor for AlC, instead of Al metal film deposition.<sup>4</sup> Al was supplied in the form of vapor

from the AlCl<sub>3</sub> Crystallization was enhanced in the effect of AlCl<sub>3</sub> vapor the crystallization was completed in 5h at 540°C.

In this work, we employ the NiCl<sub>2</sub> as a Ni source. Ni was supplied in the form of vapor from the NiCl<sub>2</sub> located in the vicinity of the a-Si films. By Ni chloride VIC process, poly-Si film was fabricated at low temperature.

#### 2. Results

100-nm-thick a-Si films were deposited on the oxidized Si wafers by low-pressure chemical vapor deposition (LPCVD) at 550°C using SiH<sub>4</sub>. The annealing process was conducted in metal chloride atmospheres. We made the metal chloride atmosphere by sublimating the NiCl<sub>2</sub> powder. In the VIC process, two heating systems are required: one for source sublimation, the other for sample annealing.

Figure 1 shows the schematic diagram of the furnace used for process. The sample annealing temperature was varied from  $400^{\circ}\text{C}$  to  $530^{\circ}\text{C}$  and the metal chloride source temperature was fixed at  $500^{\circ}\text{C}$ . Ar gas was continuously supplied before and during the annealing with a flow rate of 0.51/min.

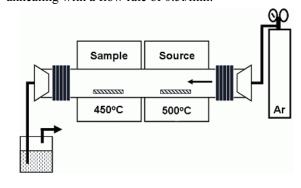


Figure 1. Schematic diagram of the furnace used for VIC process

The crystallinity of crystallized film was investigated by X-ray diffraction (XRD). The grain morphology of the poly-Si was observed by scanning electron microscope (SEM) and Optical microscope (OM). The residual metal of crystallized film was investigated by auger electron spectroscopy (AES).

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) peak intensities and SEM observations. The crystallization noticeably occurs as low as 430°C. The minimum temperature for complete crystallization in 5 h was 450°C. The crystallization was remarkably retarded below 400°C. Considering that the crystallization of a-Si film with only AlCl<sub>3</sub> vapor occurs about 540°C, the crystallization with nickel chloride was greatly enhanced.

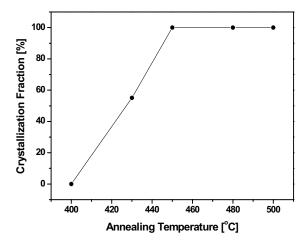


Figure 2. Crystallization fraction as a function of annealing temperature for 5h.

Figure 3 shows an OM image of fully crystallized poly-Si film annealed at  $450^{\circ}$ C for 10 h. Before observation of grain, the grain boundaries were delineated by Secco etching with a CrO<sub>3</sub>: 49%HF:  $H_2O=0.75M$ : 1: 100 solution. The grains display various octagonal disk shapes. The grain size is about 13  $\mu$ m and very uniform. The grain size by the VIC

process is much larger than that by Ni-induced lateral crystallization.

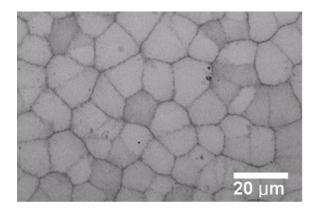
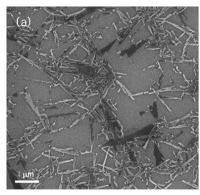


Figure 3. SEM image of fully crystallized poly-Si film annealed at 480°C for 5 h using Ni chloride vapor.

Figure 4 shows SEM images of poly-Si grain at initial stage of crystallization. The grains were observed after removing the non-crystallized a-Si region by Secco etching. Figure 4(a) shows the poly-Si film after annealing at 430°C for 3 h in an Ni chloride atmosphere and figure 4(b) shows the poly-Si film after annealing at 500°C for 1.5h using Ni solution. Using nickel solution, poly-Si needle was grown entire of film and width of needle was very narrow. But using Ni vapor, grains was grown partially and width of needle was very large. The needle size by the VIC process is much larger than that by Ni induced lateral crystallization.

Figure 5 shows AES spectra of crystallized poly-Si using Ni chloride at 450 °C for 5hous. In AES analysis, Si peak was detected but Ni peak was not found. Ni concentration of crystallized film was below the detection limit of AES analysis. Crystallized Si film has very low residual Ni concentration. So poly-Si film by VIC using Ni chloride is suitable for active layer of TFTs.



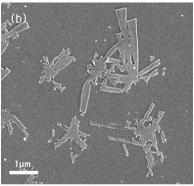


Figure 4. Initial stage of crystallization (a) using only Nickel chloride atmosphere (annealing at 430  $^{\circ}$ C for 3h) (b) using Nickel solution (annealing at 500  $^{\circ}$ C for 1.5h)

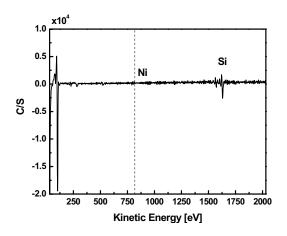


Figure 5. AES spectra of crystallized poly-Si film using Ni chloride at  $450\,^{\circ}$ C for 5h.

### 3. Conclusion

We fabricate a poly-Si film by VIC process using Ni chloride vapor. The NiCl<sub>2</sub> 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  $450^{\circ}\text{C}$ .

At the initial stage of crystallization, width of poly-Si needle using Ni vapor VIC process was very larger than that using Ni solution. Fully crystallized film had a very good microstructure and morphology at low annealing temperature. Grain size of poly-Si is very large, so the grain boundary area can be greatly reduced. And poly-Si film has very low residual metal contamination. It is expected that the leakage current in poly-Si TFTs can be lowered. This result might be one of the solutions to reduce leakage current in poly-Si TFTs. The new method might be possibly applied to poly-Si TFTs for advanced flat panel display devices.

#### 4. References

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