Effects of Oxygen in Ni Films on Ni-Induced Lateral Crystallization of Amorphous Silicon Films at Various Temperatures

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Effects of oxygen in Ni films on the Ni-induced lateral crystallization (NILC) of amorphous silicon (a-Si) films at various temperatures have been investigated. It was found that oxygen in Ni films retarded the nucleation of polycrystalline silicon (poly-Si) from a-Si, but had little effect on the growth rate of poly-Si. This is because that needed an incubation period to be reduced to Ni metal for the subsequent mediated crystallization of a-Si.

Key words: Nickel-induced lateral crystallization (NILC), amorphous silicon, polycrystalline silicon, oxygen, nickel oxide

INTRODUCTION

Low-temperature polycrystalline silicon (poly-Si) thin-film transistors (TFTs) have attracted considerable interest for their use in active matrix liquid crystal displays, because they exhibit good electrical properties and can be integrated in the peripheral circuits on inexpensive glass substrates.[1,2] Since poly-Si TFTs require glass substrates, intensive studies have been carried out to lower the crystallization temperature of Si films. For this purpose, two major methods have been used: the direct deposition of poly-Si and the deposition of amorphous silicon (a-Si) followed by thermal crystallization. The crystallization of a-Si thin films is a more promising approach to obtaining polycrystalline thin films, because it can produce larger grains and smoother surfaces.[3]

Three types of annealing processes have been used to crystallize a-Si: (1) excimer laser annealing (ELA), (2) solid phase crystallization (SPC), and (3) Ni-metal-induced lateral crystallization (NILC). Among these three processes, ELA of a-Si films appears to be very promising due to its lower thermal budget, shorter processing time, and ability to produce poly-Si films with better quality.[4] However, the equipment cost is high. As for the SPC method, it is a well-established poly-Si formation technique with several advantages over ELA, including smoother surfaces, better uniformity, and the use of the batch process in furnace annealing.[5,6] The major drawback of SPC is that a-Si films need to be annealed at 600°C for 24 h. The temperature is higher than the strain temperature of a glass substrate, and the time required to crystallize Si films is too long.

In comparison, the NILC method has a lower equipment cost than ELA and a lower thermal budget than SPC. In the NILC method, a thin Ni metal layer was deposited on the surface of the a-Si film and followed by crystallization at a temperature lower than 600°C in a nitrogen ambient atmosphere to avoid oxidation.[7–11] The Ni was usually deposited by the physical vapor deposition (PVD) method in an ultrahigh vacuum (UHV) apparatus to avoid oxidation of the Ni film.[7–11] The process is time-consuming and expensive in terms of equipment cost. To replace this PVD method, an electroless plating Ni was proposed in our previous study.[12,13] Since there was no vacuum process involved, the plating method was much simpler, faster, and less expensive than the traditional PVD method. The only question is the purity of electroless Ni, which is not as good as that of PVD Ni. Thus, the principal goal of this study is to investigate the effects of Ni purity (oxygen in the Ni films) on the NILC mechanism in order to determine the necessity of the UHV deposition system for crystallization of a-Si.

EXPERIMENT

Silicon (100) wafers were used as the substrates in this study. Wet oxide films of thickness 500 nm were grown by using a H_2/O_2 mixture at a substrate temperature of 1,050°C. Silane-based a-Si films

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with a thickness of 100 nm were then deposited by a low-pressure chemical vapor deposition system at 550°C. A lift-off process using photoresist was employed to form islands of metal films on the wafers. The photoresist was first patterned to expose selected regions of the a-Si thin film. Prior to loading the wafers into the metal deposition chamber, the native silicon oxide on the a-Si films was removed by dipping the wafers in diluted HF. Nickel or nickel oxide films were then deposited on the top of a-Si. They were designated as "NI" and "NIO," respectively. The NI film was deposited by direct current (DC) sputtering at room temperature. The total thickness deposited was about 10 nm. As for the NIO film, it was deposited by a cold DC sputter in air atmosphere.[14,15] The thickness was also about 10 nm. After the deposition of the metal film, the wafers were dipped in acetone to dissolve the photoresist and to lift off unwanted metal. Wafers were cut into 1×1 cm^2 samples and then annealed in a nitrogen atmosphere at temperatures between 500°C and 600°C.

RESULTS AND DISCUSSION

Figure 1 shows the NILC poly-Si of samples after annealing at 550°C for 12 h. The light region at the periphery of the metal islands was the poly-Si area, which was composed of needlelike Si grains. Scanning electron microscopy (SEM) was also used to study the morphology of the NILC poly-Si region. Figure 2 shows typical SEM images of the poly-Si film after being dipped in the Secco solution.[16] The solution consisted of one part by volume of a 0.15 molar solution of $K_2Cr_2O_7$ in distilled H_2O and two parts HF (49%). The morphologies of the NI sample were similar to that of the NIO sample. The only difference was the NILC lengths of the NI sample were longer than that of the NIO sample.

The NILC length perpendicular to the edge of the metal islands is plotted as a function of the annealing time in Fig. 3. The NILC rate as a function of the annealing time has been estimated by the slope of the curve in Fig. 3 and is listed in Table I. This table clearly shows that the NILC growth rates of both NI and NIO samples increased with annealing temperature.

For the NI sample, the NILC growth rate increased from 0.4 μm/h to 18 μm/h when annealing temperature increased from 500°C to 600°C. This is because the growth of NILC poly-Si is governed by the migration of $NiSi_2$ precipitates through a-Si.[17,18] Hayzelden and Batstone[17] suggested that the driving force behind NILC is that the chemical potential of Ni is lower at the $NiSi_2$/a-Si interface, whereas the chemical potential of Si atoms is lower at the $NiSi_2$/crystal silicon (c-Si) interface. In order to decrease free energy, the Ni atoms should move toward a-Si and they in turn react with a-Si to form new $NiSi_2$. The remaining Si atoms attach to the $NiSi_2$ template to form c-Si because their chemical potential is lower at the $NiSi_2$/c-Si interface. Hayzelden and Batstone[17] also showed that growth velocity is inversely proportional to $NiSi_2$ thickness, which agrees with diffusion-limited growth. In other words, the growth of NILC poly-Si is governed by Ni diffusivity in $NiSi_2$. For this reason, in this study, the increase of the NILC rate with annealing temperature was predictable since the Ni diffusivity increased with annealing temperature.

As for the NIO sample, the NILC growth rate also increased with annealing temperature, as shown in Table I. No NILC length was observed at temperatures below 500°C. When the temperature increased to 550°C, the growth rate (~3.8 μm/h) was the same as that of the NI sample, regardless of the oxygen concentration in Ni. The only difference was that the NIO sample needed a 3.6-h incubation period to start the crystallization of a-Si, whereas the NI sample did not. In other words,

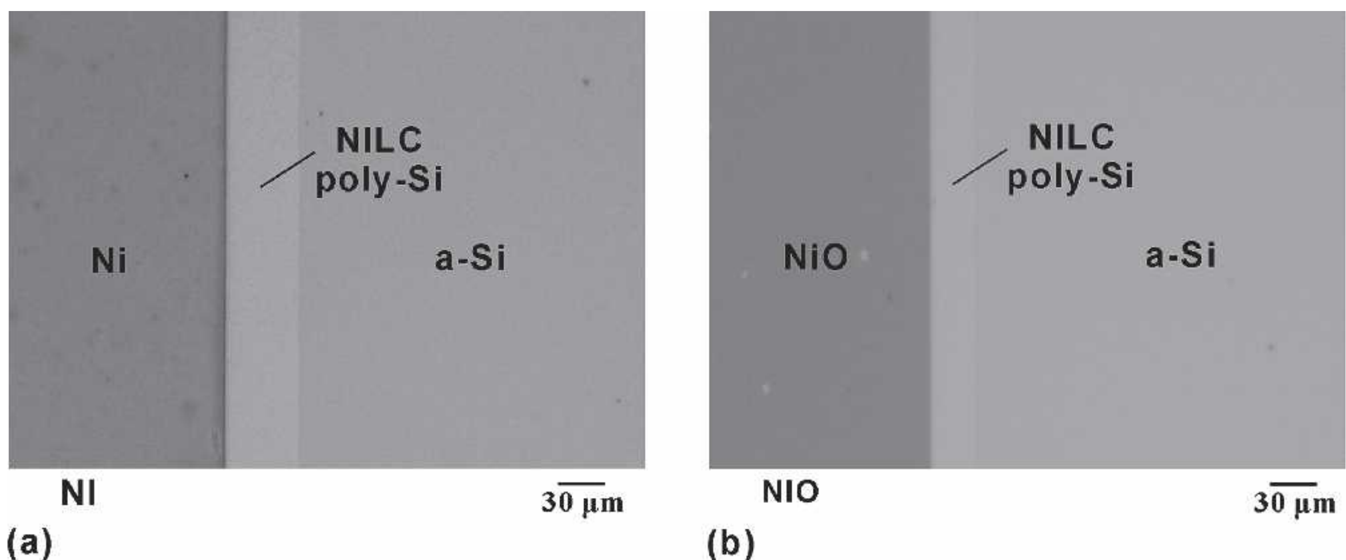


Fig. 1. Optical micrograph of samples annealed at 550°C for 12 h.

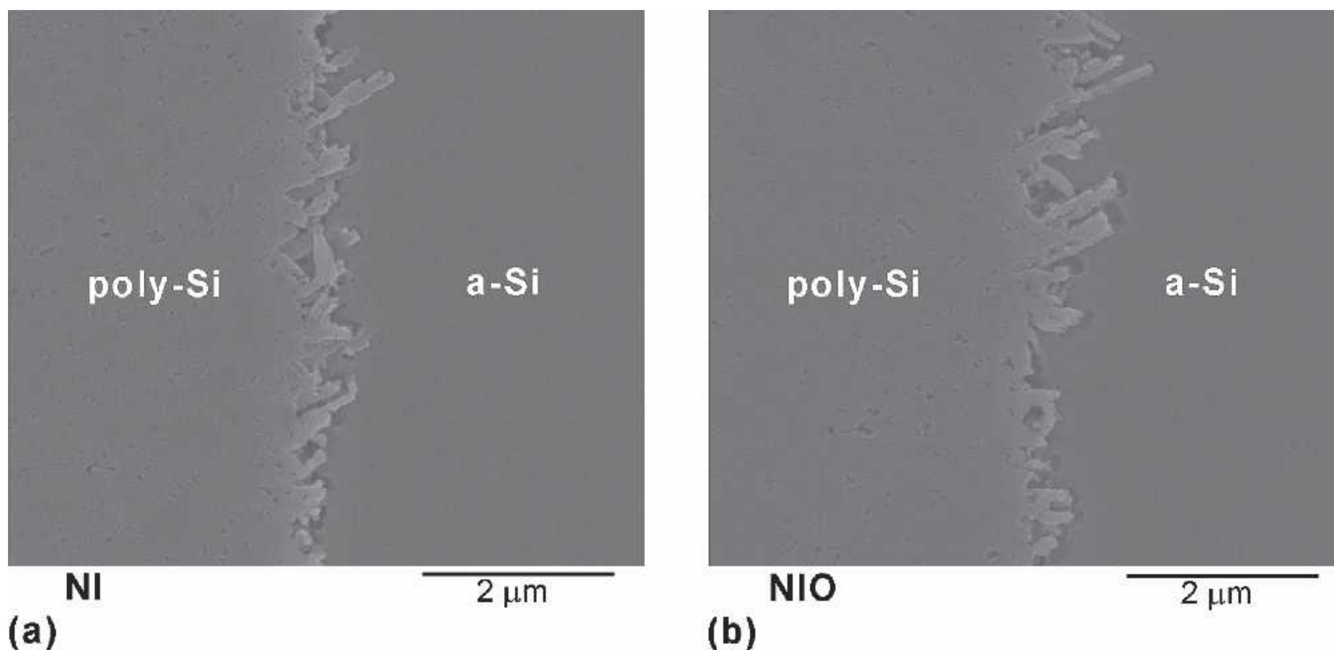


Fig. 2. SEM image of Secco-etched samples annealed at 550°C for 12 h.

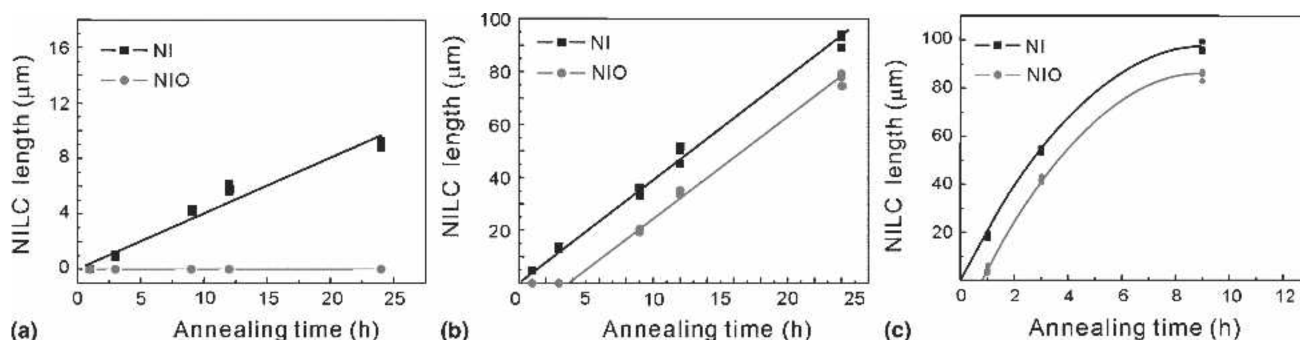


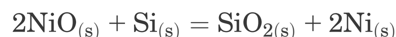
Fig. 3. NILC lengths as a function of the heat-treatment time after annealing at various temperatures: (a) 500°C, (b) 550°C, and (c) 600°C.

Table. I. NILC Rates and Incubation Periods of NI and NIO Samples

Sample	NIO	NI	NIO	NI	NIO	NI
Temperature (°C)	500	500	550	550	600	600
NILC rate (μm/h)	0	0.4	3.8	3.8	18.0	18.0
Incubation period	—	0	3.6 h	0	40 min	0

the oxygen in the Ni film retarded the "nucleation" of poly-Si from a-Si, but had little effect on the "growth rate" of poly-Si. When the temperature reached 600°C, the incubation period decreased to 40 min., and the growth rate increased to 18 μm/h, which was still the same as that of the NI sample, as shown in Table I. As shown in Fig. 3c, the NILC length was saturated after 9 h of annealing. This is because the lateral crystallization was stopped by the randomly oriented SPC grains.[19]

This incubation period phenomenon occurred because, in the Ni–silicide mediated crystallization of a-Si,[18,20] the silicide precipitates acted as nucleation sites and crystallization of silicon proceeded via the migration of the precipitates through a-Si. This required Ni to react with Si to form silicide as a nucleation site. Therefore, in the NIO sample, NiO first needed to be reduced to Ni metal for the subsequent crystallization process. From this perspective, the reaction between nickel oxide and silicon is written as follows:



$$2NiO_{(s)} + Si_{(s)} = SiO_{2(s)} + 2Ni_{(s)}$$

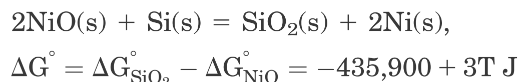
The reaction should be favorable if the change of the Gibbs free energy, ΔG°, is negative. This free energy is equal to the formation free energy of the product of the reaction minus that of the reactant. For the reaction $Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)}$, the formation (standard) free energy is[21]

$$\Delta G^{\circ}_{SiO_2} = -907{,}000 + 175T \text{ J}$$

As for the reaction $2Ni_{(s)} + O_{2(g)} = 2NiO_{(s)}$,

$$\Delta G^{\circ}_{NiO} = -471{,}200 + 172T \text{ J}$$

Thus, the change of the Gibbs free energy of the reaction



$$2NiO(s) + Si(s) = SiO_2(s) + 2Ni(s),$$
$$\Delta G^\circ = \Delta G^\circ_{SiO_2} - \Delta G^\circ_{NiO} = -435{,}900 + 3T \text{ J}$$

The changes in the Gibbs free energy for all three temperatures were negative. Because the Gibbs free energy for the reaction is negative, NiO could be reduced to Ni metal for the subsequent crystallization process. However, the entire crystallization process was retarded due to the accumulation of enough Ni metal for the subsequent mediated crystallization process.

When the annealing temperature was 600°C, after a 40-min. incubation period, the NILC growth rate of the NIO sample was 18 μm/h, which was the same as that of the NI sample. This is because the growth is limited by Ni diffusivity in $NiSi_2$, and only 5-Å-thick Ni in contact with Si was needed for the subsequent crystallization process.[11] Because the reaction byproduct, SiO_2, was left behind the Ni (silicide), it had no effect on the subsequent growth rate. When the temperature decreased to 550°C, the incubation period increased to 3.6 h because the reaction rate between NiO and Si decreased with the decrease of temperature. The NILC growth rate of the NIO sample decreased to 3.8 μm/h, which was still the same as that of the NI sample. When temperatures were lower than 500°C, we believe the reaction rate was too low to accumulate enough Ni metal for the subsequent mediated crystallization process. Therefore, no NILC length was observed. A two-step annealing process was used to test this assumption. In the first step, the NIO sample was heated to 550°C for 6 h. The NILC length was 9.6 μm. The sample was then annealed at 500°C. It was found that the elongation of NILC length did not stop at 9.6 μm, and it continued to grow. The growth rate was 0.3 μm/h, which was smaller than that of the NI sample, 0.4 μm/h. This is because the driving force for NILC is the free energy difference between crystalline Si and a-Si. After the 550°C preannealing process, the atomic rearrangement in a-Si resulted in a reduction in the energy difference, and hence the NILC rate.[22] In other words, in the NIO sample, 500°C was too low to accumulate enough Ni metal to form the $NiSi_2$ precipitates. However, once the $NiSi_2$ precipitates were formed (at 550°C), 500°C was still adequate for the subsequent mediated crystallization process.

CONCLUSIONS

In summary, two kinds of metal films (Ni and NiO) were used to study the effects of oxygen in the Ni films on the Ni induced lateral crystallization of a-Si films at various temperatures. It was found that the poly-Si morphologies of the NIO sample were similar to that of the NI sample. The only difference was that the NILC lengths of the NI sample were longer than that of the NIO sample. The NILC growth rates of both NI and NIO samples increased with annealing temperature. The oxygen concentration in Ni film did not degrade the NILC growth rate. However, it retarded the nucleation of poly-Si from a-Si. This is because NiO needed an incubation period to be reduced to Ni metal for the subsequent mediated crystallization of a-Si. The incubation period increased with the decrease in temperature. When the temperatures were lower than 500°C, the reduction rate was too low to accumulate enough Ni metal for the subsequently mediated crystallization process.

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