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Short communication

Effects of oxygen on the growth of Ni induced lateral crystallization of amorphous silicon films

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Abstract

Effects of oxygen on the growth of metal (Ni) induced lateral crystallization (MILC) of amorphous silicon have been investigated. It is found that the oxygen in the annealing ambient did not degrade the MILC length or growth rate. The oxygen existence in Ni film does not degrade the MILC growth rate either. However, it retards the nucleation of poly-Si for about 4 h. This is because that NiO needed an incubation period to be reduced to nickel metal for the subsequent mediated crystallization of a-Si process.
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Keywords: Oxygen; Amorphous silicon; Metal induced lateral crystallization (MILC); Polycrystalline silicon; Nickel and nickel oxide

1. Introduction

Low-temperature polycrystalline silicon thin film transistors (LPTS TFTs) has attracted considerable attention for active matrix liquid crystal displays (AMLCDs) application due to its good electrical properties and capability of integrating peripheral circuits on inexpensive glass substrates [1,2]. Since poly-Si TFTs should be made on glass substrates to lower the fabrication cost, intensive studies have been made to lower the crystallization temperature of amorphous silicon (a-Si) films. Metal induced lateral crystallization (MILC) method is one of these efforts. In MILC, a thin metal layer was deposited on the surface of the a-Si film and followed by crystallization in a nitrogen ambient at a temperature lower than 600 °C [3–7]. The metal most commonly used for deposition was Ni [3–7]. It was usually deposited by the physical vapor deposition (PVD) method in an ultrahigh vacuum (UHV) apparatus to avoid oxidation of Ni film [3–7]. The process is time-consuming and expensive in terms of equipment cost.

The experiment described in this letter was performed to investigate the effects of oxygen on Ni induced crystallization of a-Si in order to determine the necessity of the nitrogen ambient and UHV deposition system for crystallization of a-Si.

2. Experiment

Silicon (1 0 0) wafers were used as the substrates in this study. Wet oxide films of 500 nm thickness were grown by using a H_2/O_2 mixture at a substrate temperature of 1050 °C. Silane-based a-Si films with a thickness of 100 nm were then deposited by a low-pressure chemical vapor deposition (LPCVD) system at 550 °C. Four kinds of samples were used in this work. Their specifications are listed in Table 1. Nickel or nickel oxide films were deposited on the top of a-Si. They were designated as “Ni” and “NiO”, respectively. Prior to loading the wafers into the deposition chamber, the native silicon oxide on the a-Si films was removed by dipping the wafers in diluted HF. The Ni film was deposited by DC sputter at room temperature. The base pressure in the deposition chamber was 10^{-6} Torr, but rose to 8×10^{-3} Torr during the deposition. The total thickness deposited was about 10 nm. As for the NiO film, it was deposited by a cold DC sputter in air atmosphere [8]. The thickness was also about 10 nm. Wafers were then annealed either in a nitrogen or an oxygen atmosphere. They were labeled as “Ni-N”, “NiO-N”, “Ni-O” and “NiO-O”, respectively.

A lift-off process using photoresist was employed to form islands of Ni or NiO on the wafers. The photoresist was first patterned to expose selected regions of the a-Si thin film. After the deposition of the metal film, the wafers were dipped in acetone to dissolve the photoresist and lift off unwanted metal. Wafers were then cut into 1 cm × 1 cm samples for the subsequent heat treatment. The heat treatment was carried out at 550 °C for 1–24 h.

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Table 1
Summary of sample preparation parameters

	Ni-N	Ni-O	NiO-Ni	NiO-O
Deposition metal	Ni	Ni	NiO	NiO
Annealing ambient	Nitrogen	Oxygen	Nitrogen	Oxygen

An optical microscope was used to measure the MILC length. A scanning electron microscope (SEM) and a transmission electron microscope (TEM) were employed to observe the morphology of the MILC region.

3. Results and discussion

Fig. 1 shows the MILC induced by Ni lines with width of 300 μm. The light region at the periphery of the metal islands was the poly-Si area, which was composed of needlelike Si grains. As shown in Fig. 2, the diameter of needlelike grains was about 50 nm. SEM was also used to study the morphology of the MILC region. A typical SEM image of the poly-Si film after being dipped in the Secco solution [9] was shown in Fig. 3. The morphologies of NiO-N, Ni-O and NiO-O samples were similar to that of Ni-N set. The only difference was that the MILC lengths of Ni-N and Ni-O sets were longer than that of NiO-N and NiO-O sets.

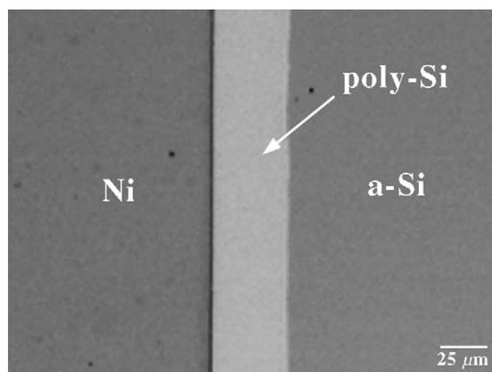


Fig. 1. Optical micrographs of Ni-N sample annealed at 550 °C for 12 h.

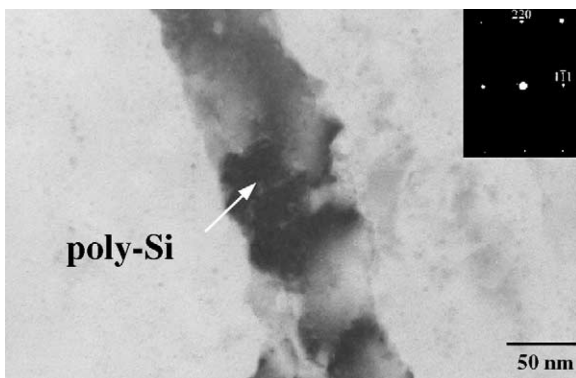


Fig. 2. TEM image and the corresponding diffraction pattern of the MILC poly-Si.

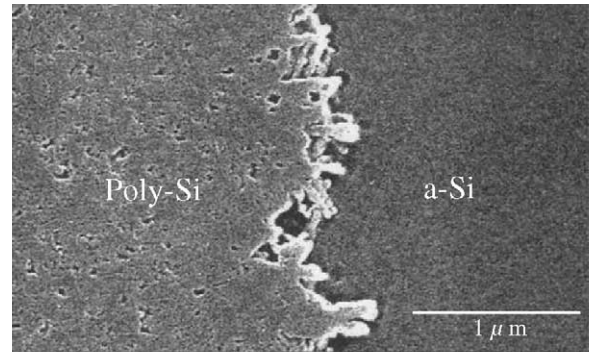


Fig. 3. SEM image of Secco-etched Ni-N sample annealed at 550 °C for 12 h.

3.1. The effect of oxygen in the annealing ambient

The MILC length perpendicular to the edge of the metal islands is plotted as a function of the annealing time in Fig. 4. The MILC rate as a function of the annealing time has been estimated by the slope of the curve in Fig. 4, and plotted in Fig. 5. It can be seen that the MILC length of Ni-N set was the same as that of Ni-O set, while that of NiO-N set was the same as that of NiO-O set. In other words, when samples were annealed at 550 °C, the oxygen ambient did not degrade the MILC growth rate.

TEM analysis revealed that an oxide layer was formed on the top of Si film. Its thickness was about 2 nm, which was similar to the value, 2 nm, simulated by SUPREM-IV program. The formation of this oxide layer will (1) decrease Si thickness and (2) create an oxide/Si interface on the top of Si. However, these two changes did not affect the growth rate of MILC. The detailed analysis is discussed in the following section.

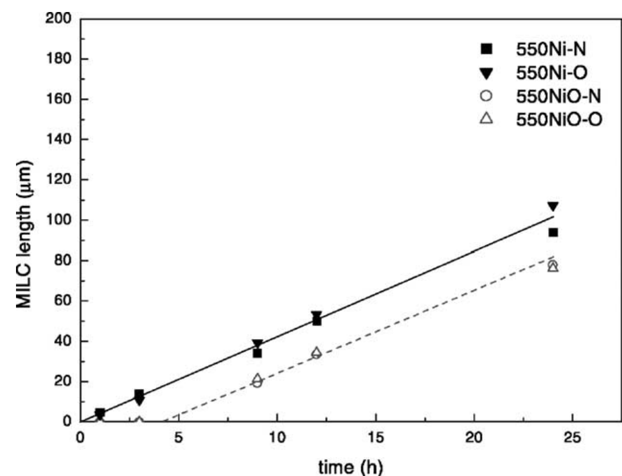


Fig. 4. The MILC length as a function of the heat treatment time.

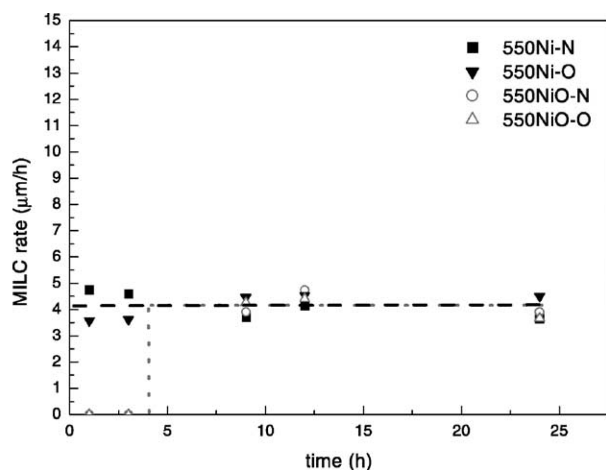


Fig. 5. The dependence of the MILC rate on the annealing time.

3.1.1. The effect of the Si thickness

The effect of the a-Si thickness on the MILC Si has been reported by Ma and Wong [3] who induced crystallization of a-Si films with different thickness. After the samples were annealed at 550 °C for 24 h, they found that the MILC length (growth rate) decreased very slowly with decreasing thickness from 100 to 30 nm. In this study, with the formation of the oxide layer, the change of a-Si thickness was about 2 nm. The growth rate only changed a little. Therefore, the difference of the MILC lengths was too little to be measured.

3.1.2. The effect of the oxide/Si interface

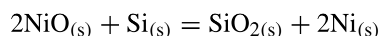
The effect of the oxide/Si on the growth of MILC Si has been reported by Jin et al. [10]. In their Ni induced crystallization of a-Si studies, two kinds of a-Si films were used: (1) 100 nm a-Si film and (2) 100 nm a-Si film capped by 100 nm of low-temperature oxide (LTO). After the samples were annealed at 500 °C for 70 h, they found that the MILC lengths of these two sets of samples were the same, meaning that the oxide/Si interface had no effect on the MILC growth rate.

Since neither Si thickness nor oxide/Si interface will degrade the MILC growth rate, the oxygen in the annealing ambient will not degrade the MILC growth rate.

3.2. The effect of the oxygen concentration in the Ni films

The oxygen existence in the Ni films deteriorates the growth of MILC Si, as shown in Figs. 4 and 5. The MILC lengths of Ni-N and Ni-O sets were always higher than those of NiO-N and NiO-O sets. However, surprisingly, all of their growth rates ($\sim$4.1 μm h^{-1}) remained the same, regardless of the oxygen concentration in Ni. The only difference was that NiO-N and NiO-O sets needed a 4 h incubation period to start the crystallization of a-Si, but Ni set did not. In other words, the oxygen in the Ni film retarded the "nucleation" of poly-Si, but had little effect on the "growth rate" of poly-Si.

This phenomenon happened because that, in the Ni-silicide mediated crystallization of a-Si [11], the silicide precipitates acted as nucleation sites and crystallization of silicon proceeded via the migration of the precipitates through the a-Si. It required Ni to react with Si to form silicide as a nucleation site. Therefore, in the NiO set, NiO first needed to be reduced to nickel 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^0, 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 [12]:

$$\Delta G^0_{SiO_2}\ (J) = -907\,000 + 175T$$

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

$$\Delta G^0_{NiO}\ (J) = -471\,200 + 172T$$

Thus the change of the Gibbs free energy of the reaction $2NiO_{(s)} + Si_{(s)} = SiO_{2(s)} + 2Ni_{(s)}$:

$$\Delta G^0\ (J) = \Delta G^0_{SiO_2} - \Delta G^0_{NiO} = -435\,900 + 3T$$

At 550 °C, the change of the Gibbs free energy

$$\Delta G^0_{550\,^\circ C}\ (J) = -433\,431$$

Since the Gibbs free energy for the reaction is negative, NiO could be reduced to nickel metal for the subsequent crystallization process. However, the whole crystallization process was retarded for about 4 h due to the accumulation of enough Ni metal for the subsequent mediated crystallization process.

After the 4 h incubation period, the growth rate of NiO system was the same as that of Ni. This is because that, in the MILC process, only 5 Å thick Ni in contact with Si was needed for the subsequent crystallization process [7]. Since the reaction byproduct, SiO_2, was left behind the Ni (silicide), it had no effect on the subsequent growth rate.

4. Summary

In summary, two kinds of annealing ambients (nitrogen and oxygen) and two kinds of metal films (Ni and NiO) were used to study the effects of oxygen on Ni induced crystallization of a-Si. It was found that the oxygen ambient did not degrade the MILC length or growth rate. In other words, it is not necessary to crystallize the a-Si in a nitrogen ambient. On the other hand, the oxygen concentration in Ni film did not degrade the MILC growth rate, either. However, it retarded the nucleation of poly-Si for about 4 h. This is because that NiO needed an incubation period to be reduced

to nickel metal for the subsequent mediated crystallization of a-Si process.

Acknowledgements

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References

[1] T. Serikawa, S. Shirai, A. Okamoto, S. Suyama, IEEE Trans. Electron Dev. 36 (1989) 1929.
[2] J.-I. Ohwada, M. Takabatake, Y.A. Ono, A. Mimura, K. Ono, N. Konisji, IEEE Trans. Electron Dev. 36 (1989) 1923.
[3] T. Ma, M. Wong, J. Appl. Phys. 91 (2002) 1236.
[4] Z. Jin, G.A. Bhay, M. Yeung, H.S. Kwok, M. Wong, J. Appl. Phys. 84 (1998) 194.
[5] J. Gu, S.Y. Chou, N. Yao, H. Zandbergen, J.K. Farrer, Appl. Phys. Lett. 81 (2002) 2235.
[6] S.-I. Jun, Y.-H. Yang, J.-B. Lee, D.-K. Choi, Appl. Phys. Lett. 75 (1999) 1104.
[7] S.-W. Lee, S.-K. Joo, IEEE Electron Dev. Lett. 17 (1996) 160.
[8] Y. Wu, J.G. Duh, J. Mater. Sci. Lett. 9 (1990) 583.
[9] F. Secco d'Aragano, J. Electron. Soc. 119 (1972) 948.
[10] Z. Jin, K. Moulding, H.S. Kwok, M. Wong, IEEE Trans. Electron Dev. 46 (1999) 78.
[11] J. Jang, S.K. Park, K.H. Kim, B.R. Cho, W.K. Kwak, S.Y. Yoon, J. Appl. Phys. 88 (2000) 3099.
[12] D.R. Gaskell, Introduction to the Thermodynamics of Materials, Taylor & Francis, Washington, DC, 1995, p. 544.