Understanding of Metal-Induced Lateral Crystallization Mechanism - A Low Temperature Crystallization Phenomenon

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Because the phase transformation temperature of amorphous silicon into poly silicon is too high for a common glass substrate, a process technology for low-temperature poly-silicon (LTPS) has to be developed for advanced flat panel display devices. Metal-induced lateral crystallization (MILC), first introduced in 1995, has been thought to be the only alternative to the laser process in fabrication of LTPS, and yet the basic reaction mechanism underlying MILC has not been clearly understood. In this work, a novel model for understanding the MILC reaction mechanism is proposed. The validity of the proposed model was evaluated through its application to various MILC-related phenomena. The concept developed in this work elucidates new poly TFT fabrication methods, by which active matrix LCDs and OLEDs can be fabricated at low temperatures such that even a plastic substrate can be used.

Key words: polysilicon, metal-induced lateral crystallization, amorphous silicon, Ni silicide, Pd silicide

1. INTRODUCTION

Thin film transistors(TFTs) are essential for the active matrix displays of liquid-crystal displays(LCDs) and for organic light emitting diodes(OLEDs). In addition, the characteristics of a flat panel display device, such as brightness, resolution, and image transport speed, are very much dependent on the electron mobility of TFTs, which in turn depends on the crystallinity of the silicon thin film substrate.

Generally, silicon thin film deposited on the glass substrate is amorphous, and the amorphous silicon(a-Si) TFTs show an electron mobility of around 0.5 cm²/V sec. When silicon thin film is crystallized into poly silicon, however, the electron mobility can be increased up to more than 200 cm²/ Vsec. In particular, OLEDs, which should be driven by the current as opposed to the voltage, as LCDs are, require high electron mobility, and this obstacle has thus far prevented OLED technology from being used in computer or TV monitors. Since a laser beam can be focused into an extremely small area to melt a silicon thin film without appreciable heating of the glass substrate, it has been thought that a method utilizing a laser could be used to prepare low-temperature poly-silicon^[1].

Current laser annealing processes, however, suffer from non-uniform crystallinity, due to the inevitable scan overlap involved, as well as surface roughness, due to the liquidsolid phase transformation of silicon. On the other hand, metal-induced lateral crystallization (MILC) is a batch process and a solid-state phase transformation. Besides, MILC does not require extra equipment, such as an expensive laser. For these reasons, MILC is generally agreed to be more appropriate for industrial application than laser techniques, even though further decrease in the leakage current and the crystallization temperature is desirable^[2]. Much progress has been made on the application of the MILC phenomenon to poly TFT fabrication; however, only a few reports have addressed the basic reaction mechanism involved in MILC^[3].

In this paper, a new MILC reaction model is proposed, and a report is provided on the application of the proposed model to some MILC-related phenomena that have not been understood. In addition, this paper reports on experiments that were carried out to prove the validity of the proposed model, which may lead to a new MILC process that allows for a reduction of the annealing temperature currently involved.

2. EXPERIMENTAL PROCEDURE

Amorphous silicon thin films, each of 600-Å thickness, were deposited on a glass substrate using an LPCVD or a PECVD system. Silane (SiH₄) gas was used as a source gas and hydrogen was used as a carrier gas. The substrate temperature was kept at about 450 °C A Ni thin film of 50-Å thickness was deposited after the lithography for the lift off technique. A conventional tube furnace was used for MILC, which was carried out at the temperature of 500 or 550 °C in

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hydrogen ambient. External stress was mechanically applied to the glass during MILC annealing. Ni or Pd dots formed in between the two electrodes, and a DC electrical field was applied. Doping was performed with an ion mass doping system (IMDS), which was locally made. The RF power was fixed at 150 W, and the DC voltage between the grids was 20 KeV. The doping time was varied from 1 min to 4 min to vary the dopant concentration. The dose amount was identified through SIMS and a sheet resistance measurement. The length after the crystallization was measured under an optical microscope and confirmed with SEM whenever necessary. TEM was used to examine the lateral crystallization behavior and the crystallinity.

3. RESULTS AND DISCUSSION

3.1. MILC phenomenon

Metal-induced crystallization (MIC) techniques have been used since 1964. Unfortunately, however, such techniques cannot be applied to TFT fabrication, because TFTs prepared with MIC techniques have shown high leakage current, due to metal contamination, thus precluding the practical use of such TFTs^[4]. MILC can be distinguished from MIC in that MILC occurs through a lateral phase transformation from the MIC region, and this lateral crystallization is mediated by the silicide formed in the MIC region^[5]. Hence, MILC is called a catalytic phase transformation, and poly crystals formed via MILC are free from metal contamination. When Ni or Pd is used as a catalyst for MILC, the growth rate is about 5 μ m/hr at a temperature of 550 °C and $2 \ \mu m$ /hr at 500 °C^[2]. Isotope experiments performed by R. Pretorius et al. confirmed that the MILC region was free from metal contamination^[6]. The low leakage current of MILC TFTs also proves that the MILC region is free from metal contamination^[2].

3.2. MILC reaction model

The silicide mediated lateral crystallization is shown in fig. 1. At the tip of the lateral crystallization, there is a silicide of less than 50 Å in thickness, which moves into the amorphous silicon leaving the poly silicon behind. The schematic drawing for this reaction is illustrated in fig. 2. For the catalytic phase transformation to occur, three different atomic fluxes are required in the system. Firstly, the bond breaking of a-Si atoms and migration of each atom towards the interface between a-Si and the silicide designated as /1/ in fig. 2 (F1). Migrated silicon atoms are to be adsorbed at the silicide surface to create the metal vacancies. Secondly, the hopping of the abovementioned created metal vacancies inside the silicide to reach the interface between the silicide and poly silicon designated as /2/ (F2). Hopping of the metal vacancies should be coupled with the metal ions in the silicide. Finally, the rearranging of the dissociated silicon atoms at $\frac{12}{100}$ to be





(b)

Fig. 1. TEM bright field image of MILC a) TEM of MILC tip. Arrow indicates growth direction, which is [111] b) Bright field image of MILC poly silicon. Diffraction pattern at right hand upper corner reveals a single crystal (111) plane in the grain.



Fig. 2. A schematic illustration of the MILC reaction model.

attached to the dangling bonds of the poly crystal (F3). Phase transformation of one atomic layer can be completed by the rearrangement of dissociated silicon atoms at /2/. In a steady state, F1 should be equal to F2 and F3.



Fig. 3. Pd effect on Ni-MILC.

Since there is a volume expansion at /1/ and shrinkage at /2/, corresponding tensile and compressive stresses would be created. For Pd-MILC, the volume is calculated to expand by two times at /2/ and to contract in half at /1/. Therefore the tensile stress drives the bond breaking of a-Si and the migration of silicon atoms for adsorption at the silicide surface of /1/, while compressive stress built at /2/ would facilitate the atomic rearrangement. For Ni-MILC, the respective volumes occupied by one silicon atom in crystalline, in nickel silicide, and in amorphous silicon are calculated to be 20.0, 19.9, and 20.3. This means that almost no volume change occurs at either interface /1/ or /2/ for Ni MILC. This fact is related to the MILC growth rate and the adjacent metal effect, which will be discussed in detail later.

Vacancy motion inside the silicide, which has to be coupled with the metal ions in the reverse direction, can be driven by the thermodynamic equilibrium potential difference between /1/ and /2/. It is known that a-Si can accommodate more metal elements than poly-Si, thermodynamically, so that the charged metal ions have to move towards /1/.^[7] The kinetics of this hopping reaction may change, however, with the presence of an externally applied energy, such as an electric or magnetic field. Flux F3 is expected to occur spontaneously, even though it can be promoted by the compressive stress at /2/. A determination of the rate-controlling step has never been experimented but F1 is thought to be the one even though F2 is the most sensitive step upon the external conditions such as an applied stress etc.

3.3. MILC related phenomena and the model

3.3.1. Effect of the spacing of metal catalysts on the MILC rate

The MILC rate is dependent on the Pd spacing: the smaller the spacing, the higher the MILC rate. The critical distance over which no appreciable effect is to be observed depends

Fig. 4. External stress effect on MILC rate (a) tensile stress (b) without external stress (c) compressive stress.

on the annealing temperature and time. According to the MILC reaction model, the tensile stress is to be created at /1/ and each /1/ from the spaced Pd is in face to face so that the tensile stress would be accumulated in between to promote the bond breaking of a-Si and migration of silicon atoms towards each /1/. Hence, F1 will be enhanced by the spaced Pd, which causes a considerable increase in the MILC rate. It is quite interesting to notice that without the spaced Pd, almost no appreciable lateral growth can be observed in Pd-MILC. For Ni-MILC, where a relatively small volume change would occur at the interface /1/ and /2/ with MILC, relatively less effect of adjacent Ni on the Ni MILC rate without any help from adjacent Ni is about 5 um/hr, as mentioned earlier.

It can be seen in Fig. 4 that when the tensile stress is applied at a right angle to the growth direction of Ni-MILC, i.e., moving in the direction of /1/, the growth rate becomes four times faster than that without any stress. When the tensile stress is applied in a direction parallel to the moving direction of /1/, a slight increase in the growth rate can be observed. In addition, when a compressive stress is applied, the growth rate is reduced to almost half of that without any external stress.

3.3.2. The electrical field effect on MILC rate

It has been found that the MILC rate towards the positive electrode is considerably faster than that towards the negative electrode when a DC electric field is applied to the system, as shown in fig. 5. According to our model, the metal ions in the silicide should move to /1/ and the metal vacancies to /2/ for a MILC reaction to occur. Since Ni ions are negatively charged in the nickel silicide and Ni vacancies are positively charged, the MILC rate can be promoted with an



Fig. 5. Electric field effect on the MILC rate.

applied electric field when the reaction occurs towards the positive electrode. If /1/ moves towards the negative electrode, however, the columbic force might hinder the movement of metal ions towards /1/ inside the silicide, thus preventing the MILC reaction.

3.3.3. Doping effect on the MILC rate

The MILC rate in the boron-doped a-Si is three to four times faster than that in undoped a-Si, while in the phosphorous-doped a-Si, no appreciable lateral growth can be observed. Boron is an acceptor and it is supposed to be negatively charged in crystallized silicon, whereas phosphorous is a donor and is positively charged. At /2/ the negatively charged boron would attract the positively charged Ni vacancies towards /2/ and repel the negatively charged Ni ions towards /1/. According to the proposed model, these conditions are desirable for MILC growth. With phosphorous doping, however, opposite movements would occur which would prevent a MILC reaction.

4. CONCLUSION

It has been known that MILC is a good alternative to laser annealing in the fabrication of low-temperature poly silicon. In this work, a basic MILC reaction model has been proposed for the first time. Accordingly, the catalytic phase transformation occurs by the propagation of metal silicide, which can be activated through a balance of three fluxes: atomic arrangement flux, vacancy-hopping flux, and diffusion flux. The proposed model has been applied to various MILC related phenomena that have not been clearly understood up to now. The geometric effect, electrical field effect, and doping effect can all be explained by the basic mechanism suggested in this work. The crystallization temperature can be lowered even further by application of the basic model concept. It is expected that further reduction of the crystallization temperature through the model will enable us to fabricate TFTs on plastic substrates in the near future.

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REFERENCES

- C. T. Angelis, C. A. Dimitriadis, M. Miyasaka, F. V. Farmakis, G. Kamarinos, J. Brini, and J. Stoemenos, *J. Appl. Phys.* 86, 4600 (1999).
- 2. S. W. Lee and S. K. Joo, *IEEE Electron Device Lett.* 17, 160 (1996).
- 3. A. R. Joshi, T. Krishnamohan, and K. C. Sarawat, *J. Appl. Phys.* **93**, 165 (2003).
- C. R. Kagan and P. Andry, *Thin-film Transistors*, p. 165, Marcel, Dekker Inc., New York (2003).
- 5. C. Hayzelden and J. L. Bastone, *J. Appl. Phys.* **73**, 8279 (1993).
- 6. R. Pretorius, Z. L. Liau, S. S. Lau, and M-A. Nicolet, *Appl. Phys. Lett.* **29**, 598 (1976).
- 7. S. W. Lee, Y. C. Jeon, and S. K. Joo, *Appl. Phys. Lett.* 66, 1671 (1995).