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Solution-based metal induced crystallization of a-Si*

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This paper investigates a simplified metal induced crystallization (MIC) of a-Si, named solution-based MIC (S-MIC). The nickel inducing source was formed on a-Si from salt solution dissolved in de-ionized water or ethanol. a-Si thin film was deposited with low pressure chemical vapour deposition or plasma enhanced chemical vapour deposition as precursor material for MIC. It finds that the content of nickel source formed on a-Si can be controlled by solution concentration and dipping time. The dependence of crystallization rate of a-Si on annealing time illustrated that the linear density of nickel source was another critical factor that affects the crystallization of a-Si, besides the diffusion of nickel disilicide. The highest electron Hall mobility of thus prepared S-MIC poly-Si is 45.6 $\mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$. By using this S-MIC poly-Si, thin film transistors and display scan drivers were made, and their characteristics are presented.

Keywords: Ni-salt source, metal induced crystallization (MIC), poly-Si, TFT
PACC: 7360, 7360F, 7360L, 7360P

1. Introduction

Macro-electronics, composed of thin film transistors (TFTs) in large area, has attracted much attention since Le Comber[1] from the University of Dundee, UK declared that 'the macro-electronics age is coming' in 1989.[1] Its applications in active matrix displays (AMDs) have been rapidly developed.[2,3] The functions and the degree of integration of active matrix liquid crystal displays have gone up almost by Moore's Law,[4] which is only ∼20 years later than the development trend of very large scale integration.

In the information age, even small portable electronic products are expected to be able to display high content information. In this area, poly-Si TFTs are better candidate than a-Si TFTs, because of their higher mobility[5] which allows integration of peripheral circuits with the active matrix on the same glass substrate. Meanwhile, for current-driving organic light emitting diode display, high driving capability of pixel circuit is desirable. Although the application of poly-Si TFTs in AMD have been well demonstrated, the high cost, low yield and complicated fabrication processes have limited its development in mass production. To simplify the TFT fabrication processes, a novel low cost metal induced crystallization (MIC) of a-Si is introduced in this paper.

Normally, the inducing metal source is deposited by physical methods, e.g. sputtering or evaporation. These deposition processes need to be performed in a high vacuum system,[6] which is one of the bottlenecks in achieving high yield on poly-Si TFTs. Recently, it was found that MIC of a-Si can be implemented by dipping a-Si in chemical solution of nickel salt to form the inducing metal source on the surface of a-Si,[7−11] which is named solution-based metal induced crystallization (S-MIC).[7−11] S-MIC can be batch-processed in air. Thus the formation of poly-Si is simplified, and accordingly fabrication cost decreased and production yield increased.[8,9] In this paper, the electrical properties of S-MIC poly-Si thin film material and TFTs are presented, and the mechanism of S-MIC is discussed.

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2. Sample fabrication

The precursor to form S-MIC poly-Si is 50 nm–100 nm thick amorphous silicon (a-Si) film deposited by Low Pressure Chemical Vapour Deposition (LPCVD) at 450°C or Very High Frequency Plasma Enhanced Chemical Vapour Deposition (VHF-PECVD) at 200–250°C. After dipped in $Ni(CH_3COO)_2$ or $Ni(NO_3)_2$ solution[9] and re-cleaned with deionized (DI) water rinser, the samples were furnace-annealed in nitrogen atmosphere at 550–590°C. The crystallized samples were etched by TMAH or Secco for observing grain status with the optical microscope (Olympus STM6-LM-F31). The crystallization quality of thus prepared poly-Si was characterized with Raman spectrum, x-ray diffraction (XRD), Hall mobility and conductivity. The characteristics of TFTs made on this S-MIC poly-Si were measured with HP4156 semiconductor parameter analyser.

3. Results and discussions

Figure 1 shows the surface microscope photos of Si thin film taken after the Si thin film had been annealed for 2 hours, 8 hours and 18 hours respectively. These surface photos show that the crystallization of a-Si started from some isolated nucleus (see the small dots in Fig.1 (2h)). Then the grains did not radially grow in a-Si at isotropic crystallization rate (Fig.1 (8h)), until the grains touched each other (Fig.1 (18h)).

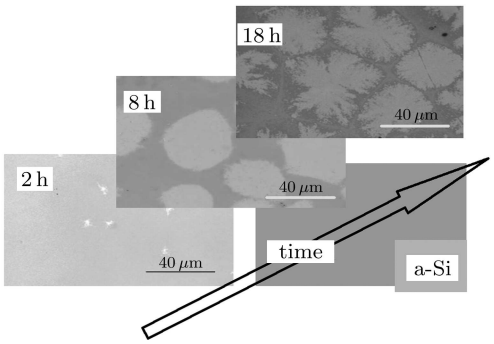
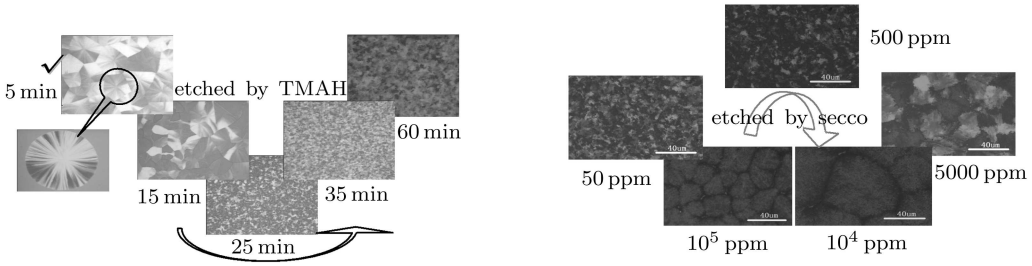


Fig.1. Growth of grain size with annealing time induced by chemical Ni source at 550°C.

3.1. Effects of dipping conditions

It was found that the dipping conditions of Ni-salt solution obviously affected the grain size and the shape of S-MIC poly-Si. As summarized in Fig.2, the shape of crystallized grain can be categorized into two types: large grains with disc-like shape,[7,9] and small grains with 'wadding-like' shape. When the solution concentration was fixed at 50,000 ppm, the grain size decreased with dipping time, and the grain shape changed from 'disc-like' to 'wadding-like'. When the dipping time was fixed at 10 minutes, the grain size first increased, and then decreased with solution concentration. As mentioned in Ref.[9], the crystalline grains were significantly affected by the content of Ni inducing source adhered to the surface of a-Si. We believe that the content of Ni inducing source on the surface of a-Si increases with dipping time and solution concentration. So the change of grain size and shape with the dipping conditions reveals that large disc-like grain can only be formed at appropriate content of Ni inducing source, but wadding-like small grain can be formed at very low or very high content of Ni inducing source.

The location and condition of Ni inducing source on a-Si surface also have impact on the dynamic process of S-MIC. As well known, the crystallization of a-Si is mediated by the migration of nickel disilicide ($NiSi_2$), so S-MIC dynamic mechanism should be relative to the diffusion of $NiSi_2$ in a-Si.[7] Accordingly,



(a) fixed at 50000 ppm (b) fixed at 10 min

Fig.2. Grain size and shape vs dipping conditions: (a) solution concentration fixed at 50,000 ppm, (b) dipping time fixed at 10 minutes.

there should be 1/2 power relationship between the crystallization length and the annealing time, if the mechanism of S-MIC is mainly dominated by diffusion of $NiSi_2$. However, as shown in Fig.3, the power relationship between the crystallization length and the annealing time is not 0.5 but ∼0.7, which was deduced from the result of laterally S-MIC experiments at 550°C.[12] This result suggests that the dynamics of S-MIC should be based on some mechanisms other than $NiSi_2$ diffusion. We think that one of the other key factors is the content of Ni inducing source. This was confirmed by an experiment hereinafter.

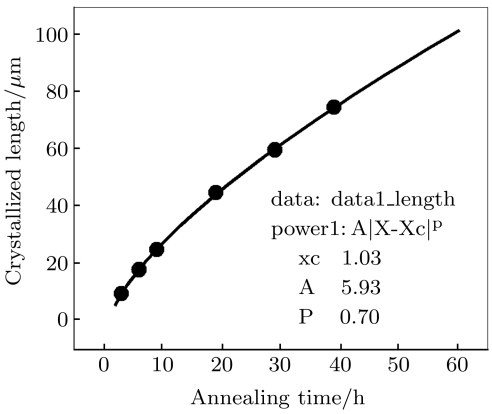


Fig.3. Change of crystallization length with annealing time.

Three kinds of the inducing holes with different diameters were patterned on three samples before they were dipped in Ni-salt solution. As shown in Figs.4(a), 4(b) and 4(c), the diameter of the inducing holes increased from (a) to (c), but the subsequent S-MIC were made under the same conditions of Ni salt concentration of 1×10^4 ppm, dipping time of 10 minutes, annealing temperature of 550°C and annealing time of 4 hours.

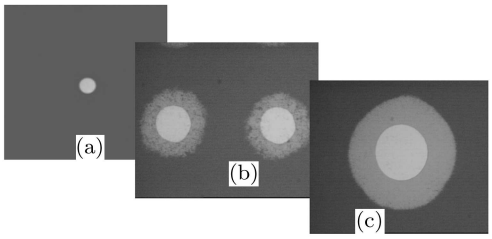


Fig.4. Microscopic photos of crystallized poly-Si samples with different diameter inducing hole.

It was found that the size of the inducing hole also affected the dynamic process of S-MIC. When the diameter of the inducing hole was small, lateral crystallization of a-Si was not observed (shown in Fig.4(a)). With the increase of the diameter of the inducing hole, a laterally crystallized poly-Si area, like a ringed halation (shown in Fig.4(b)) around the inducing hole, was observed. The halation area looks like a mixture of a-Si and poly-Si, because some red brown microareas whose colour was similar to a-Si were observed in the halation. The edge of halation could not be observed in focus with microscope. With further increase in the diameter of the inducing hole, a clear crystallized poly-Si area was observed as shown in Fig.4(c). It is well known that the density of Ni atoms is required to be above a threshold to perform metal-induced lateral crystallization (MILC) of a-Si.[10] Because the dipping conditions are the same for these three samples, we think the area density D_A of Ni inducing source deposited on the surface of these three a-Si samples should be equal to each other. Thus the linear density D_L at the edge of the inducing hole should increase with the diameter $d(D_L = D_A{\cdot}\pi{\cdot}(d/2)^2/(\pi{\cdot}d) = D_A{\cdot}d/4)$. This suggests that the linear density of Ni source in some region in the MILC front could not be high enough to induce the sequential crystallization, if the inducing hole is not large enough. Thus a mixed phase of a-Si and poly-Si was obtained, shown as a halation in Fig.4(b). If the inducing hole is large enough, the linear density is high enough for full lateral crystallization of a-Si. Figure 4 also indicates that the crystallization rate was reduced by decreasing the linear density of Ni source. All these experimental results imply that the linear density of Ni source at the MILC front is a critical factor to obtain high quality poly-Si.

3.2. Electrical characteristics of S-MIC poly-Si thin film

The dipping conditions have much effect on the electrical characteristics of S-MIC poly-Si, because they influence the grain structure of S-MIC poly-Si (as shown in Fig.2). Figure 5(a) shows the effect of dipping time on the Hall mobility of S-MIC poly-Si. The mobility of disc-like grains is much larger than that of wadding-like grains. The larger the grain, the higher the Hall mobility is. The largest grain S-MIC poly-Si we have prepared has the highest electron Hall mobility of $45.6\,cm^2/(V\cdot s)$ and the highest hole Hall mobility of $27.1\,cm^2/(V\cdot s)$.

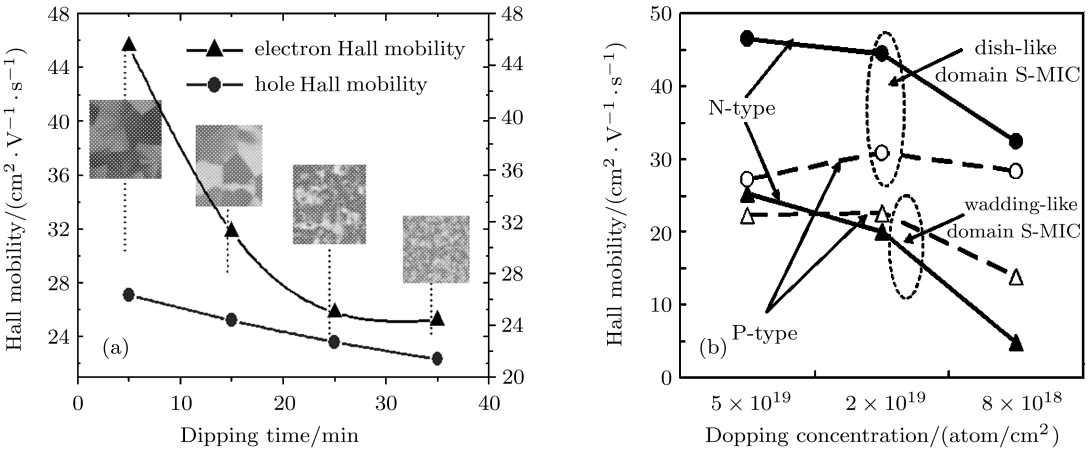


Fig.5. Dependence of Hall mobility on dipping time (a) and dopant concentration (b).

Figure 5(b) shows the dependence of the Hall mobility of S-MIC poly-Si with disc-like grain and wadding-like grain on the doping concentration. Compared to boron doped S-MIC poly-Si, the electron Hall mobility of phosphorous doped (N-type) S-MIC poly-Si increases with the dopant concentration at much higher rate. This should be attributed to the Ni gettering effect induced by phosphorous, which led to the improvement of the quality of S-MIC poly-Si and was enhanced by the increase of the phosphorous doping concentration.

3.3. S-MIC poly-Si TFTs

S-MIC poly-Si was used to make active islands of P- and N-type TFTs. Figure 6 shows the transfer characteristics of thus prepared S-MIC poly-Si TFT. Both P- and N-type TFTs have $I_{\rm on}/I_{\rm off}$ ratio of $\sim10^7$. N-type TFTs have field effective mobility $\mu_{\rm FE}$ of $\sim81\,{\rm cm}^2/({\rm V}\cdot{\rm s})$, and P-type TFTs have $\mu_{\rm FE}$ of $\sim73\,{\rm cm}^2/({\rm V}\cdot{\rm s})$. They also have nearly uniform space distribution of $I_{\rm off}$.[13] Performances of these devices are comparable to those presented in Refs.[7–9].

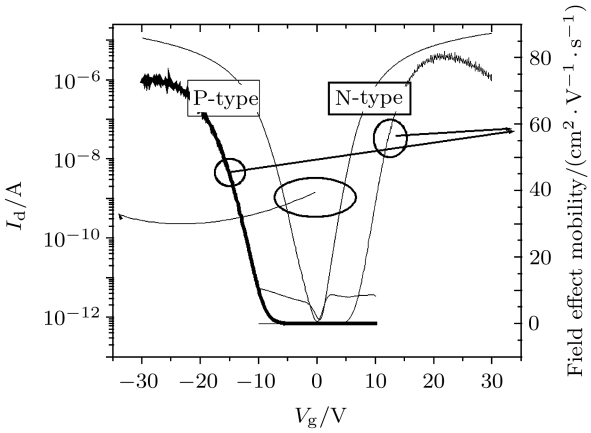
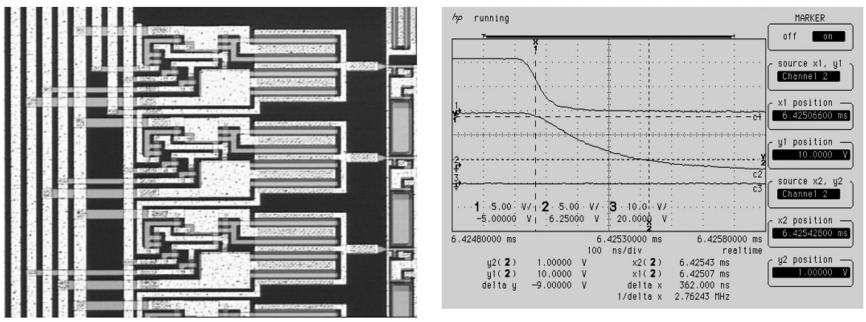


Fig.6. Transfer $I-V$ curves and $\mu_{\rm FE}$ of P- and N- type S-MIC poly-Si TFT.

A scan driver for active matrix organic light emitting diode display (AMOLED) was prepared with full P-type S-MIC TFTs. A microscopic photo of part of the scan driver circuit is shown in Fig.7(a).



(a) (b)

Fig.7. Photos of part of scan driver (a), and measured input and output signal pulses (b).

The decay time of the scan driver is 365 ns as shown in Fig.7(b). So the total row scan time can reach 0.8 μs, and the row frequency can be up to 1.25 MHz. If frame frequency is set at 60 Hz, the driver can scan more than 20,000 row lines. This means that the S-MIC poly-Si TFT scan circuit would be able to drive 3G (normal VGA = 640 × 480 mode, just 480 lines) or 4G mobile-phone (SVGA = 800 × 600 mode, 600 lines).

4. Conclusion

- A simplified S-MIC method to make poly-Si has been studied.
- 45.6 $\mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$ high electron Hall mobility and 30–40 μm large grain S-MIC poly-Si thin film were obtained.
- The content of Ni inducing source on the surface of a-Si affects the formation of the crystalline nucleation, the grain size of S-MIC poly-Si, and the crystallization rate.
- S-MIC Poly-Si TFTs have $I_{\mathrm{on}}/I_{\mathrm{off}}$ ratio of 10^7 and μ_{FE} of $\sim 81.7\,\mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$ (N-type).
- A scan driver for AMOLED using full P-type TFTs has been demonstrated. Its row frequency can reach 1.25 MHz, which is suitable for application in high quality mobile phone.

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