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Dynamic Ni gettered by PSG from S-MIC poly-Si and its TFTs*

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A dynamic phosphor-silicate glass (PSG) gettering method is proposed in which the processes of the gettering of Ni by PSG and the crystallizing of α-Si into poly-Si by Ni take place simultaneously. The effects of PSG gettering process on the performances of solution-based metal induced crystallized (S-MIC) poly-Si materials and their thin film transistors (TFTs) are discussed. The crystallization rate is much reduced due to the fact that the Ni as a medium source of crystallization is extracted by the PSG during crystallization at the same time. The boundary between two neighbouring grains in S-MIC poly-Si with PSG looks blurrier than without PSG. Compared with the TFTs made from S-MIC poly-Si without PSG gettering, the TFTs made with PSG gettering has a reduced gate induced leakage current.

Keywords: metal induced crystallization, polycrystalline silicon, nickel gettering, phosphor-silicate glass (PSG)

PACC: 7360, 7360F, 7360L, 7360P

1. Introduction

Solution-based metal induced crystallization (S-MIC) is a cost-effective method of manufacturing poly-Si.[1,2] As is well known, the MIC process happens at the interface of amorphous phase and crystalline phase induced by Nickel Silicide ($NiSi_2$). Ni as a source to induce crystallization prefers to transfer itself from crystalline $NiSi_2$ to a Ni element and reacts with sideward a-Si to form a new $NiSi_2$ because the free-energy of Ni at $NiSi_2$/a-Si interface is lower than that at $NiSi_2$/c-Si interface as explained by Hayzelden *et al.*[3,4] The free-energy of atom Si at the interface of $NiSi_2$/a-Si is higher than that at the interface of $NiSi_2$/c-Si, so a-Si trends to change into crystalline grain induced by the medium $NiSi_2$, which also drives Ni to reacting with subsequent a-Si. Consequently, with the crystallized medium $NiSi_2$ migrating in a-Si continually at a suitable temperature, the crystalline Si grain will be left behind the $NiSi_2$ migrated. In short, when $NiSi_2$ migrates toward and arrives at a-Si, poly-crystalline Si is left behind. Therefore, the crystalline grain will grow larger and larger and then stop until it collides with neighbouring grains. The grain-boundary forms at the place where the induced fronts of two neighbouring grains meet each other. The Ni concentration within the induced front is higher than that within the MIC region, which will degrade the performances of poly-Si TFTs made in this area.[5,6]

In this paper, a dynamic PSG gettering of the residual Ni in S-MIC poly-Si is proposed. The effects of PSG gettering process on the performances of solution-based metal induced crystallized poly-Si are discussed. The performances of SMIC TFTs made separately with and without Ni gettering are compared.

2. Preparation of SMIC poly-Si material and device

The S-MIC method is adopted to prepare a pre-poly-Si film in order to extract the nickel residue as

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derivant metal in the film. A 50 nm thick a-Si active layer was deposited by low-pressure chemical vapour deposition (LPCVD) at 550°C on 4-inch c-Si wafers covered with 500 nm thick thermal oxide. After dipping in 1% hydrogen fluoride solution for 1 min to remove the native oxide, the samples were soaked in nickel nitrate solution for 5 min and then annealed at 550°C for 3 h in a nitrogen atmosphere. After the sample had been etched in Secco solution, we observed the grains status by using an optical microscope of mode Olympus STM6-LM-F31 and found that the crystalline grains were separated from each other as shown in Fig.1. We call this kind of poly-Si film partly crystallized Si.

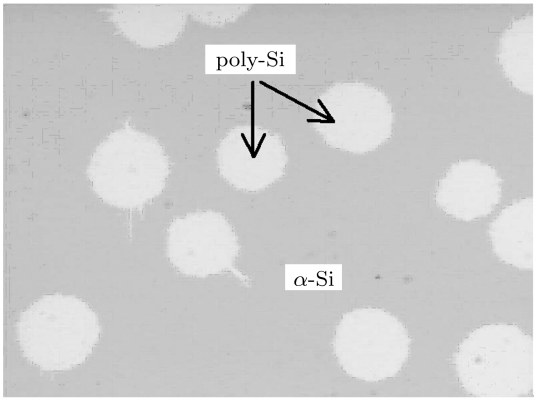


Fig.1. Image of partly crystallized Si thin film.

After the partly crystallized Si had been fabricated, a 700 nm thick PSG was then deposited on the film. For comparison, the poly-Si film covered with PSG was divided into two parts. One had no PSG which was removed by 777 enchant (composed of CH_3COOH, NH_4F and glycol), the other had the PSG, which was kept on the poly-Si film. And then both of them experienced by a further-annealing (called by the second crystallization) at 590°C for 4 h in a nitrogen atmosphere. In the end, the PSG layer was removed and the two parts (with and without PSG covered in the second crystallization step) were etched with tetramethyl ammonium hydroxide (TMAH) etchant for 3 min at room temperature so as to be able to observe the grain structure of the poly-Si material. The sample was called 'comparison sample'.

By controlling the soaking time in nickel nitrate solution with a certain density of Ni, two kinds of S-MIC crystallized poly-Si with different grain shapes were obtained: dish-like and floc -like grain structure.[3]

We prepared four kinds of samples and divided them into two species as dish-like and floc-like structures, each species with two samples. The samples were soaked in 37% HCl for 3 h to get rid of the remaining nickel on the poly-Si surface. Then a 700 nm thick PSG layer was deposited from the surface of one sample with dish-like and floc-like grain structures. Subsequently, the four samples were all annealed at 590° for 4 h for nickel gettering and the second crystallization simultaneously. After that, the PSG covered on the surface of two samples was etched with 777 etchant at room temperature. Thus, four types of poly-Si samples were prepared: (a) Type-A: dish-like grain with PSG gettering, (b) Type-B: dish-like grain without PSG gettering, (c) Type-C: floc-like grain with PSG gettering, and (d) Type-D: floc-like grain without PSG gettering.

Four kinds of transistors whose active layers were made from the above different kinds of S-MIC poly-Si thin films were prepared.

The above four kinds of poly-Si films were patterned into active islands through their wet etching with Freckle enchant. Then a 100 nm thick low temperature oxide (LTO) was subsequently deposited on these islands by using LPCVD at 425°C as the gate insulator after the native oxide had been removed by 1% HF. Following the deposition of a 280 nm thick LPCVD poly-Si layer which had been patterned into gate electrodes, phosphorus and boron with a dose of $4 \times 10^{15}/\mathrm{cm}^2$ were implanted into the source, drain and gate regions for N- and P-type TFTs, separately. A 500 nm thick LTO isolation layer was deposited and the dopants were activated. Contact holes had opened before a 500 nm thick aluminium layer with 1% Si was subsequently sputtered and patterned as contacts. Contact sintering was then performed in forming gas at 420°C for 30 min.

3. Results and discussion

The surface morphology of the poly-Si material called 'comparison sample', etched with TMAH, is shown in Fig.2. The region on the left-hand side of the dashed line was not covered by the PSG while the region on the right-hand side was covered by the PSG. The circled part at the grain centre shows the edge of

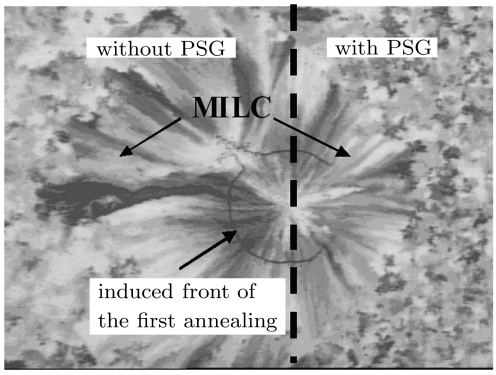


Fig.2. The surface morphology of S-MIC poly-Si covered with and without PSG after etched with TMAH.

disc-like crystalline grain after annealed at 550°C for 3 h for the first crystallization. It can be seen that the disc-like grain formed during the first annealing continues growing expitally during the second crystallization step. The crystallized grain size without PSG in the left region in Fig.2 was as large as 60–70 μm after the second annealing, while that in the right region was only 15–17 μm after annealed under the same condition. The crystallization rate with PSG was much reduced because part of nickel elements were gettered out by PSG during its second crystallization process. This demonstrates that the PSG can getter some Ni elements out of the poly-Si thin film at the time when a-Si was further crystallized during the second furnace annealing. So it is the reason why the method is called a 'dynamic Ni gettering process', the process in which the extraction of nickel by PSG and the further induced crystallization take place simultaneously.

The colour difference in the right region is less than in the left region. Because the etching selectivity of TMAH etchant is dependent on crystalline orientations of silicon crystal, or rather, the crystalline grains with the different orientations display different colours after etched by TMAH at room temperature. The less colour difference for the S-MIC poly-Si with PSG means the less difference of crystalline orientation for S-MIC poly-Si with PSG than without PSG.

Shown in Fig.3 are the surface morphologies of two collided neighbouring grains in the whole surface of S-MIC poly-Si covered separately with and without PSG after etched with TMAH. No obvious induced front can be observed in S-MIC poly-Si with PSG for the first crystallization and the second crystallization. But the boundary for the two neighbouring grains in S-MIC poly-Si with PSG (Fig.2(b)) looks blurrier and track less obvious than without PSG (Fig.2(a)). It can be convinced that the reduction of Ni in the front of induced crystallization by PSG gettering should cause the decrease of the crystallization rate, and it would also dispel the traces of conflicting grains because of the grain-boundary improvement.

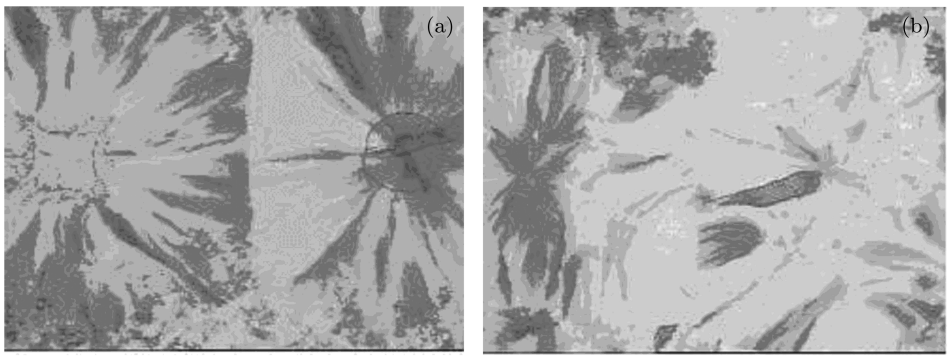


Fig.3. The surface morphologies of two neighbouring domains in S-MIC poly-Si covered without PSG (a) and with PSG (b) after etched with TMAH.

The effect of Ni gettered on the performances of TFTs whose active layer was made from this kind of material is shown in Fig.4, in which the transfer characteristics of SMIC poly-Si TFTs and their field-effect mobility are displayed.

Figure 4(a) shows the I–V curves with and without Ni gettered, respectively, corresponding to one couple of curves a and b and another couple of curves c and d. The two couples of curves both are very similar to each other. When they are enlarged, a little differ-

ence could be observed as shown in the insets. The transfer characteristic curves of TFTs with PSG gettering shift toward the left by 0.3–0.5 V with respect to those of TFTs without gettering, which means that the gettering of Ni can reduce its thermal speed $V_{\rm th}$ and improve the sub-threshold slop. This shift is probably results from the decrease of nickel so that there is the little improvement of the grain-boundary effect on the transportation characteristic of charges in the channel. Otherwise, a distinct effect of Ni gettering can emerge to improve the field effect mobility ($\mu_{\rm FE}$) shown in Fig.4(b).

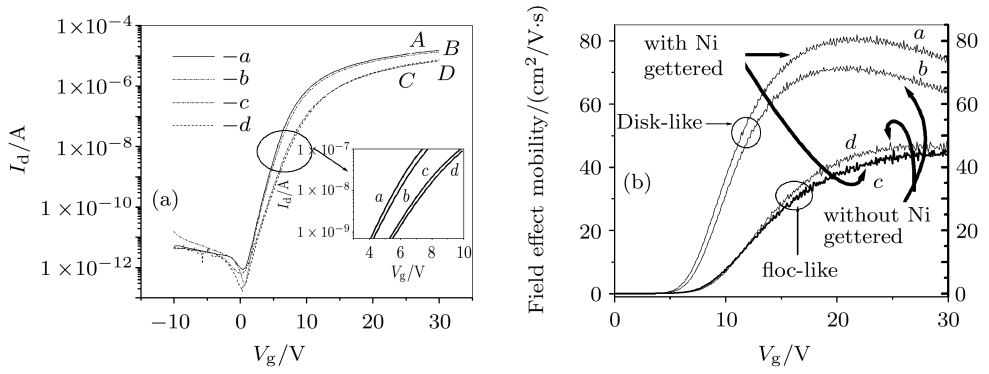


Fig.4. The effect of PSG gettering on S-MIC poly-Si TFTs: (a) $I_{\rm d}$–V curves and (b) $\mu_{\rm FE}$–V.

The N-channel TFTs with dish-like domain poly-Si exhibit a maximal field effect mobility of about $\sim$80 cm^2/Vs near 20 V. The $\mu_{\rm FE}$ of TFTs with PSG gettering can be increased by about 10 cm^2/Vs compared with that without PSG gettering on an average. For the TFTs made from the poly-Si with floc-like grain, the maximal field-effect mobilities are a little more than 45 cm^2/V.s which are shown by curves 'c' and 'd'. That means that for floc-like grain poly-Si TFT, the effect of PSG gettering on mobility could appear, but not obviously.

For these two kinds of TFTs with different grain structures (disc-like and floc-like), the different effects of nickel gettering on the mobility improvement would be related with grain structure. Because of the large grain size and better crystal properties for disc-like grains, the property of the material would be restricted by the interface between the crystal grain boundaries. In this case, the inosculation of the collided grains interface treated by PSG gettering can be seen from Fig.3(b). The PSG gettering could decrease the Ni metal content and mitigate the recombination effect, resulting in the mobility improvement as shown in Fig.4. For the floc-like grain structure, there are a lot of un-perfective defects everywhere in the film, so the effect of PSG gettering to improve the grain boundary character, and so to improve device performances could not show obvious distinction in recent PSG treatment condition. Thus the PSG condition needs optimizing in the future.

As shown in Fig.4, the Ni gettering process does not improve their I–V characteristics so much. Normally, I–V performance of TFTs mainly depends on the quality of active layer material and its interface with the gate-insulator. The effect of Ni gettering on I–V curves cannot be observed obviously but the distinction in crystallized structure between disc-like and floc-like grains can be founded in their I–V curves. It is suggested that maybe there remained just such a little Ni content in the poly-Si film with disc-like grains obtained by using the S-MIC method, that the gettering effect on I–V curves cannot be observed obviously. Perhaps, the inconspicuous effect of PSG gettering on I–V curves of S-MIC poly-Si TFTs can be used to testify whether there remains a little Ni content in the SMIC material. If so, the poly-Si materials crystallized by using the S-MIC method contain a low Ni content, which is suitable for the manufacturing of the TFTs.

Leakage current of TFTs is very important for their application in flat panel displays. Figure 5 shows the gate induced drain leakage (GIDL) currents of N-type poly-Si TFT with PSG and without PSG separately. Besides the single gate TFT, the GIDL currents of four-finger multi-gate TFTs are also shown in the same figure. The leakage currents are shown from the I–V curves measured respectively at $V_{\rm d} = 5$, and -5 V. Figure 5(a) shows a comparison of leakage

currents of N-type poly-Si TFTs with disc-like crystallization between with and without PSG gettering for single gate TFTs. Figure 5(b) exhibits such a comparison between with and without PSG gettering for four-gate TFTs and Fig.5(c) indicates such a comparison between single gate and four-gate TFTs with PSG gettering. Their active layers are all made from SMIC poly-Si with disc-like grains. As shown in these figures, the GIDL currents of TFT with PSG gettering decrease by half to one order of magnitude compared with those of TFTs without PSG gettering. Meanwhile, the spatial distributions of the GIDL currents are also improved by PSG gettering (see the leakage current curves of single gate TFTs without PSG gettering in Fig.5(a) . We believe that these improvements are due to the decrease of residual Ni concentration so that the grain-boundaries are improved. The four-finger multi-gate device structure can reduce the leakage current more obviously as shown in Figs.5(b) and 5(c).

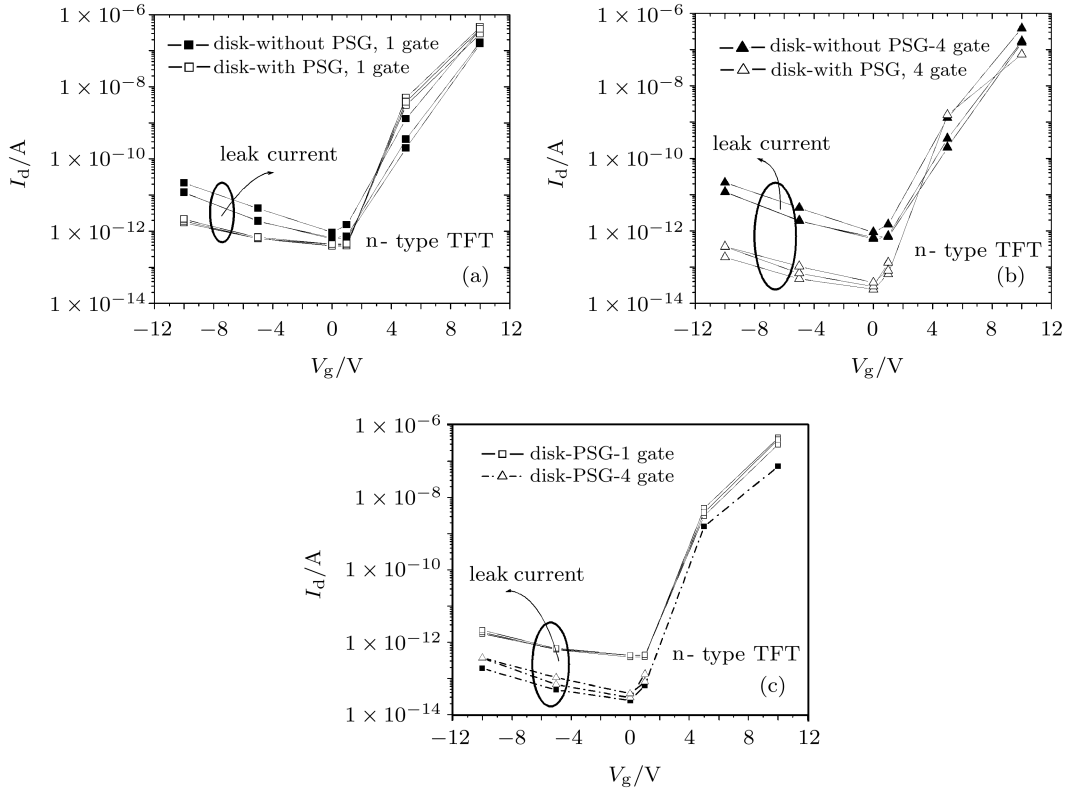
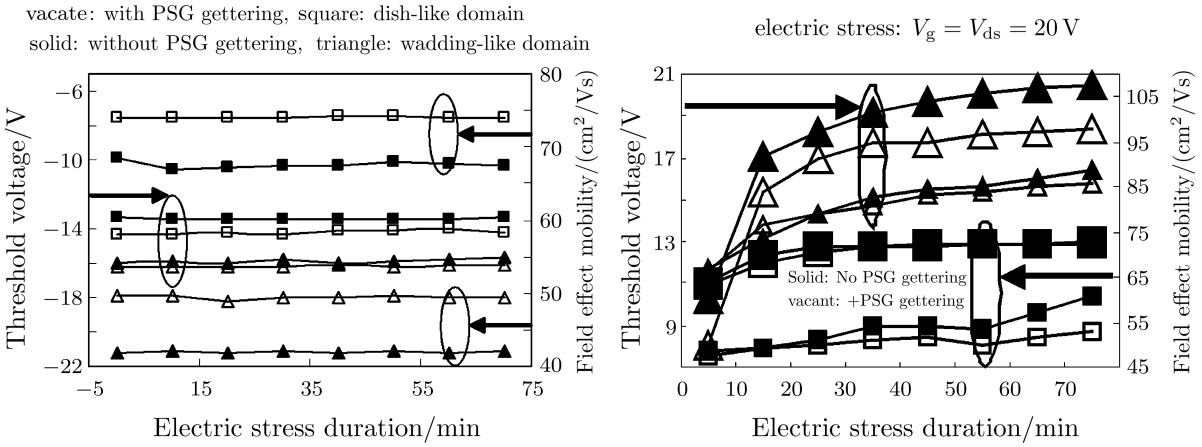


Fig.5. A comparison of leakage current of n-type poly-Si TFTs with disc-like crystallization between with and without PSG gettering for single gate(a), four-gates (b)and (c) the leakage currents of single and four-gate TFTs.

The stabilities of four different kinds of poly-Si TFTs were tested under different values of gate stress and hot-carrier bias-stress. No change in threshold voltage and field-effect mobility for both n-channel and p-channel SMIC poly-Si TFTs was found under the condition of gate stress at $V_d = V_s = 0\,V$, $V_g = \pm 20\,V$ for one hour (the relevant curves are omitted). The test under hot-carrier bias-stress condition was carried out at $V_g = V_d = -20\,V$ for p-type TFTs and $V_g = V_d = 20\,V$ for n-TFTs, respectively. The threshold voltage and field-effect mobility are extracted from the low voltage transfer characteristic curves of TFTs (with $W/L = 30$, and $T_{ox} = 100\,nm$) measured every ten minutes. The stability characteristics for four kinds of poly-Si TFTs under the different values of hot-carrier bias-stress are shown in Fig.6, in which the changes of the threshold voltage and field effect mobility with stress duration are shown, especially in the first 20 min. The p-type TFTs with and without PSG gettering all reveal good stability (see Fig.6(a)), but for N-TFTs, just the TFT with PSG gettering shows a little better stability than TFT without PSG gettering over the hot carrier stress duration (see Fig.6(b)). It is the reason why the P-type TFTs can be used in AMOLED (active matrix organic light emitting display) and periphery driver circuits of SOP-LCD (System-on-panel liquid crystal display) recently.[7]



(a) p-type S-MIC poly-Si TFT (bias condition: $V_g = V_{ds} = -20$ V) (b) n-type S-MIC poly-Si TFT

Fig.6. The effect of hot-carrier bias stress on the field-effect mobility and the threshold voltage shift for the p-type (a) and n-type S-MIC TFT (b) versus bias stress duration.

4. Summary

(1) The effects of PSG gettering process on the performances of solution-based metal induced crystallized poly-Si materials and thin film transistors made from them are discussed in this paper.

(2) The crystallization rate is much reduced by the PSG gettering effect.

(3) The boundary between two neighbouring grains in S-MIC poly-Si with PSG looks blurrier than without PSG. It would suggest that an amalgamation effect of grain interface occurs due to the fact that Ni is gettered out there.

(4) The effect of PSG gettering on I–V characteristics of several TFTs is not obvious, which indicates that there remains a little of Ni content in S-MIC poly-Si film. This is an excellent merit of S-MIC method for application.

(5) Compared with the TFTs made from S-MIC poly-Si without PSG gettering, the TFTs made with PSG gettering have a reduced gate induced leakage current and the stability improved a little under the hot carrier stress.

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