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Optimizing Structure and Processes of Nickel Induced Lateral Crystallization

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Abstract: The structure and processes of nickel induced lateral crystallization are studied. The structure of metal induced lateral crystallization(MILC) is improved by opening a seed window on the buried oxide, which is helpfu to get superior quality of large grain poly-Si at low temperature. By optimizing the temperature and time of annealing based on others' pervious work, the large grain poly-Si with few defects are obtained, and the typical grain size is 70 ~ 80μm. The methods of etching $NiSi_2$ which is created after the long time annealing are also studied for the first time. Finally, a method is successfully chosen to reduce the possible contamination of Ni and to guarantee the MILC for the submicron VLSI application.

Key words: nickel; metal induced lateral crystallization; grain boundaries; seed widow; $NiSi_2$

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1 Introduction

Silicon-on-insulator (SOI) metal-oxide-semiconductor field-effect transistors with ultra-thin channel layers have various advantages. These include high mobility, kink elimination, enhanced saturation current, steeper sub-threshold slope and low threshold voltage[1]. Similar beneficial effects have also been observed in poly-Si TFTs with ultra-thin channel layers. However, the conventional poly-TFT has poor field effect mobility and high leakage current due to the grain boundaries existing in the channel region[2]. The grain sizes are on the order of the device sizes or smaller. The random distribution of the grain sizes and grain boundary location leads to an unacceptable degradation of device performance for the submicron VLSI application.

Many researchers have attempted to provide superior quality poly-Si film. Near single-crystalline property poly-Si TFTs have been fabricated by the techniques such as solid phase crystallization (SPC)[3] and laser annealing[4]. Metal induced crystallization (MIC) has been studied in the past by using trace metals such as Ni, Ge, Al, Au and Pb[5~9]. However, the grain sizes are still small compared to the sizes of transistors. Recently, poly-Si film with large grain was formed by the re-crystallization of amorphous silicon (a-Si) through metal induced lateral crystallization (MILC) at an elevated temperature[10]. This method can greatly decrease the metal contamination in the active area, because the region of re-crystallization is on the side of the region covered by metal, and is simple to be integrated into the CMOS technology. The grain size of the resulting film is significantly

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enhanced and is much larger than the transistor size. There are still some metal atoms in the MILC region, but the number of metal atoms is so small that the performances of the transistor fabricated by this technology do not degrade. Researchers in Hong Kong have tested this result by successfully fabricating gate-all-around transistors with MILC[11].

In the MILC process, the grain size, grain-boundary direction and position are determined by the re-crystallization process and the subsequent annealing process. Researchers at the Hong Kong University of Science and Technology have done a great deal of work, studying the mechanism and process of MILC[12,13]. Based on their researches, we improve the structure of crystallization by opening a seed window on the buried oxide, connecting the a-Si with the single crystal silicon of the substrate, and studying the effects of the two-step annealing on the re-crystallization. Finally we optimize the process and parameters of MILC, obtaining a poly-Si grain size of 70~ 80μm with less defects when compared to the conventional process. The $NiSi_2$, created at the seeding areas following the long time annealing process, is successfully removed through etching. This greatly decreases the possible metal contamination in the poly-Si layer, guaranteeing the MILC for the submicron VLSI application.

2 Experiment

A 120nm thermal oxide was grown on the bulk silicon substrate to serve as the buried oxide. Then the wafers were split into two groups. One is without seed windows connecting with the substrate, illustrated as Fig. 1. The other is with the seed widows at the buried oxide, which makes the a-Si connecting with the single crystal silicon of the substrate, illustrated as Fig. 2. Then 100nm amorphous silicon film was subsequently deposited by low-pressure chemical vapor deposition (LPCVD) at 550℃. The wafers were covered by a layer of 300nm low temperature oxide (LTO) for both groups of wafers deposited at 400℃. After the lithography, the exposed oxide was removed in a HF solution, and 5nm of nickel was sputtered on the a-Si surface. MILC process was carried out subsequently. This process included two annealing steps: at the first step, the wafers were annealed at a lower temperature for 60h in the N_2 ambient, then the unreacted Ni was completely removed in a heated H_2SO_4 solution. In order to enlarge the silicon grain size, the wafers were subsequently annealed at a higher temperature for a shorter time. Finally, the $NiSi_2$ was removed by wet etching to reduce the possible contamination of Ni.

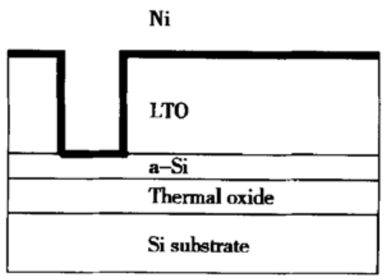

Fig. 1 Structure of MILC process

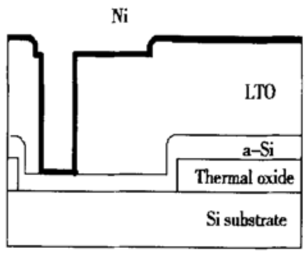

Fig. 2 Improved structure of MILC process

To observe the poly-Si grain sizes and grain boundaries after the re-crystallization, we used Secco etching solution to etch the poly-Si because the Secco etching rate varies according to different orientation of the silicon crystals. After etching for a while, the poly-Si surface topography was rough, and the grain boundaries were clearly seen by using scanning electron microscope (SEM).

3 Result and discussion

To obtain the uniform distribution of large grain of poly-Si and guarantee the MILC for the submicron VLSI application, we studied the following structure and processes of MILC technology.

3.1 Temperature and time of the two-step annealing

The first step of annealing taked a long time at a low temperature, which transfered the amorphous silicon to the large grain poly-Si. Some researches[14, 15] have shown that if the annealing temperature is too low (< 500℃), the MILC rate is slow; if the temperature is too high (> 600℃), the a-Si can nucleate by themselves. This self-nucleation greatly limit the dissolution of nickel atoms in the a-Si. Thus the grain size after MILC is much smaller than that under low temperature. So we chose the annealing temperature between 530℃ to 560℃. The annealing time was 60h to enhance the grain size. According to the result of experiments, the slight variety of temperature did not effect the crystallization during this long time annealing. So we set the annealing temperature at 560℃ for 60h to gain higher MILC rate. Finally we obtained large grain poly-Si as 60~ 70μm. The Fig. 3 illustrates the results. In the figure the large grains are distributed in a radial direction, the long axes of these grains are perpendicular to the local edge of the Ni strip, grain size is long but narrow with the width of 2~ 3μm, and the distribution is not uniform. In the region where is far from the nickel strip with the radius above 70μm there are the poly-Si without MILC.

In previous work[16] the time and temperature of second step of annealing is 30min and 900℃. In our experiments, under this condition the uniform distribution of poly-Si grain was improved, but the enhance of the grain length was not obvious comparing with the result of the first annealing step. We lengthened the annealing time and found when the time was more than 60min, the poly-Si grain length can be enlarged to 70~ 80μm with the width of 3~ 7μm as shown in Fig. 4. And when the annealing time was more than 120min, there was no improvement of the re-crystallization. We finally determined the condition is 60min at 900℃.

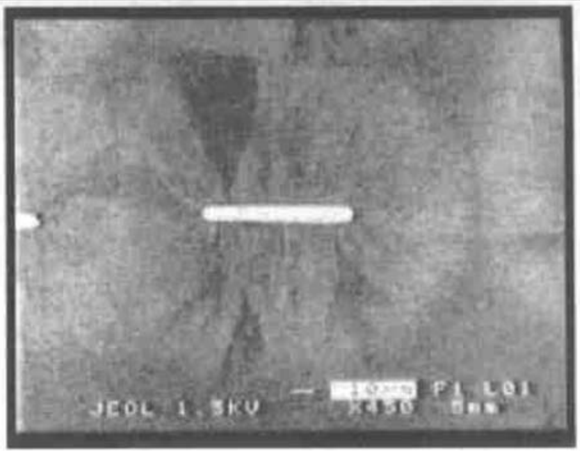

Fig. 3　SEM picture of the poly-Si surface in MILC region after Secco etching　The sample was heat treated at 560℃ for 60h

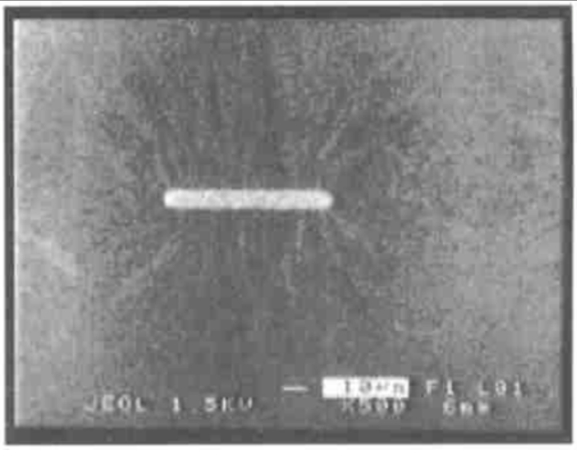

Fig. 4　SEM picture of the poly-Si surface in MILC region after Secco etching　The sample was second heat treated at 900℃ for 60min

3.2 Structure improvement of MILC

To obtain better quality of the large grain poly-Si, we studied and improved the structure for MILC illustrated as in Fig. 2. Before CVD the a-Si, we opened a seed window on the thermal oxide. The a-Si was connected with the single crystal silicon on the substrate through this seed window. After the two steps of annealing with the previous determined condition, we still got large grain poly-Si with the length of 70~ 80μm as shown in Fig. 5, which is almost the same length as in Fig. 4. The result shows that the topography of the a-Si film has little effect on the dissolution of the Ni in the a-Si layer.

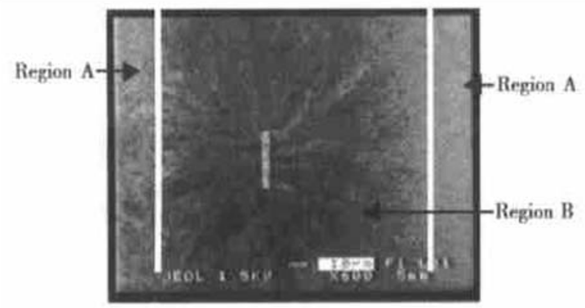

Fig. 5 SEM picture of the poly-Si surface after Secco etching The sample was treated after the MILC process with the seed window on thermal oxide. The white lines indicate the boundary of the MILC region, while the Region A is the region without MILC and the Region B is the one with MILC.

In the experiment we found that after the MILC process the uniform distribution of grain boundaries in the Fig. 5 was better than that in the Fig. 4. The amplified SEM pictures of the grain boundaries of the two structures after the MILC are shown in Fig. 7 and Fig. 6, respectively. To show the difference between the region without and with MILC clearly, we chose the location that is exactly the boundaries at the front-end of the MILC region, as shown in these two pictures. In the pictures, we can clearly see the grain boundaries between poly-Si with the small grain size and with much larger size, at the left side and the right side of the pictures respectively. In the region without the metal induced lateral crystallization, the poly-Si film are separated grains with the grain size less than 0.1μm, in the MILC region the grain sizes are much larger than those in the region without MILC. These results show how much the MILC enlarge the grain size of the poly-Si.

By comparing the two pictures we can see

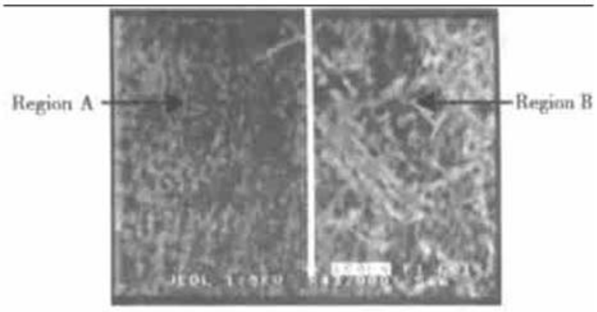

Fig. 6 SEM picture of the poly-Si surface after Secco etching at the boundary region of the MILC without the seed window The white line indicates the boundary of the MILC region, while the Region A is the region without MILC and the Region B is the one with MILC.

there are much more defects in Fig. 6[11] without seed windows than those in Fig. 7 with seed windows. This phenomenon takes place not only at the grain boundaries of the MILC, but also within the large grain of poly-Si, where the distribution of defects is similar with the boundary region shown in Fig. 6 and Fig. 7. The reason that the seeding structure is with less defects comparing with that without seed windows is that the co-effect of the Solid Phase Epitaxy (SPE) and the MILC facilitate the formation of supecion quality large grain poly-Si film.

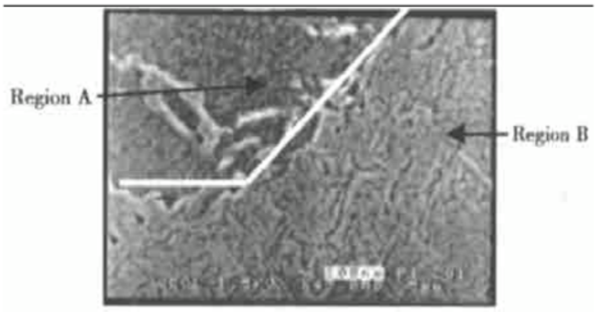

Fig. 7 SEM picture of the poly-Si surface after Secco etching at the boundary region of the MILC with the seed window The white lines indicate the boundary of the MILC region, while the Region A is the region without MILC and the Region B is the one with MILC.

Puglisi *et al.*[17] found at 560℃ of annealing temperature, the SPE is slow and the crystallization rate is about $5\times10^{-6}\mu m/s$, but with the Ni precipitates, the SPE growth rate can speed up to $1\times10^{-3}\mu m/s$. In our experiments, at the early stage of the heat treatment, Ni atoms diffuse into a-Si film from both vertical and lateral direction. The Ni atoms in the a-Si can easily bond with the a-Si, this low-energy bond facilitates the growth of SPE through the seed window where the a-Si is connected with the substrate. At the same time, the Ni reacts with the amorphous silicon and converts itself into $NiSi_2$. Then the small grains of silicon crystal can nucleate and grow along the interface between the $NiSi_2$ and the a-Si around it, and the nucleation was aided by the small lattice mismatch between $NiSi_2$ and crystalline silicon, which is only 0.4%[18]. When annealing continues for a long time, as the $NiSi_2$ is very unstable at the low temperature(500~ 600℃), the $NiSi_2$ bond is easy to break up, which makes Ni atoms in the $NiSi_2$ separated with Si. The Ni atoms subsequently diffuse into the a-Si region and continue to react with a-Si to form new $NiSi_2$, repeating the $NiSi_2$ form and break processes. At the edges of the Ni covered region, some Ni atoms can move laterally into the a-Si region that is not originally covered by Ni, along the path of the moving Ni atoms the a-Si will be re-crystallized, so the MILC is the process of transport of Ni atoms. This is the mechanism of MILC[12,15].

In summary, the SPE makes the orientation of all the re-crystallized silicon similar with the single crystal silicon (100) of the substrate and greatly decrease the defects at the grain boundaries and interior of the grain of the poly-Si; the MILC process enlarges the grain size up to tens of micron. Thus we can get superior quality large grain poly-Si at low temperature.

3.3 Reservation of the LTO caps

The work in Ref. [14] shows when the first annealing time is longer than 20h, whether the LTO caps are removed has little effect on the MILC rate. But they removed the LTO caps before the second annealing, and discussion about whether this removing benefits the MILC process was not given. Comparing the process without the LTO caps and that with the LTO caps, we find the MILC rate and quality are almost the same, indicating that the removing of the LTO caps does not have negative effect on MILC process. But in such high ambient as 900℃, the exposed silicon is easily contaminated, so we think the LTO caps should be reserved to cover the silicon till the last 900℃ treatment is completed.

3.4 Removing of $NiSi_2$ after MILC

After MILC process, there are lots of Ni atoms in the metal induced crystallization region just under the Ni strips. These metal contaminations keep the MILC process from VLSI application. How to remove these metal atoms is an important problem for the Si technology. Treated for a long time at high temperature, the resultant $NiSi_2$ are difficult to remove by using conventional etching methods, such as Cl_2 plasma etching and royal water wet etching. Thus the $NiSi_2$ removing becomes a challenging task to be resolved, and till now there is no report on this problem.

We have done a great deal of work to acquire a helpful method to remove the $NiSi_2$ that is formed after the long time heat treatment. Finally we have found three ways as following: (1) the chemical mechanical polish (CMP). The $NiSi_2$ can be removed by using the CMP. But this method can not remove $NiSi_2$ selectively. (2) Ar ion physical bombardment. The Ar ion sputtering can etch the $NiSi_2$ in the poly-Si, but the rate is slow. (3) the heated HF wet etching. This is a practical way to remove the $NiSi_2$. After the MILC is too steady to react with HF at room temperature, the HF solution do not etch the $NiSi_2$ until heated reaching 80℃. This wet etching not only remove the $NiSi_2$ in the MIC region, but also remove the small quantity of the Ni atom in the MILC region. So this etching is also a simple and useful way to observe the distribution of Ni atom in the poly-Si layer. Finally we successfully removed the Ni in the poly-Si for the first time.

4 Conclusion

Using nickel as the induced metal of MILC can obtain thin poly-silicon film with large grain size. We improve the structure for MILC by opening a seed window where the amorphous silicon is connected with the single crystal silicon substrate, which facilitates the superior quality large grain poly-silicon formed. By optimization of the time and temperature in the MILC process the grain size of the poly-silicon in MILC region is with the length of about 70~ 80μm, and the defects in the MILC are much less comparing with conventional process. For the first time we use HF solution to etch the $NiSi_2$ formed after MILC at 80℃, greatly removing the Ni atom in the poly-silicon layery. Thus we make the MILC for VLSI application and sub-micro double-gate structure research.

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金属 Ni 诱导横向晶化的结构及工艺进程的优化

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摘要: 研究了用 Ni 进行金属诱导横向晶化(MILC)制备大尺寸多晶硅晶粒的结构改进和工艺条件优化,改进了 MILC 的结构,通过在埋层氧化层上开出与衬底相连的籽晶区,减少了大晶粒多晶硅中的缺陷分布;同时在前人的基础上优化了退火温度及时间,用 Secco 腐蚀液观察了晶粒大小和间界分布,最后得到了质量更好的大晶粒多晶硅,其大小在 70~ 80μm 左右. 同时讨论了 MILC 后生成的 $NiSi_2$ 的去除方法,成功地去除了高温退火后生成的 $NiSi_2$,大大减小了 Ni 在多晶硅层中的分布,保证了将 MILC 方法成功应用于实现深亚微米器件的研究中.

关键词: 金属镍; 金属诱导横向晶化 (MILC); 晶粒间界; 籽晶区; $NiSi_2$

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