

Influence of the oxidation in the metal silicide/Si₃N₄ interfaces on the etching profile

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Abstract

Metal silicide has been proposed, studied and used as gate, word, and bit-line materials since it has considerably low resistance compared with the conventional materials like polysilicon. However, there are several serious problems encountered because the silicide is oxidized and forms a native oxide (SiO₂) layer at the interface between metal silicide and Si₃N₄ film. In this study, we have introduced 10 slm N₂ gas from top to bottom of the modified quartz tube in order to decrease the oxygen concentration in the tube by using the long injector system. The result shows that there is no oxidation occurred when the flow rate of N₂ gas is sufficiently high.

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1. Introduction

As the density of integrated circuits has been continuously increasing, the resistances of the con-

ducting lines are also much increased because of very small widths and thicknesses of the lines. That, in turn, causes undesirable degradation in bandwidth and electrical characteristics of the IC devices. To resolve such a problem, there have been much efforts to replace the conventional polysilicon with more conductive metal silicide such as TiSi₂ or WSi_x [1–4]. These new materials have been tried as gate, word, and bit-lines in

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ULSI DRAM devices, too. The thin films of metal silicide (TiSi_2 and WSi_x) are, however, oxidized while they are being coated by the Si_3N_4 film that is used as etching masks or spacers in the fabrication process of DRAM.

This oxidation is caused by the reaction of Si (silicon) atoms in the metal silicide film and oxygen molecules that are present in the quartz tube where the deposition of Si_3N_4 film is being carried out. Therefore the degree of oxidation greatly depends on the concentration of oxygen gas inside the tube and stand-by temperature of the deposition equipment.

If we maintain the stand-by temperature below 400°C , there is no oxidation taking place since metal silicide film is oxidized when temperature is at least as high as 450°C . However, this temperature is very low compared to the film deposition temperature (750 – 800°C) and particles can be generated by the lifting of resident Si_3N_4 films on the inner wall of the quartz tube. Moreover, the low stand-by temperature also decreases the throughput of processing very much. Hence the temperature control is not likely to be a practical solution for the oxidation problem.

Meanwhile, the oxidation of metal silicide could be suppressed when the concentration of oxygen in the tube was kept under several ppm [5]. The method was found to be effective when the stand-by temperature and deposition temperature of Si_3N_4 film were as high as 650°C and 750 – 800°C , respectively.

In this work, we have modified the conventional equipment for Si_3N_4 deposition into equipment shown in Fig. 1(b) in order to reduce the oxygen concentration in the tube. With our new deposition equipment, the oxidation of metal silicide has been prevented and the characteristics of Si_3N_4 film have also been improved by reduction of oxygen atoms inside the film.

2. Experiment

2.1. Modification of the quartz tube for reducing the oxygen concentration

As already mentioned, two primary factors determining the oxidation are the amount of oxygen in the quartz tube and stand-by temperature of the deposition equipment. In this experiment, we tried to suppress the oxidation of metal silicide by decreasing the oxygen concentration. The deposition equipment used in the experiment was a vertical-type LPCVD (Low Pressure Chemical Vapor Deposition, Kokusai Co., DJ-802V-D) whose quartz tubes were quite general ones (Fig. 1(a)). In the deposition process of Si_3N_4 films, the source (SiH_2Cl_2 , NH_3) and carrier (N_2) gases are introduced into the inner tube and exhausted through the outer tube. In this process, however, the oxygen molecules flow into the quartz tube while loading the boat where silicon wafers are installed. Furthermore, there was already a considerable amount of oxygen present in the tube, too. These oxygen molecules react with underlying metal silicide to form the oxidized metal silicide film during the deposition process. The oxide also penetrates into the Si_3N_4 film and degrades the electrical isolation characteristics of the Si_3N_4 .

To eliminate such problems, we have replaced the conventional quartz tube of twofold configuration with a single-tube configuration and made the source and carrier gas flow from the upper part to the lower part of the tube by using a long injector (Fig. 1(b)). With this new configuration, N_2 gas could be provided into the tube through the injector while the wafer-installed boat was loaded. The flow of N_2 gas took the oxygen molecules away that were present in the tube. With sufficient supply

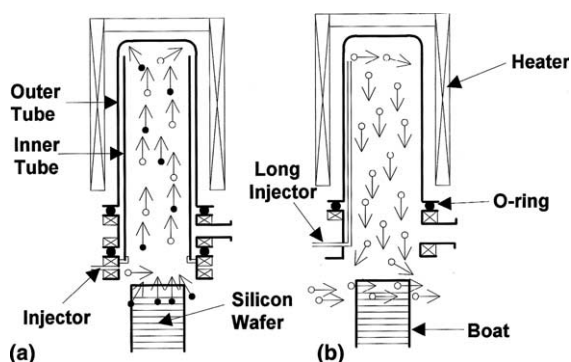


Fig. 1. A schematic diagram of the conventional furnace (a), and improved furnace using the long injector (b) (•: O_2 , ○: N_2).

of N_2 gas, the concentration of oxygen in the tube was decreased down to several ppm. In addition, we have installed the N_2 curtain line at the entrance of the quartz tube in order to shut out the influx of oxygen gas accompanied by the incoming boat.

Since the modified equipment has only a single tube, the operation and maintenance has become much easier. Furthermore, the uniformity of the deposited film can also be improved because Si and N_2 can be supplied in an independent way when the source gases are introduced into the quartz tube through the injector [6].

2.2. Deposition of polysilicon film for estimation of oxygen concentration

To estimate the oxygen concentration in quartz tube, a polysilicon film was deposited by using the standard process where the pure SiH_4 gas (99.999 %) was supplied without any H_2 or N_2 impurities. The deposition temperature was around 625 °C and the pressure was kept between 0.2 and 0.4 Torr. The flow rate of SiH_4 gas was 20–40 cm^3/min , which made the deposition rate around 100 Å/min. The stand-by temperature of the quartz tube was set at 400 °C. The phase of thin film deposited below 600 °C becomes amorphous [7–10] which may be crystallized if the film has sufficient thermal treatment in subsequent processes. Since this crystallization, however, may take place in a random and unstable manner, there remain many amorphous domains over the layer. Hence the deposition temperature has been determined to be 625 °C that is high enough to guarantee a perfect polysilicon layer [11–13].

To form a polysilicon film of low oxygen concentration, the air in the tube has been replaced by N_2 gas by supplying N_2 gas at rate of 20 slm (standard liter per minute). Then a large amount of N_2 gas was flowed from top to down of the quartz tube by using a long injector as is shown in Fig. 1(b) during the loading process of silicon wafers, which is succeeded by the standard polysilicon deposition process mentioned earlier. The thickness of the film was about 1000 Å. The oxygen content of the polysilicon film has been measured by using Secondary Ion Mass Spectrometer

(SIMS) analysis and compared with that of polysilicon film deposited in a conventional way.

2.3. Detailed oxidation mechanism of metal silicide film

To fabricate the gate lines made of $TiSi_2$ [14] in DRAM devices, thin layers of polysilicon/RF-etch/ TiN / $TiSi_2$ films are deposited as is shown in Fig. 2(a). Then the Si_3N_4 layer is deposited for use of the etching mask. In this process, the oxygen present in the tube reacts with Si in $TiSi_2$ film to form a native oxide layer over the $TiSi_2$ film. Although the thickness of the native oxide between $TiSi_2$ and Si_3N_4 layer is very thin, the oxide has very low chemical activity against the etching elements of $TiSi_2$. Hence the $TiSi_2$ layer cannot be removed uniformly when it is etched under the Si_3N_4 mask, which makes it difficult to form the gate line with good electrical characteristics. As the packing density of the devices is getting higher, this problem is also getting more serious since the relative variation of the gate line width becomes much larger.

Likewise, the word or bit-line of WSi_x [15–17] is fabricated from the $TiN/WSi_x/PE-Si_3N_4$ layers as

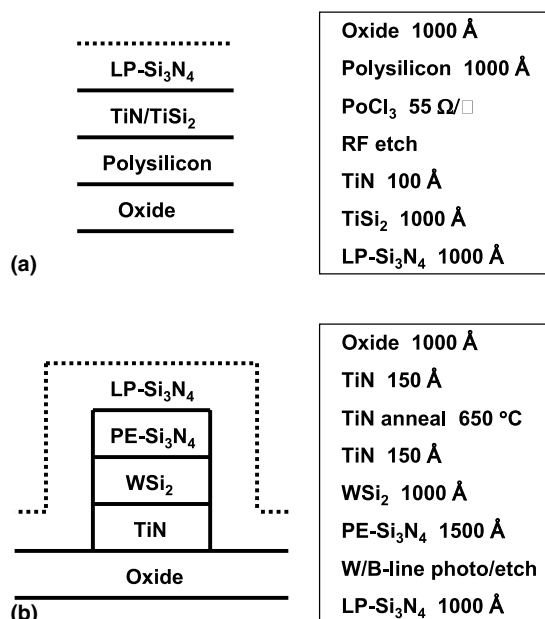


Fig. 2. Process sequences of the gate line (a), and word/bit-line (b) by using the silicide films.

in Fig. 2(b). After the patterning using the photolithography and etching, the spacer Si_3N_4 film is deposited. In this process, the native oxide is growing by the reaction of the oxygen gas in the tube and the Si in WSi_x film. The primary problem of the native oxide in this case is the stress between Si_3N_4 and WSi_x surfaces during the spacer-forming process, which results in the lifting of the spacer film.

To resolve the problems of the native oxide, we have controlled the flow rate of N_2 gas that drives out the oxygen gas in the tube. For each Si_3N_4 deposition, N_2 gas was supplied through the long injector at a flow rate selected between 1 and 20 slm. The stand-by temperature of the deposition equipment was set to be 650 °C for all cases. After deposition, the Si_3N_4 film was patterned to make a mask with which the etching of the underlying metal silicide layer was carried out subsequently. Then the etching profiles were observed by using the Scanning Electron Microscope (SEM) to check whether the native oxide layer had been formed or not for each case.

3. Results and discussion

Thin polysilicon layers formed by LPCVD equipment generally have oxygen and carbon impurities with concentration of 10^{17} – 10^{18} cm^{-3} . There are also 10^{15} – 10^{16} silicon dangling bonds in a cubic centimeter [18]. The same is true for the Si_3N_4 layer made from SiH_2Cl_2 and NH_3 gases. The impurities and dangle bonds in the thin films build up the deep traps in energy band that degrade the electrical characteristics of the thin films [19,20].

In our work, we have replaced the twofold quartz tube to single-tube configuration. It has been found that the configuration of the tubes has little effect on the characteristics of the deposition layer if other parameters such as etch rate and deposition rate are same.

Fig. 3(a) shows the concentration of oxygen in the polysilicon layer measured by SIMS. The layer was deposited in the conventional equipment (two-fold-tube configuration) and the thickness was 1000 Å that is thick enough to measure the electri-

cal characteristics. On the other hand, Fig. 3(b) is the result obtained with modified equipment (single-tube configuration) where N_2 gas had been flowing through the tube at rate of 20 slm to shut out the external oxygens accompanying with the incoming wafer boat. As you can see, the concentration of oxygen in polysilicon film deposited in the modified equipment is about $7 \times 10^{15} \text{ cm}^{-3}$ which is ~ 30 times smaller than that of the conventional equipment. The result confirms that the flow of N_2 gas is very effective to remove the oxygen gas in the tube.

Next to verify the effect of N_2 gas on the growth of native oxide, we have deposited Si_3N_4 layer on the metal silicide after the N_2 gas flow through

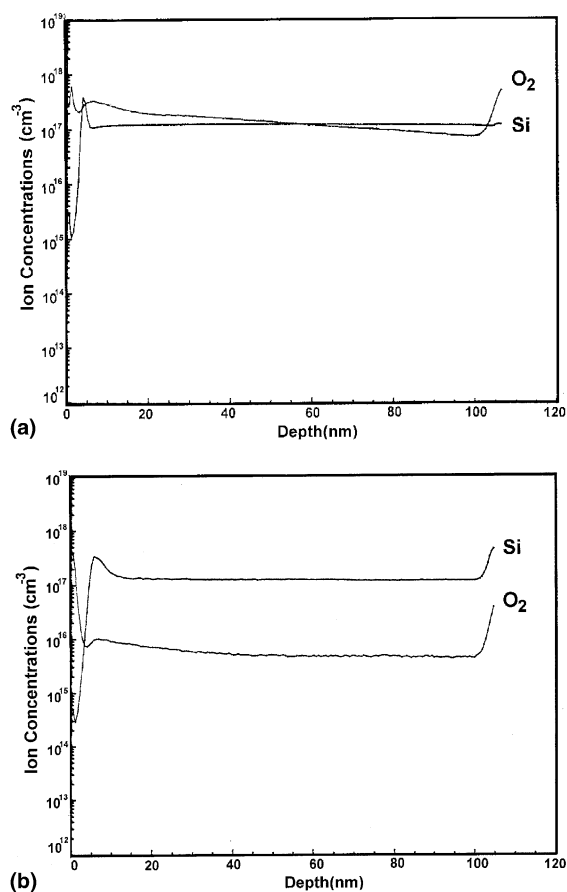


Fig. 3. (a) SIMS profile of oxygen concentration in the polysilicon film formed in the conventional furnace. (b) SIMS profile of oxygen concentration in the polysilicon film deposited in the modified equipment (with long injector) with 20 slm N_2 gas.

the long injector and observed the etched profile. We have carried out the experiment under many values of the flow rate to obtain some quantitative data. The flow rates tested were 1, 3, 5, 8, 10, and 20 slm. The stand-by temperature of deposition equipment was set to be 650 °C taking into account the efficiency and throughput of the equipment.

Fig. 4 is the SEM photograph of the gate patterning consisting of underlying TiSi_2 layer and Si_3N_4 mask layer. Fig. 4(a) is a pattern when the flow rate of N_2 gas was 5 slm. As you can see, there are obscure marks of the native oxide on the TiSi_2 surface and the edge of etching profile is not clean, which means there was a considerable amount of native oxide formed on the surface. On the other hand, the surface and etching profile are very clean when the flow rate was 10 slm, as you can see in Fig. 4(b).

In Fig. 5, there is a Si_3N_4 film over WSi_x layer. With additional lithography and etching process, we can make word or bit-lines made of WSi_x , where Si_3N_4 film is required to form the spacers. The figure shows similar result with the case of TiSi_2 gate. When the flow rate of N_2 gas was 3 slm during the wafer loading, WSi_x film so severely lifted and penetrated the upper Si_3N_4 layer that the pattern could not be identified. However, the lifting gets weaker as the flow rate increases and there is no lifting observed when the flow rate was equal or higher than 10 slm.

As a whole, it has been found in our experimental data that the sufficient N_2 gas flow lowers the concentration of oxygen in the tube and obviously suppresses the growth of the undesirable native oxide when depositing Si_3N_4 film over metal silicide layer.

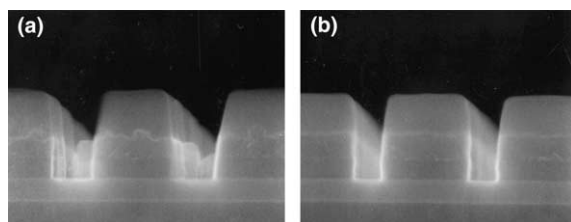


Fig. 4. Scanning electron micrographs of $\text{TiSi}_2/\text{Si}_3\text{N}_4$ interface in the gate patterning process for the N_2 -gas flow rates of (a) 5 slm, and (b) 10 slm.

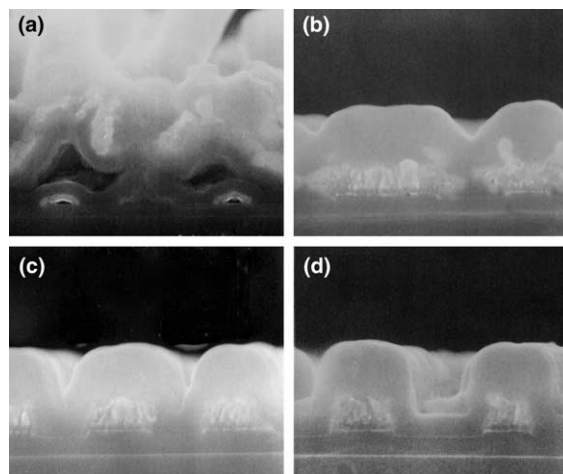


Fig. 5. Scanning electron micrographs of $\text{WSi}_x/\text{Si}_3\text{N}_4$ interface in the word-line and bit-line process for the N_2 gas flow rates of (a) 3 slm, (b) 5 slm, (c) 8 slm, and (d) 10 slm.

4. Conclusions

As the density of integrated circuits has been increasing, a lot of efforts have been tried to replace the polysilicon with metal silicide as a material for gate and word/bit-lines. Although the metal silicide has a much lower resistance compared with the polysilicon, it is easily oxidized by the oxygen gas in the quartz tube, which causes a lot of problems in the subsequent processes and electrical characteristics.

To prevent the oxidation, it had been proposed to lower the stand-by and deposition temperature of the CVD equipment. However, the operation in the low temperature also has many disadvantages like generation of Si_3N_4 particles, extremely low throughput.

Hence in our work, we have proposed the method of suppressing the undesirable oxidation by removing the oxygen gas in the quartz tube. To control the oxygen concentration in the tube, the configuration and structure of deposition equipment has been modified. Supplying the N_2 gas through the long injector, the oxygen in the quartz tube was exhaled and incoming oxygen gas was blocked. The measured oxygen content in the polysilicon indicated that the oxygen in the tube was decreased very much when N_2 gas was supplied through the injector. From the subsequent

experiments, it has been found that there is no oxidation observed at the flow rate higher than 10 slm, which means no native oxide, no lifting of WSi_x film and clean etching profiles.

We expect that our new method can be a practical solution in the metal silicide processing because the oxidation can be suppressed by simple modification of the equipment without any drawback such as particle generation or reduction of throughput.

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