Modification of thin oxide films of MOS structure by high-field injection and irradiation

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Abstract. We have investigated processes of modification and changing of the charge state of MOS structures having a multilayer gate dielectric based on a thermal SiO₂ film doped with phosphorus under conditions of different modes of high-field electron injection and an electron irradiation. We have determined that negative charge, accumulating in the phosphosilicate glass (PSG) ultra thin film of the MOS structures having the two-layer gate dielectric SiO₂-PSG under conditions of both high-field tunneling injection of electrons and electron irradiation, could be used for a modification of devices having the same structure (e.g. correction of threshold voltage, increase of charge stability and breakdown voltage of MOS structure). We have shown that when thickness of PSG film increased, a raising of the electron traps density occurred, but the value of the cross-section of electron traps was the same. It was established that in order to obtain MOS structures with high thermal stability, one has to anneal them at 200 °C after performing irradiation treatment.

1. Introduction

Doping of the gate dielectric, based on thermal silicone dioxide, by phosphorus can be applied especially in order to stabilize the characteristics of devices [1–6]. Phosphosilicate glass (PSG) film can take place also in case of using polycrystalline silicon gates doped by phosphorus [7]. The fact of the PSG film presence considerably changes the character of charge state changing of MOS structures under both the high-field tunneling injection of electrons in dielectric and irradiation in comparison with the structures based on thermal SiO₂ films which are not doped with phosphorus. Currently the gate dielectric based on SiO₂ passivated by ultra thin PSG film is widely used for field effect devices based on SiC [3, 4]. The main problem in creation of the dielectric films for the semiconductor devices based on the MOS structures allowing the parameters of the devices to be controlled by the high-field injection modification and the irradiation modification after their manufacturing is fabrication of the required optimal structure of the dielectric film providing the effective trapping of the charge carriers on the traps and having the high injection and irradiation stability as well as low charge defectiveness [2,3,6–8]. Everything mentioned above is a cause of demand for an integrated and comprehensive study of the technological process of SiO₂ films doping with phosphorus and also the SiO₂-PSG structure study in order to optimize the parameters of the dielectric film needed to increase the stability and reliability of MOS devices.

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In this work we have considered a method of MOS structures modification based on SiO₂ film doped by phosphorus under the high-field tunneling injection of electrons into the gate dielectric and modification by the irradiation of crystals with low-energy electrons. Also, we have studied the influence of SiO₂ phosphorous doping modes on the characteristics of MOS structures.

2. Materials and experimental techniques

The tested MOS capacitors were fabricated on Si (100) n-type wafers with a resistivity of 4.5 Ω·cm. As the gate dielectric, we used both a thermal silicon dioxide film and SiO₂ film passivated by phosphosilicate glass. Silicon dioxide having the thickness of 7±50 nm was thermally grown by using a dry oxidation at 850÷1000 °C. PSG film having the thickness of 3±22 nm was produced by doping with phosphorus from POCl₃-O₂ at 900 °C. In order to obtain experimental samples having different PSG thickness, the doping time by phosphorus was ranged from 1.5 to 7 min. After that the wafers were exposed to nitrogen annealing at 1000 °C. As the gates we used both a polysilicon (Si*) film doped with phosphorous up to 20 Ω/□ and an aluminium film. The gates had the square dimensions of 10⁻⁴ × 10⁻² cm².

The thickness of the PSG film was calculated as the difference between thicknesses of the insulating film before and after selective etching in a mixture of HNO₃ (33 ml), HF (44 ml), and distilled water (923 ml) [8].

In order to realize the injection modifications of MOS structures, we used the Fowler-Nordheim high-field injection of electrons from the silicon substrate [9–11] by a constant current pulse of 0.1 µA/cm² to 10 mA/cm². During the injection process we monitored a value of voltage dropping on MOS structure that allowed us to obtain information about a change of the charge state of the dielectric film straightly at the time of the modification process. So as to determine the amount of thermostable components of an accumulated negative charge in the dielectric film after the injection and radiation treatments, the MOS structures were annealed in a range of temperatures of 150÷250 °C within the time from 3 to 30 minutes. We monitored the changes of the charge state of MOS structures by using the C-V technique and multilevel current stress technique [11]. The latter technique was to apply a special form of a current pulse to a sample, providing a charge of MOS capacity and subsequent high-field FN electron injection into the dielectric which generally carried out in the constant-current mode. During FN injection we measured the shift of the voltage drop on the MOS structure ΔV_I, characterizing a change of the charge state of MOS structure [2, 6, 11]. From the C-V characteristics, we determined voltage shift (ΔV.ss) characterizing the surface state charge.

In order to study the influence of electron irradiation on characteristics of the MOS structures, we used a scanning electron microscope Carl Zeiss EVO 40. Using the microscope, we carried out the irradiation of the MOS structures by electrons with energy from 15 to 20 keV having a beam current of 8 nA and a fluence up to 5 · 10¹⁴ cm⁻².

3. Experimental results and discussion

In this work we implemented a comparative study of the charge state modification of MOS structures by both the high-field tunnel injection of electrons into the gate dielectric and the electron irradiation of the MOS structures. A distinctiveness of the MOS structures having the two-layer dielectric SiO₂-PSG, being under high-field electron injection, is the accumulation of negative charge in the PSG film [1, 6, 7, 12]. In accordance with the assumptions made in [6, 12], the electrons injected into the insulator are captured by the positively charged groups located in the PSG film. Apparently these electron traps make a major contribution to the value of an accumulated negative charge in the PSG film and these traps have the capture cross section \( \sigma_1 = 1.4 \cdot 10^{-15} \text{ cm}^2 \) [8, 12, 13]. As shown in [12], along with the traps of the first type in the two-layer dielectric SiO₂-PSG there exist electron traps having capture cross section of \( \sigma_2 = 3.2 \cdot 10^{-16} \text{ cm}^2 \) which are observed under the injection of electrons from Si. One of possible
explanations for the presence of electron traps of the second type can be the impact of molecules of POCl$_3$ on the SiO$_2$ structure [6] and, as consequence of that, a reconstruction of the silicon oxide structure near the SiO$_2$-PSG interface occurs what leads to the appearance of the dangling bonds of oxygen. These dangling bonds might be electron traps.

Fig. 1 shows the dependencies of the shift of a voltage drop on the MOS structure in time of the injection process modification by constant current (1), the voltage shift provided by the integrated charge in the surface states (2) and a change of these dependencies after annealing at 200 °C (1′, 2′) on the density of injected electrons. In order to implement the mode of high-field electrons injection from the silicon substrate to the gate of MOS structure, the pulse of constant current having density of 1 μA/cm$^2$ was applied. In figure 1 the density of injected electrons was defined as $N = Q_{inj}/q$, where $q$ is the electron charge; $Q_{inj}$ is the density of injected charge.

We used the irradiation with 15 to 20 keV electrons what guaranteed us a track length of more than the thickness of the gate. We ascertained the fact that the irradiation of MOS structures having SiO$_2$-PSG film by electrons possessing energy enough to pass through the gate dielectric film significantly increased the density of surface states at the Si-SiO$_2$ interface as well as the accumulation of a negative charge in the volume of gate dielectric in PSG film. Fig. 2 shows the dependencies of the shift of voltage drop on the MOS structure under conditions of the irradiation modification (1), the voltage shift provided by the integrated charge located on the surface states (2) and also a change of these dependencies after annealing at 200 °C (1′, 2′) on the fluence of electrons (in that case the energy of electrons is 18 keV) (2, 2′). In order to measure $\Delta V_I$ and $\Delta V_{ss}$ in case of irradiation modification, the process of irradiation was interrupted. During the interruption short impulse of current of 1 μA/cm$^2$ was applied to MOS structure (to determine $\Delta V_I$) [14]. Then we measured $\Delta V_{ss}$ by using of C-V characteristics. Measurements had negligible effect to the process of irradiation modification. As distinct from the high energy irradiation by electrons [15], in conditions of the low energy irradiation a change of the charge state of MOS structure is basically caused by the ionizing processes. The observed physical processes in case of the low energy irradiation in many respects are identical effects occurring in case of the high field electron injection [1].

Fig. 1 and fig. 2 show that in time of the irradiation by electrons, lower density of negative charge is accumulated in the gate dielectric in comparison with the high-field electron injection. Curves 1′ in fig. 1 and fig. 2 characterize the thermostable component of negative charge. Fig. 1 and fig. 2 demonstrate that the thermostable component of negative charge accumulated under the injection modification (curves 1′) highly exceeds the charge accumulated during irradiation by electrons. Therefore the modification by injection is more effective and under certain conditions of the injection causes less degradation of MOS structures (figures 1 and 2, curves 2). However the irradiation by electrons allows carrying out the group crystal treatment right on a semiconductor wafer. That significantly increases productivity of the treatment.

During the process of electrons injection from silicon if the thickness of PSG layer grows then the range of possible values of the threshold voltage of MOS transistors increases. However in order to ensure acceptable values of the surface state density, the value of injected charge at the time of adjusting of the threshold voltage should not exceed 0.3 μC/cm$^2$. The range of current exposure during changing of the charge state of MOS devices should be limited between $10^{-7} \div 10^{-5}$ A/cm$^2$. The decrease of the current stress density is accompanied by technical difficulties of implementation and is impractical as a result of the significant increase at the time of injection of the desired amount of charge. An increase of the injection current density leads to significant increment probability of the sample breakdown probability as well as to the build-up of the surface states density at the Si-SiO$_2$ interface [12] during the injection of electrons from Si.

Fig. 3 shows the dependences of the shift of voltage drop on the MOS structure at the time of the tunnel injection of electrons from silicon by a current pulse 1 μA/cm$^2$ on the value of
Figure 1. The dependencies of the shift of voltage drop on the MOS structure during the modification by the constant injection current (1), shift of the voltage caused by the integrated charge located on the surface states (2) and a change of these dependencies after annealing at 200 °C (1′,2′) on the number of injected electrons.

Figure 2. The dependencies of the shift of the voltage drop on the MOS structure in time of the radiation modification (1), the shift of the voltage caused by the integrated charge located on the surface states (2) and a change of these dependencies after annealing at 200 °C (1′,2′) on the fluence of electrons curves (2,2′).

Figure 3. The dependencies of the shift of the voltage drop on the MOS structure having the thickness of the gate dielectric SiO$_2$-PSG of 40 nm at the time of the modification by constant injection current on density of injected charge for a different thickness of PSG film: 1 — 5 nm; 2 — 9 nm; 3 — 13 nm; 4 — 22 nm.

the injected charge for MOS structures in case of different PSG film thickness in case the total thickness of the gate dielectric SiO$_2$-PSG equals 40 nm. Fig. 3 shows the fact that the increase of PSG film thickness leads to extension of a range of $\Delta V_I$ possible changes on the same amount of injected charge.

Interrupting the process of injection at a certain distance of time (process of interruption does not affect the experimental curves) we were measuring the shift of flat-band voltage $\Delta V_{FB}$ by using C-V characteristics and also the change of voltage applied to the sample under the injection by the same current density at the negative polarity at the gate $\Delta V_I$ (−). The analysis of the obtained dependencies revealed that the centroid of the negative charge located in the PSG film closer to the SiO$_2$-PSG interface. We ascertained the fact that the accumulation of
negative charge for all curves in Fig. 3 was mostly caused by presence of electron traps having the cross section $1.4 \cdot 10^{-15}$ cm$^2$.

We found that both the density of accumulating negative charge and the density of the thermostable part of accumulating negative charge (after annealing) increased in case of raising of doping time of SiO$_2$ by phosphorus what leads to the increasing of the PSG film thickness. But the increasing of the PSG film thickness is not acceptable for thin gate dielectric films because this might be a reason of deterioration of the gate dielectric charge stability and deterioration of the gate dielectric-semiconductor interface. If the concentration of phosphorus in the PSG film is more than 1.5% then it might leads to polarization effect and decrease of charge stability of the gate dielectric [5, 8, 12].

We estimated the relaxation time constant of negative charge having high-temperature stability in the range of operating temperatures for MOS devices with due regard for the curves of the thermally stimulated depolarization currents [8]. The estimated value of the relaxation time is larger than $4 \cdot 10^8$ sec. Therefore, in order to obtain MOS devices having high-temperature stability after correction of the structures charge state, it is needed to anneal the MOS devices at temperatures not lower than 200 °C. Also, modification of the characteristics needs to be performed taking into account the relaxation of the charge part during annealing.

Accumulation in the volume of gate dielectric a desired density of the thermostable component of negative charge allows us to adjust the threshold voltage of MOS transistors and increase the breakdown voltage of the gate dielectric as well as reduce the probability of breakdown by healing “weak spots” due to the accumulation of negative charge [10, 12, 16]. Fig. 4 shows the histograms of the MOS structures distribution by the charge-to-breakdown ($Q_{BD}$) for the samples having SiO$_2$ gate dielectric (1) and for the samples having two-layer SiO$_2$-PSG gate dielectric (2).

![Figure 4. The histograms of the MOS structures distribution by the charge-to-breakdown for the samples having SiO$_2$ gate dielectric (1) and for the samples having two-layer SiO$_2$-PSG gate dielectric (2).](image)

Fig. 4 shows the fact that the two-layer gate dielectric SiO$_2$-PSG allows to increase the average amount of charge injected into the dielectric before its breakdown and also allows to reduce the number of defective structures having a small value of the charge injected before breakdown. This effect is explained by the healing of “weak spots” in the gate dielectric due to the accumulation of negative charge and consequently by reducing the value of the local injection currents flowing in places of defects and leading to breakdown of the gate dielectric. As a result of the trapping of injected charge the potential barrier interfering the localization of currents in fields of long damages at the substrate interface raises.
4. Conclusions
We have established that the negative charge, accumulated in the PSG film in MOS structures having two-layer gate dielectric SiO$_2$-PSG at the time of both the high-field tunnel injection of electrons and the electron irradiation, could be used for modification of MOS devices. We have shown that the application of the high-field injection of electrons in order to modify the MOS structures charge state was more preferable than the usage of electron irradiation because in this case we could make an individual adjustment of the characteristics of each device. Also, by using selected modes of the high-field injection one may significantly reduce related degradation processes. We have ascertained the fact that both the density of the accumulated negative charge and the density of its thermostable component increased with the growth of a doping level of SiO$_2$ by phosphorus. The growth of a doping level of SiO$_2$ by phosphorus led to the increase of the PSG film thickness. We have shown that the application of two-layer SiO$_2$-PSG gate dielectric allowed to increase the average value of charge injected into the dielectric before charge-to-breakdown and to reduce the number of defective structures having a small value of the charge-to-breakdown. This effect is explained by the healing of “weak spots” in the gate dielectric due to the accumulation of negative charge and consequently by reduction of the value of the local injection currents.

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