Proc. of the X Int. Conf. - Ion Implantation and other Applications of Ions and Electrons, Kazimierz Dolny 2014

Modification of MOS Devices by High-Field Electron Injection and Arc Plasma Jet Treatment

V.V. ANDREEV^{*a*,*}, G.G. BONDARENKO^{*b*}, V.M. MASLOVSKY^{*c*} AND A.A. STOLYAROV^{*a*} ^{*a*}Bauman Moscow State Technical University, Kaluga Branch 2, Bazhenov St., Kaluga, 248000, Russia

^bNational Research University, Higher School of Economics, 20, Myasnitskaya Str., Moscow 101000, Russia

^cZelenograd Research Institute of Physical Problems, Moscow, 124460, Russia

Methods of modification of gate dielectrics of the MOS structures by high-field electron injection and arc plasma jet treatment were studied. It is possible to use them for correction of parameters, decreasing defects number and increasing reliability of MOS devices. It was found that the negative charge accumulated in the film of the phosphorus-silicate glass of the MOS structures with the two-layer gate dielectric SiO₂-phosphorus-silicate glass under the high-field electron injection can be used for modification of devices with the same structures. It is shown that the injection-thermal treatment allows to find and exclude MOS structures with defects of isolation and charge defects. Arc plasma jet treatment was found to improve characteristics of the MOS devices. These treatments increase injection and radiation resistance of the gate dielectric by creating the needed density of electron traps in the bulk of SiO₂ film.

DOI: 10.12693/APhysPolA.128.887 PACS: 73.40.Qv,73.40.Gk

1. Introduction

A perspective way for solving a task of creating semiconductor devices with the parameters which can be modified after their production is the development of dielectric films which are able to be changed in their charge state and maintain the accumulated charge for a long time during the process of exploitation [1–5]. Another perspective way is development of new methods of modification of MOS structures characteristics [4, 5]. At the present time a significant part of the research is devoted to the problem of the MOS structure characteristics improvement using special treatment like plasma treatment, irradiation, thermal treatment and so on. In view of development of new methods of plasma treatment (one of these is arc plasma jet treatment) it is possible to change the features of MOS structures [4].

In this work research of change of the charge state of the MOS devices as a result of the high-field injection treatment and following annealing as well as plasma treatment was carried out. The ways to improve gate dielectric characteristics of the MOS structures were found.

2. Experimental techniques and samples

Test MOS capacitors fabricated on Si *n*-type wafers having resistivity of 4.5 Ω cm with thermal silicon dioxide and with SiO₂ passivated by a phosphorus silicate glass (PSG) film were used. Silicon dioxide of a 10–50 nm thickness was thermally grown, using dry and wet oxidation at 850 ÷ 1000 °C. PSG film was produced by doping phosphorus from POCl₃–O₂ vapour at 900 °C. In order to obtain experimental samples of different PSG thickness, the phosphorus doping time ranged from 3 to 6 min. As gates with square dimensions of $10^{-4} \div 10^{-2}$ cm², polysilicon (Si^{*}) film, doped with phosphorous up to 20 Ω/\Box and aluminium film was used.

For injection modification of the MOS structures the Fowler–Nordheim (FN) tunnel injection of electrons from the silicon substrate was used [4, 6]. In the injection process voltage on the MOS structure was monitored that allowed us to obtain information about the change in the charge state of the dielectric film directly in the process of modification. For determining the amount of thermostable components with accumulated negative charge in the dielectric after the injection, the MOS structures were annealed at a temperature of 200 °C for a time from 3 to 30 min.

Changes of the charge state of the MOS structures were monitored using the C-V and multilevel current stress techniques [6, 7]. During FN injection at constant current the shift in voltage on the MOS structure, ΔV_I , characterizing the change in MOS structure charge state [7] was measured.

In this paper there was applied a new technology of surface treatment of semiconductor wafers, i.e. arc plasma jet treatment (APJT) [4], using Ar-plasma flow, which is formed with a multi-generator electric arc at the atmospheric pressure. Hydrodynamically continuous high enthalpy (10^4 J/deg) and low temperature (2×10^4 K) plasma jet was used during APJT. Transport of charged and neutral excited particles to the surface was carried out by diffusion through a thin boundary layer of the plasma. Thus a very high flux density (about 10^{20} cm⁻² s⁻¹) of the active particles with the kinetic energies < 0.1 eV was reacted with the surface. In this case the energy flux density was very high

^{*}corresponding author; e-mail: andreev@bmstu-kaluga.ru

(about 10^3 W/cm^2), too. The flux of photons was above $10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ in the range of long-wave ultraviolet. The change in surface temperature during the treatment was controlled by a speed of crossing the wafer by plasma jet and usually it did not exceed 200 K.

3. Experimental results and discussion

Previous studies [4–6] showed that the negative charge accumulated in the PSG film of the MOS structures with the two-layer gate dielectric SiO_2 -PSG under high-field electron injection can be used for correcting the threshold voltage of MOS devices. To fabricate devices with high thermal-stability after FN injection modification of charge state they must be annealed at a temperature of about 200 °C [6].

In Fig. 1 the shift of the voltage of the MOS structure during the modification vs. the density of injection charge under the high-field electron injection from the silicon substrate and followed by annealing at 200°C for the samples with different concentrations of phosphorus in the PSG film is shown. As can be seen in Fig. 1, the increase of phosphorus concentration in the PSG film leads to an increase of density of both negative charge captured in the dielectric (curve 2) and the thermostable components of negative charge (curve 2'). However, the growth of a phosphorus concentration increases the thickness of the PSG film [4]. At present time gate oxide thickness decreases constantly and thick PSG films are not applied. Therefore an increase of the threshold voltage correction range of MOSFETs is advantageously made by controlling the ratio between the thickness of SiO_2 and the PSG films, shifting the centroid of negative charge to the Si-SiO₂ interface.

Another way of high-field injection application for modification of the dielectric films of MOS structures is the usage of injection-thermal treatment (ITT), which allows to increase the reliability of MOS devices and identify samples containing charge defects [6]. The injection thermal treatment of MOS-structures corresponds to the high-field injection into dielectric of the determined charge density of electrons, followed by high temperature (200 °C) annealing of samples. ITT can replace the radiation treatment of MOS devices [7].

Figure 2 shows the histograms of the MOS structures distribution by the charge-to-breakdown for the samples without treatment (1), after injection treatment (2) and injection-thermal treatment (3). As can be seen from Fig. 2, injection treatment eliminates the charge structure defects leading to breakdown (the density of chargeto-breakdown less than 0.1 mC/cm^2), and thus significantly increases the reliability of devices and integrated circuits. However, such treatment without annealing slightly decreases the injection hardening of structures and devices based on them (histogram 2, Fig. 2). The decrease of hardening is explained by degradation of both the charge of the dielectric film and the $Si-SiO_2$ interface under FN injection [1, 6]. For elimination of the degradation processes we annealed the sample after the treatment at 200 °C for 30 min. As can be seen from Fig. 2,



Fig. 1. The shift of the voltage of the MOS structure during the modification vs. the density of injection charge under the high-field electron injection from the silicon substrate (curves 1,2) and followed by annealing at 200 °C (curve 1',2') for samples with different concentrations of phosphorus in the film PSG: (1,1') = 0.7%; (2,2') = 1%.



Fig. 2. Histograms of MOS structures distribution by the charge-to-breakdown for the samples without treatment (1), after injection treatment (2) and injection-thermal treatment (3).

histogram 3, after the annealing recovery of the injection hardening takes place. ITT allows to detect and eliminate the structure with leading to breakdown defects in the dielectric and thus the resource injection of samples is not practically reduced. As a result, the usage of ITT can lead to significant increase of injection and radiation resistance of MOS structures.

It was found that under certain modes APJT can significantly improve stability of the MOS structure charge and increase such an important parameter as the amount of charge-to-breakdown for the sample. Figure 3 shows the histograms of MOS structures distribution by the charge-to-breakdown for the samples without (1) and after APJT treatment (2). As can be seen from Fig. 3, after the APJT, the maximum value of the charge-to-breakdown of the sample can be increased more than one order of magnitude.



Fig. 3. Histograms of MOS structures distribution by the charge-to-breakdown for the samples without treatment (1) and after arc plasma jet treatment (2).



Fig. 4. The distribution of the charge-to-breakdown Q_{BD} (1,2 curves) and the relaxation time of the unsteady capacitance (1', 2' curves) of the MOS structures by the diameter of the semiconductor wafer which is normal to trajectory of the treatment of the wafer by plasma (the area of the contact with plasma $x/D = 0.2 \div 0.5$). 1, 1' — the curves for the 1st wafer; 2, 2' — the curves for the 2nd wafer.

For the investigations of APJT effect, measurement of the time relaxation of unsteady capacity and the chargeto-breakdown in the same MOS-structures before and after treatment were carried out. Figure 4 shows the relaxation time (τ) profilogram of the unsteady capacity of the MOS structure, recorded by the diameter of the wafer perpendicular to the trajectory of the plasma jet after APJT. The initial value of relaxation time was $2 \div 3$ s for

wafer 1 and $3 \div 4$ s for wafer 2. The area of direct contact of the plasma jet with wafer ranged $x/D = 0.2 \div 0.5$, where D is the wafer diameter, and x is the distance from its edge. In accordance with the results of [2] the generated carrier lifetime is proportional to the relaxation time of unsteady capacity. Significant reduction in the generated carrier lifetime in the region outside the plasma jet impacts is associated with the generation of surface states at the interface of $Si-SiO_2$ under the influence of the plasma radiation (visible light and short-wave ultraviolet) and with change of their charge state. The increase of the density of surface states in structures with internal mechanical stresses can occur due to transport of holes formed in the oxide to the $Si-SiO_2$ interface. Capture of holes by localized states formed strained Si–O bonds, causing movement of atoms from the local to the absolute minimum of the free energy, which leads to trivalent silicon forming surface states.

The most interesting fact is that the resulting distribution of τ is correlated with the distribution of $Q_{\rm BD}$, detectable on the same wafers along a diameter perpendicular to the trajectory of the plasma jet (Fig. 4). The initial value was of the $Q_{\rm BD} = 0.2 \div 0.6$ C/cm².

Thus, a new and important result is that APJT can increase by several times the charge stability of MOS structures. This is a result of the ability of capture electrons in the oxide, which prevents the growth of current under the dielectric pre-breakdown condition. Accumulation of negative charge as a result of capture of electron traps oxide shows the time dependence of the voltage on the MOS structure under constant current FN injection (Fig. 4). The increase of the concentration of hydroxyl groups after APJT seems quite natural. As a result of APJT, an increase in breakdown voltage of the gate dielectric is also observed, which is quite natural explanation for the formation of a negative charge in the formed oxide. The results indicate that in the areas outside the contact with the plasma jet, there was observed significant degradation of parameters associated with the generation of surface states in local areas with a high concentration of broken bonds under the action of ultraviolet radiation from the plasma [4]. These surface states are annealed in the direct contact with the plasma jet, due to transport of electronic excitations to the Si-SiO₂ interface [4]. Another important result is that for the first time a correlation between $Q_{\rm BD}$ and τ was found due, apparently, to the fact that both of these quantities are determined by the charge state of the interface. Thus APJT leads to the significant change of the generated currents in the surface area of silicon and an evolution of defects at the Si–SiO₂ interface.

4. Conclusions

A new method of modification of the MOS structure with the two-layer gate dielectric SiO_2 -PSG using highfield tunneling injection of electrons into the gate under constant current stress was proposed. During modification this method allows to monitor change of the MOS transistors features and taking into account the reduction of the part of the charge allows the precise correction of the threshold voltage of the MOS transistors. It was shown that the injection-thermal treatment makes it possible to find and exclude the MOS structures with the leading to breakdown defects of the isolation and the charge defects. At that reliability of the MOS devices does not decrease. It was found that the ITT enables the injection and radiation stability of the MOS devices increase due to modification of the dielectric film. It was found that the arc plasma jet treatment can improve the characteristics of the MOS devices increasing the injection and radiation stability of the gate dielectric due to creation the required density of the electron traps in the bulk of SiO₂ films.

Acknowledgments

This work was supported by the Ministry of Education and Science of the Russian Federation. The study was implemented in the framework of the Basic Research Program of the National Research University Higher School of Economics (HSE).

References

- S. Lombardo, J.H. Stathis, P. Linder, K.L. Pey, F. Palumbo, C.H. Tung, J. Appl. Phys. 98, 121301 (2005).
- [2] V.V. Afanas'ev, A. Stesmans, J. Appl. Phys. 102, 081301 (2007).
- [3] V.A. Gritsenko, *Phys.-Usp.* **52**, 869 (2009).
- [4] G.G. Bondarenko, V.V. Andreev, V.M. Maslovsky, A.A. Stolyarov, V.E. Drach, *Thin Solid Films* 427, 377 (2003).
- [5] G.G. Bondarenko, V.V. Andreev, V.E. Drach, S.A. Loskutov, M.A. Stolyarov, *Thin Solid Films* 515, 670 (2006).
- [6] V.V. Andreev, G.G. Bondarenko, V.M. Maslovsky, A.A. Stolyarov, Acta Phys. Pol. A 125, 1371 (2014).
- [7] V.V. Andreev, G.G. Bondarenko, V.M. Maslovsky, A.A. Stolyarov, *IOP Conf. Ser. Mater. Sci. Eng.* 41, 012017 (2012).
- [8] United States Military Standard MIL-STD-883H Method 1019.8.