PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 19, № 4 (2018) P. 352-357
DOI: 10.15330/pcss.19.4.352-357

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 19, № 4 (2018) С. 352-357

UDK: 621.382.82
ISSN 1729-4428

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Thermal Field Stabilization of the Threshold Voltage of the Field Transistors of the Submicron Technology of the LSI

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On the basis of the analysis of the volume correspondence of the phases in the active gate system Si-SiO_2, the possibility of obtaining a negative charge in the shutter system of submicron LSI is shown. Such a technological method has been experimentally verified at low temperature oxidation of silicon, which is patented. Studies have established that the magnitude of charge at the interphase boundary can be significantly influenced by introducing into the oxidizing atmosphere of halogen-containing compounds.

Article acted received 02.12.2018; accepted for publication 15.12.2018.

I. Charging properties of the boundary of the Si- SiO_2 submicron structure of the LSI

Further reduction of the MES transistors now requires a more detailed study and improvement of the technological processes by which the charge state of the semiconductor-dielectric interface boundary is formed, in particular how to control the nature and concentration of these charges, since this charge state determines the sign and the magnitude of the threshold voltage of the supply of LSI/ VLSI . Charges formed in the oxide of the shutter, significantly affect the currents of losses, threshold voltage, superficial recombination, stability of the parameters. Today, the problem of creating a partition boundary with given electrophysical parameters is mainly determined empirically with high experimental costs.

We know that the effective charge in the thermal oxide on the electrostatic silicon substrate orientations (111) and (100) is positive. On the contrary, the introduction of a stable negative charge in SiO_2 represents a rather complicated and difficult technological problem. The introduction of fluorine, chlorine, arsenic and some other impurities into oxide, in addition to allowing an efficient negative charge, does not allow its stability to be achieved, this charge is already eliminated by low temperature annealing at T = 200-300^{0}C or optical (photon) action. Meanwhile, obtaining a stable negative charge in a large degree would result in high technological efficiency in the regulation of the threshold voltage of field transistors.

Today, there are several approaches to solving this problem in the sub-micron technology of the LSI/ VLSI. One option suggests the implantation of ions into a film of thermally grown oxide at a relative temperature of iodine ions. The second option for the formation of a negative charge in SiO_2 was carried out by ion implantation (Ca^+). In addition, in a series of works where they tried to obtain a negative charge by doping substrates-Si Pd, Rh, Nd, and others, it was possible only to reduce the positive charge in oxide, rather than the formation of a negative charge in a pure form that does not solve the problem in general.

In this paper, the possibility of obtaining a negative charge at the boundary of the Si-SiO_2 section was investigated on the basis of the analysis of the nature of the defects occurring on the interphase boundary. The analysis was carried out within the framework of ensuring the principle of the bulk correspondence of crystalline lattices and their deformations, which allows to establish qualitatively the connections between the structures of the interface boundary and its electrophysical parameters using diagnostic methods.

Here it is believed that there is a thin quasicrystalline oxide layer with a distorted structure between the semiconductor Si-lining and the amorphous-oxide film. The results of the calculation of such a model on the concentrations of defects of the boundary of the Si-SiO_2 section during the installation of various modifications of silicon dioxide are presented in Table 1.

The data presented in the table show that only low-temperature α-quartz at the interface of mono Si (100)

Table 1

Concentration of defects with unclosed bonds at the interface of Si- SiO_2

№	Lining/orientation	Built-in oxide	Inconsistency $\Delta N^{n.v.}_{v}$ * 10-14cm^{-2}	Note
1	Si(111)	α is quartz (000)	-0.68	SiO_2 - thermal.
		β - tridymite (0001)	+0.56	
		β - cryostolite (111)	+0.57	
2	Si(100)	α - quartz (0001)	-0.10	
		α - cristobalite (100)	+1.15	
		β - cristobalite (111)	+0.12	

and Si (111) from all modifications of SiO_x should cause a negative charge. Therefore, in order to obtain a purely negative charge, in our opinion, it is necessary to ensure the growth of SiO_2 oxide at a possibly lower temperature, which will reduce the probability of formation in the oxide film of α-crystallobalite. This can be done technologically.

In the role of the low-temperature oxidation method, we selected ion-beam synthesis of SiO_2 using ionic sources such as Radikal or Istra. Experimental installation "Vertical" with the use of these sources allowed to receive the collimation beams of ions with an energy of up to 200eV and a current density of 0.5-5mA / cm^2, as set forth in the author's monograph "Sub-and Nanomicon Technology of Structures of the WSI" - Ivano-Frankivsk: City of HB-2010 - 454s. It is the application of low-energy ions that also contributed to a sharp decrease in radiation defects, and in the process of forming SiO_2 dioxide, the liner carrier can be cooled cryogenically (liquid nitrogen at 77°K). Therefore, taking into account the ion bombardment and heat release, the radiation during oxidation was maintained at a temperature below the Si substrate (that is, <300^{O}K). Experiments were carried out on Si-substrates of the brand KEF-4.5 (100), providing a minimum threshold voltage U_T.

To activate the oxidation process, ionization of oxygen by Xe^+ ions with energy of 25-50 eV was used. The design of the installation allowed the addition of a reactor chamber, along with oxygen (exact dew < -70^{0}C) halogenated gases (CCl_4, SF_6, freon). To eliminate the influence of natural oxide through the formation of SiO_2, it was bleed by bombardment with Xe^+ (milling) ions with the addition of halogenated gases. The scrubbing of the natural silicon oxide layer prior to the growth of the low temperature new ion beam method is used in high-quality MES technology of the sub-micron structures of the LSI to obtain accurate high-stability SiO_2 films as a screw dielectric. The magnitude of the charge in the oxide was determined by the volt-ampere characteristics of the mercury or indium probe.

Our research has found that unlike thermal oxide, we obtained SiO_2 films of 8-12 nm in thickness. already characterized by an effective negative charge, whose magnitude practically did not change with thermal annealing to T ≤ 450-500^{0}C. This corresponds entirely to our theoretical considerations described above regarding the connection of negative Q_s to the formation of the phase of α-quartz, which is thermodynamically more distinct at atmospheric pressure to a temperature of 573^{0}C.

The results obtained by us testify to the very fundamental importance of using ion-beam technology with ion sources and low cryogenic temperatures for the substrate for a negative charge. It is the cryogenic temperatures that provide the formation of a negative charge, by which you can adjust the threshold voltage MON-transistors submicron technology LSI.

We also investigated the influence on the electrophysical parameters of obtaining structures of halogen-containing gases introduced into the oxidizing medium (2-3% vol.). As is well known in the research, ions of halogens can leave (unclosed) unbound ligaments at the interface and reduce the density of surface states Q_s. It was found that the addition of tetrachloride carbon (CCl_4) has little effect on the Q_s value and it is virtually impossible to obtain a negative charge. In the presence of sulfur hexafluoride (SF_6), the voltage characteristics are shifted toward negative voltages, as illustrated by Fig. 1.

This allows for a certain concentration of SF_6 in the gas stream (7 - 10 % vol.) To receive zero and negative threshold voltage U_T. On this technology, we obtained a

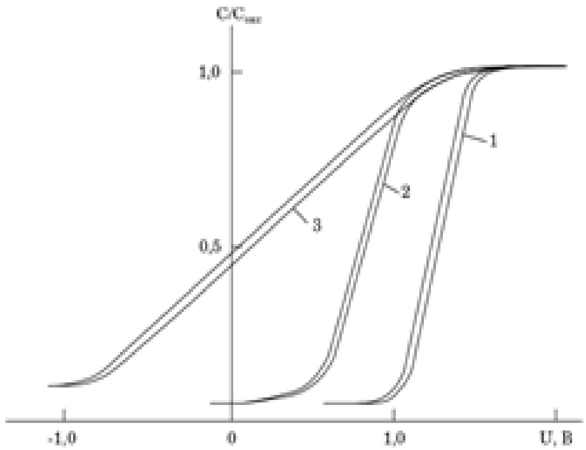

Fig. 1. Volt-fantastic characteristics of Si- SiO_2 structures:1 - without halogen compounds; 2 – O_2 + CCl_4; 3 – O_2 + SF_6.

patent for utility model N27540 "Method for obtaining n-MES transistors with negative threshold voltage" of 12.11.2007, which allowed to adjust the field voltage for n-MOS transistors to zero and negative values.

The threshold voltage offset (voltage of the ΔU_{FB} plane zones) obviously can not be related to the charge of the ions introduced into the oxide themselves, since in this case it would have been expected to shift it in the opposite direction, as the oxidation theory says. Here, fluorine ions (F^-), which have smaller size and higher mobility compared to chlorine ions (Cl^-), can more effectively penetrate the boundary of the Si-SiO_2 section and cause a change in the structure of the transition layer, which causes the appearance of dipole centers of the opposite orientation (that is, the transformation of α-quartz into α-crystallo-base). Such transitions, while preserving the orientation of the Si-substrate, are known. Therefore, the probability of this transformation is increased by an order of magnitude due to the presence of a sufficiently large concentration of point defects that cause mechanical stresses (here the density of fast surface states (DFSS) was obtained at our level at $10^{12}eV^{-1}sm^{-2}$), as well as the presence of impurity atoms (because the interphase boundary becomes an effective layer), which effectively stabilize one or another modification of oxide. The decrease of Q_s is also related to the recalculation of complex dipole centers that arise due to bulk inconsistencies attracted by directional dipoles that form halogen ions with uncontrolled metal ions (Na^+, Cu^+ and others), which are digested from the volume semiconductor substrate.

The results of our research indicate that the formation of a stable negative charge on the boundary of Si- SiO_2 in the conditions of ion-beam silicon oxide at a cryogenic temperature (below room temperature). This allows us to develop a method for adjusting the threshold voltage of the n-MES transistors in a sufficiently spherical interval from U_t = -1,0B to U_t = + 1,5B. An interesting method here is n-MOS transistors with a threshold voltage Ut = 0. In addition, the charge charge Q_s on the boundary of Si- SiO_2 can be influenced by the introduction of the oxidizing amorphous of halogen-containing compounds. It should be noted here that ion-radiation deposition of SiO_2 can be replaced by multi-charge implantation of fluorine ions (F^{--}) at a cryogenic temperature determined by the corresponding patent.

II. Electrophysical characteristics of MDN devices with a warp dielectric obtained by photonic-thermal oxidation of silicon

Today, in perspective technological processes, which must meet the requirements of modern serial production of sub-micron structures of the LSI / VLSI, requirements are set for the achievement of extremely high structural and electrophysical parameters of functional layers of such structures.

In this article, an analysis of the electrophysical characteristics of MDS of condensers as test structures is carried out, the pseudo-oxide of which is formed as a result of the photonic-thermal oxidation (PTO) Si substrate for sub-micron structures of the LSI, which reduces the oxidation temperature.

The test MPN-capacitors, which were formed using FT technology, were characterized (depending on the electrode area) by the average values of breakdown fields (voltages) of EPR from 12 to 15.8 MW / cm. The electric field applied to the MDS-capacitors varied at a rate of 2MV / cm / sec, and the electrical breakdown itself was recorded at a current level of 5 μA. Dispersion of the breakdown fields of the measured structures of MDS capacitors, given in Fig. 2a, has a fairly small value ($\sigma \leq$ 2MV / cm), which suggests a fairly high quality of the warp dielectric. The dispersion of the perforated fields of already thermal oxides is $\sigma \geq$ 2MV / cm, and the range of EPR = 6-9MV / cm. A positive feature of the FTO is also the complete absence of micropores in such an oxide, which are recorded in the experiment as an electrical breakdown of the dielectric in fields less than ≤ 5MV / cm.

The VAC of an MDN-capacitor with a submerged photonic-thermal dielectric already has two regions: (Fig. 2b). Analysis of the second region of the VAC, recorded by the Fowler-Nordheim Law for the tunneling of charge carriers through a triangular barrier, characterized by a dispersion field σ = 3.2 * 108 V / cm, significantly exceeding the measured values for the barrier, silicon-thermal oxide (2.6 * 106 V / cm). Such experimental data indicate a high increase in the potential barrier of silicon-photonic-thermal oxide. In this case, the current density, which is equal to 2 * 10-9 A / cm^2, corresponds to the electric field obtained 8MV / cm (Fig. 2b), satisfies the requirements of the pouring dielectric of the storage capacitor of dynamic PL and microprocessor systems (MP and MK).

VFH of MDN-capacitors with submerged photonic-thermal oxide indicates the high quality of the received thin films of silicon dioxide SiO_2 and the boundary of the Si-SiO_2 section: the values of the plane U_{FB} = -0.22 - (-0.25) B, the density of the inset embedded in the charge within the limits of the accuracy of our experiment (1-2) * 1010 zar / cm^2, the density of surface states in the middle of the band gap in mono-Si was $N_{ss} = 4 * 10^{10}$ $eB^{-1}cm^{-2}$ (Fig. 2c). This value of Nss is calculated on the low-frequency VHF (10 kHz).

Also, the measurement and thermopole stability of MDN structures at a load of 3MV / cm at a temperature of + 150^0C and lasting for 30 minutes. The results of this experiment showed a slight change in the voltage of the plane zones ($\Delta U_{FB} = \Delta U_{ps}$), namely, the value $\Delta U_{FB} \leq$ 45mV. Measurement of all MDN condensers already with thermal oxide was given by the magnitude of the plane zones ΔU_{FB} = -0.4 - (-0.55V), the density of surface states in the middle of the band gap N_{ss} = (6-9) * 1010 eV^{-1} sm^{-2} and thermopole the stability of the flat zones ΔU_{FB}> 115 mV at the above-stated load.

Thus, the obtained results indicate that the photonic-thermal oxidation of the submerged dielectric is extremely promising for the formation of sub-micron structures of LSI / VLSI. It should also be noted that the use of photonic processing of an excimer laser (ArF and KrF) with a range of wavelengths of 193 and 247nm allows lowering the temperature to the level of 570-

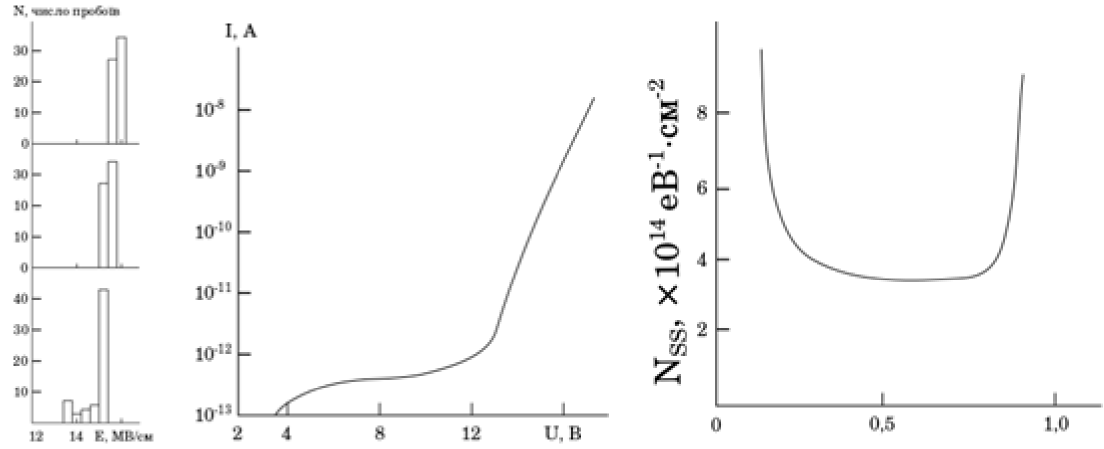

Fig. 2. a) histograms of breakdown fields for MDN-capacitors with the area of 30x30; 50x50; 150x100 microns (I-III) and with a SiO_2 thickness of 12.5 nm; b) VAC of MDN-structures with a thickness of bare metal oxide of 15 nm; c) Distribution of the density of surface states by energy in the forbidden zone.

620^0C, which, with an endurance of 10-25 seconds, completely eliminates the blurring of the concentration profiles.

III. Sub-SiO_2-SiO_xNy-SiO_2 sub-mixture system as a high-quality dielectric of storage capacitors of operational memory circuits (OMC)

Further increasing the degree of integration of the LSI, in particular the memory circuits, leads to the search for new ways in the technology of preparation and formation of high-quality dielectric of storage capacitors of operational memory circuits (OMC). Here the main requirements for this dielectric are: low defect density, high electrical strength and high thermal stability in the wide temperature range (-60 - (+125)^{0}C). In addition, such a dielectric should have high barrier properties in relation to rapidly diffusing admixtures of boron and phosphorus. To solve such a difficult task, it is necessary, on the one hand, to develop a technology for preparing the surface of silicon substrates to provide a minimum thickness of the surface interphase region Si-SiO_2 and a minimum surface charge density when forming the self-winding dielectric. The technology of forming a three-layer oxide oxynitride-silicon oxide requires several steps: 1) the stage of purification and preparation of an atomic clean surface of mono-Si; 2) stage of formation of a three-layer structure in a single process-microcycle; 3) test measurements of the electrophysical parameters of the formed dielectric (test diagnostics).

The first stage involves purifying and preparing a clean atomic surface using chemical and plasmachemical treatment. The essence of chemical treatment consists in the oxidation of heavy metals and complex organic compounds using perhidroglycerol-permanganate solution of herb in the deionized form in the ratio H_2O_2 : CH_3COOOH : H_2O = 3 : 1 : 1 with nitrogen and UV irradiation of the solution:

$$CH_4 + CO_2 + O_3 + 2H_2 \uparrow + M_cO, \qquad (1)$$

Ozone O_3, which is formed by this reaction, intensively reacts with complex organic compounds, turning them into more simple, easily soluble in a perhydrooxide solution in deionized water. On the other hand, the rehydrolyzate of H_2O_2 and the parietal cascade of CH_3COOOH act as strong oxidizers of quantities and transition metals that are responsible for the mobile charge in oxide during thermal tests.

Finishing plasmochemical treatment of Si substrates is carried out in a high-frequency plasma reactor at a frequency of 13.56 MHz or 2.4 GHz in a plasma of oxygen and hydrogen (O_2 + H_2) in a ratio of 2: 1. It is the oxygen plasma that leads to the purification of organic compounds that have already been introduced with deionized water, and the hydrogen plasma restores natural oxide to the minimum possible Si-SiO_2 limit, reducing its deformation, voltage, and charge state Q_S.

To reduce the deformation phenomena and the charge state of the Si-SiO_2 boundary, in the second stage, rapid thermal oxidation with the use of the photon "Impulse-3" on Xenon lamps KNP16 / 250 in an atmosphere of dry oxygen, ultraviolet irradiation (mercury lamp DRS-250) is carried out at a temperature T = 950 - 1100^{0}C for 3-5 minutes at an oxide growth rate of 0.6 mm / min. In this case, the thickness of ultrahigh oxide is 2-3nm. Analysis of the data presented in Fig. 3 a, b indicates that the thickness of the oxyhydride film and its refractive index n, which withstands repeated oxidation, can be reduced to 1-3 mm in comparison with conventional thermal oxidation. It is precisely in the case of rapid thermal oxidation (RTO) thermomechanical stresses and deformations at the interface of Si-SiO_2 can be reduced to a level that positively ensures the thermopole stability of the CV-characteristics of such a screw dielectric, maintaining its high strength at the level (12-14) MV / cm at The instability of the voltage of the plane zones $\Delta U_{fb} \leq$ (-25 - (-60)) mV. All electrophysical measurements were made on test capacitors with polysilicon and polycydeal gates with an area of 10^{-4}-10^{-}

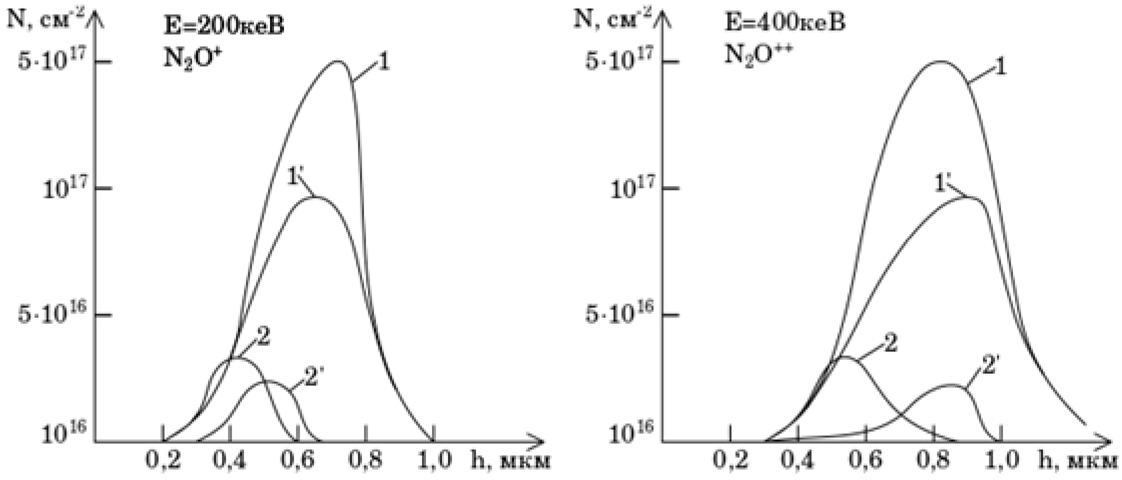

Fig. 3. Concentration profiles of atoms of oxygen (1) and gas atoms (2) to (1,2) and after (1', 2') of fast impulse activation for a dose of $2*10^{17}$ cm^{-2} for: a) N_2O^+ at E = 200 keV; b) N_2O^+ at E = 400 кеВ.

$^1cm^{-2}$.. This formation of the three-layer structure of SiO_2-SiO_xNy-SiO_2 allowed to greatly reduce the density of surface states to the level (1-2) * 10^{10} eV^{-1} sm^{-2}.

It is this level that provides the geter effect of the oxynitride layer. This is the originality of this technology of such an inverted dielectric and allows you to maintain a level of threshold voltage at the level U_T = 0,6-0,65V for n-MOS transistors of OMC circuits.

Conclusions

1. Literary analysis of sources for the purpose of increasing the electrophysical parameters of the warp dielectric during the formation of n-MES transistors of sub-micron technology of LIS / VLSI;

2. Based on experimental research, the possibility of forming n-MOS transistors with a negative (zero) threshold voltage $U_T \leq 0$ is established;

3. Two technological processes by which n-MOS transistors with negative threshold voltage can be formed 1) the process of ion-beam oxidation with the introduction of halogenated gases in the gas stream of ion sources "Istra" and "Radical", in particular SF6 sulfate; 2) the process of multiply charged ion implantation of the submerged dielectric SiO_2 by fluorine ions (F^{--}) with subsequent photon annealing;

4. To improve the quality of the die-casting dielectric for sub-micron technology of LSI / VLSI, a technological process of photonic-thermal oxidation (PTO) is proposed that eliminates the diffusion shift of the concentration profiles;

5. The high-quality technology of forming a dielectric in the form of a three-layer SiO_2-SiO_xN_y-SiO_2 structure based on fast photonic oxidation, in which oxynitride plays the role of an internal heater for purification of the charge state of the interphase boundary of Si-SiO_2, is proposed.

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Термопольова стабілізація порогової напруги польових транзисторів субмікронної технології ВІС

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На основі аналізу об'ємної відповідності фаз в діючій затворній системі Si-SiO_2 показана можливість отримання від'ємного заряду в затворній системі субмікронних ВІС. Такий технологічний метод експериментально провірений при низькотемпературному оксидуванні кремнію, на що отримано патент на винахід. Дослідженнями встановлено, що на величину заряду на міжфазній межі можна суттєво впливати шляхом введення в окислювальну атмосферу галогеновмісних сполук.