Influence of γ -irradiation and ultrasound treatment on current transport in Au-SiO₂-Si structure

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Abstract

Keywords: metal—semiconductor structures, Si-SiO2 interface, ultrasound influence, $\gamma-{\rm rays}$

1. Introduction

It is well known that the defects are crucial for the semiconductor devices performance. Thus electrical characteristics of metal-oxide-semiconductor (MOS) structure are extremely sensitive to the interface state density. The formation of lattice defects near the interface caused by the irradiation is very harmful for such device performance and leads to the current mechanism change frequently [1–6]. The radiation defects (RDs) are known to be able to effectively interact with elastic acoustic vibrations. E.g. the RDs are annealed by acoustic waves treatment at temperature, which is much lower than ones in the case of ultrasound-free heating. Such phenomenon is observed in the single crystal of Si [7–9], Ge [10] as well as semiconductor [11, 12] and alkaline halide [13] compounds. Usually it deals with a decay of radiation-formed complexes and acoustically induced (AI) diffusion of defects to a sink. Besides, the possibility of parameter recovery of irradiated barrier structures by ultrasound treatment (UST) is shown. So, the active ultrasound effects are observed in the solar cells [14, 15], LEDs [16, 17], and Schottky diodes [18, 19]. The industrially important Si-SiO₂ system is under consideration as well. Particularly, the AI change of the Si-SiO₂ interface defects [20-22] and minority carrier lifetime [23-25] are reported.

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Some attention is paid to the UST of silicon MOS structures, which have been irradiated by 60 Co γ -rays [26, 27]. The decrease of the both radiation—induced charge in the dielectric layer and generation lifetime in the silicon, and the insignificant growth of the surface recombination rate after UST have been determined by capacitancevoltage characteristics measurements [26, 27].

The first aim of our work is to investigate experimentally the UST influence on a charge transfer in the irradiated $\text{Au-SiO}_2\text{-Si}$ structures. In contrast to the cited study [26, 27], our results are obtained i) for systems with a significantly higher RD concentration (see Section 2); ii) for operating mode of diode, that is, when the current was present. It should be noted to, that our some result was reported previously [25]. But this work is focused on the modification of charge transfer mechanisms as well as the defect structure due to irradiation and UST.

On the other hand, in the silicon solar cell industry, the efficiency of a cell is restricted by the recombination of carriers [28]. The silicon surface is often highly recombination active due to the abundance of band–gap states that exist due to dangling bonds. The number of band–gap states can be reduced by introducing a dielectric coating. The alneal is one of the most effective methods of passivating the Si–SiO₂ interface [28–30]. This reaction is reported to release atomic hydrogen that is then free to diffuse across the oxide and passivate dangling bonds at the oxide–silicon interface [29–31]. In this work, it is demonstrated that it is possible to enhance the hydrogen diffusion by ultrasound. Therefore, acousto–alneal can be a effective processing step.

2. Experimental and calculation details

Experiments were performed on n-type (111)—oriented crystalline float-zone Si with residual boron (B) impurity concentration of about $10^{12}~\rm cm^{-3}$ and doping phosphorus (P) impurity concentration of $2\cdot 10^{12}~\rm cm^{-3}$. The corresponding resistivity is 4000 $\Omega\cdot\rm cm$. A bulk silicon material was divided into several rectangular—shaped samples of approximately $1\times 5\times 10~\rm mm^3$. The MOS structures were formed by chemical etching of the upper Si surfaces using HF-HNO₃-CH₃COOH solutions (HF:HNO₃:CH₃COOH = 3:5:3), followed by the surface oxidation due to the exposure to ambient air for 24 hours and the Au vacuum evaporation. GaZn—eutectic Ohmic contacts were rubbed on the bottom surfaces of the samples.

The samples were γ -irradiated (60 Co source) at nominal room temperature to the dose $5 \cdot 10^7$ rad. The measurement on the reference bulk sample shown that the conductivity has been reduced to about 0.5 of the initial value after irradiation. As it was mentioned above, the ultrasonical recovering of the γ -irradiated silicon MOS structures has been investigated [26, 27] early. The structures Si–SiO₂, which have been produced by thermal oxidation of silicon, were under consideration [26, 27] as well. But the more heavy degradation and the higher RD concentration were expected in the our case. The main reasons are following. i) The high doze was used ($5 \cdot 10^7$ rad in our case as against 10^6 rad in [26, 27] case). ii) The semiconductor resistivity was greater (4000 Ω ·cm as

against $0.2-0.5~\Omega\cdot\text{cm}$); therefore the non–ionizing energy losses was larger as well. iii) It is known [32], that the surface defect density, which is γ –induced in Si–SiO₂, is about $10^{12}~\text{eV/cm}$ for 10^7 rad in the case of (111)–oriented substrate ant this value is much more then one for (100)–substrate, which is used in cited study.

The UST of the irradiated structure was done by attaching the piezoelectric transducer to one side of the sample. An epoxy glue was used as the bonding medium, providing the rigid coupling of the transducer to the sample. The thickness resonant of the transducers was 4 MHz. A radio–frequency voltage supplied from a generator drives the transducer, resulting in vibrations of the coupled transducer-sample system. UST was carried out by a two consecutive loading–unloading cycles, 30 min each; so the total UST time $t_{\rm UST}$ was equal to 30 min or 60 min. The density of acoustic energy flux W_{US} in Si was equal to about 2 W/cm². The sample temperature was measured with a copper–constantan thermocouple directly attached to the surface and did not exceed 350 K. The more details about the sample and UST setup are presented elsewhere [25].

The characteristics of the Au-SiO₂-Si structure, after γ -irradiation and after UST, were investigated using an current-voltage (I-V) technique. The forward and reverse bias characteristics were measured in current range from 10^{-9} to 10^{-3} A with a voltage step of 0.01 V at 295 K.

The data non-linear fitting were done by using the method of modified artificial bee colony [33].

3. Results and Discussion

Fig. 1 shows IV characteristics for both initial and irradiated Au–SiO₂–Si structure as well as after the sequent USTs. One can see that IV characteristic for non-irradiated sample is typical for Schottky diode: the forward current is caused by a thermionic emission (TE) over barrier, the reverse current value is determined by barrier height lowering, which occur due to the electric field (log $I \sim V^{1/2}$) [34, 35]. The forward branch was fitted by the following equation [34]

$$I = I_s \left\{ \exp\left[\frac{q(V - IR_s)}{nkT}\right] - 1 \right\}, \tag{1}$$

where I_s is the saturation current, R_s is the series resistance, n is the ideality factor, the other symbols have their usual meanings. The fitting results are shown on Fig. 1,b and d by solid lines, the obtained parameters values are listed in Table 1. It should be noted that the oxide layer presence does not allow to determinate the barrier height by help the saturation current value only, since the tunneling must be taken into account as well [36, 37].

In addition, the real current value for the non-irradiated structure exceeds ones, which is expected from Eq. (1) — see Fig. 1. The redundant current is most likely to be caused by the tunneling through the SiO_2 layer and can be

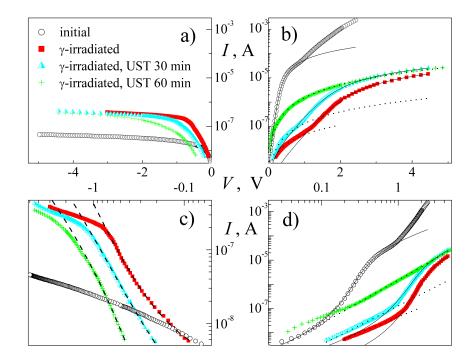


Figure 1: The logarithmical (a, b) and double-logarithmical (c, d) plots of the reverse (a, c) and forward I-V characteristics for Au–SiO₂–Si structure before and after γ –irradiation and UST. T=300 K. The marks are the experimental results, and the solid, dashed, and dotted lines are the TE, TAT, and SCLC fitted curves using Eq. (1), (??), and (3) correspondingly.

Table 1: Extracted parameters for the $\mathrm{Au}\mathrm{-SiO}_2\mathrm{-Si}$ structure

Structure status				
γ -irradiation	_	+	+	+
UST	_	_	+	+
$t_{\mathrm{UST}},\mathrm{min}$	_	_	30	60
Parameter				
$I_s, 10^{-9} A$	3.3	1.1	4.9	
$R_s, 10^4$	1.1	13	8.8	
n	1.7	10.3	9.9	
$m_{ m F}$		1.3	1.6	1.8
$I_0, 10^{-8}$ A		4.5	13	150
$I_{0,\mathrm{TAT}}$, a.u.		1	0.14	0.04
U_d , B		0.73	0.44	0.12
R_{TAT} , a.u.		1	0.54	0.33

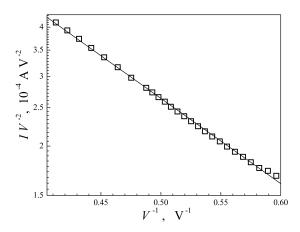


Figure 2: The Fowler-Nordheim plot of the forward branch for non–irrradiated Au–SiO $_2$ –Si structure at V>1,6 V. The line is the least–squares linear fitting.

described as [34, 38]:

$$\ln\left(\frac{I}{F_m^2}\right) \propto -\frac{4\sqrt{2m^*}(qE_{\text{eff}})^{3/2}}{3\hbar qF_m} \,,\tag{2}$$

where F_m is the electric field, $E_{\rm eff}$ is the effective tunneling energy. The linearity of the Fowler–Nordheim plot of the forward current at large bias is this assumption evidence — see Fig. 2. It was taken into account when plotting that the electric field in a oxide layer is proportional to the applied voltage $F_m \propto V$.

The γ -irradiation has a considerable effect on the current behavior — see Fig. 1. The changes are pronounced for the reverse branch especially and the I-V characteristic modification is the evidence of a transformation of the current transport mechanism. Thus the forward I-V dependence, expected according to TE model, is observed at V>1 V only and the current value is much more then ones in non–irradiated case. The fitting of the V>1 V region by Eq. (1) show that the irradiation leads to significant increase in both series resistance and ideality factor values — see Table 1 data. And the former significantly exceeds the resistance change, which was observed in the bulk samples. The ideality factor increase deals with the RDs formation and results in the observed TE current decreasing. Note that the effect of the radiation induced decreasing of MOS structure current is known [39].

Pintilie, et al. [40] have investigated the RD formation by 60 Co γ -radiation in silicon. The both growth method and resistivity have been analogous to structure under our investigation and the dose $9 \cdot 10^7$ rad have been used. It have been shown that complexes VO_i , ${}_iC_s$, H-centre (V_2O_i), Γ -centre, and interstitial defect $I^{0/-}$ are the main radiation defects. The latest one is a secondary defect and its appearance leads to a conductivity compensation (inversion) [40].

In our case the series resistance change in a range one order of magnitude above causes the reduction of voltage drop in the dielectric layer. As a result, the electric field intensity was ceased to be sufficient for effective Fowler–Nordheim tunneling and the corresponding current component is not observed after irradiation.

Fig. 1,d show that the forward I-V characteristic of irradiated structures at low biases (V<1 V) is enough good described by a power law

$$I = I_0 V^{m_F},$$
 (3)

where $m_{\rm F} = \frac{V}{I} \frac{\partial V}{\partial I}$ is the power–law parameter. The relation (3) is typical for the space charge limited current (SCLC) [41–43] and the $m_{\rm F}$ value is connected with the energy distribution of traps, which emit carriers. E.g. the value $m_{\rm F} \approx 1, 3$, which is observed for the investigated structure after γ -irradiation and before UST, is evident of the exponentially distributed traps. It is known [41–43] that the I_0 depend on the total trap concentration N_t

$$I_0 \sim 1/N_t^{m_{\rm F}-1},$$
 (4)

and the temperature dependency of power-law parameter is defined by equation

$$m_{\rm F} = 1 + T_c/T,\tag{5}$$

where T_c is the characteristic temperature parameter of the trap distribution; notably the trap concentration per unit energy range at an energy E above the valence band is proportional to $\exp(-E/kT_c)$.

The SCLC current-voltage relation is often written as [42]

$$I(V,T) = C \exp\left(-\frac{E_x}{kT}\right) V^{m_F(T)},\tag{6}$$

where C is the constant, E_x is the activation energy that defined by the level position of the filled traps to the conductivity band. Fig. 3 shows the temperature dependence of the forward current. Eq. (5) was taken into account when Fig. 3 plotting. One can see that the experimental data are in good agreement with the fitting curve by Eq. (6) for value $E_x = (0, 32 \pm 0, 01)$ eV.

The γ -irradiation of Si–SiO₂ structures is known [32] to lead to a mechanical stress relaxation, a trap filling, and a new charged defect generation. It is believed [44, 45] that the negative charge is trapped at the interface while the positive charge accumulates at E'-centers, E'_{δ} -centers, and three strained bond related centers. However, the E' and E'_{δ} concentration considerably overrides the bond related centers concentration in the case of defect formation by photons (X- and γ -rays) [44]. It should be noted that the low temperature as well as low partial oxygen pressure result in the thin SiO₂ layer formation in the structure under investigation. But it is known [46] that RDs, which appears in thin and thick layers, are the same.

Note that the hydrogen content is the key factor of a generation of the electrically active RDs in silicon MOS structures [46] and the SiO_2 layers, which are grown by thermal oxidation, are rich in an atomic hydrogen [32]. The irradiation is known [47, 48] to lead to the breaking of $\equiv Si-H$ bonds at the

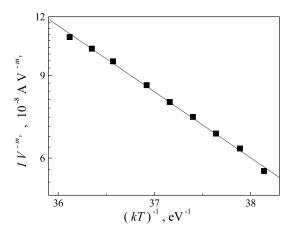


Figure 3: Temperature dependence of SCLC–current for γ –irradiated Au–SiO₂–Si structure before UST at V=0,4 V. The line is the least–squares linear fitting.

Si–SiO₂ interface and subsequent diffusion of released H species into the oxide bulk. The resulting unsaturated bonds \equiv Si– act as electronic traps. Generally such defects are distinguished by the orientation of the silicon substrate. It is considered [49] that P_b centers appear at (111)–oriented substrate interface whereas P_{b1} and P_{b0} centers are a typical in the case of (100)–oriented substrate. Both P_{b0} and P_{b1} are chemically identical to the P_b center, however the difference in an electrical activity is observed.

The non–monotonic energy distribution of the interface levels is observed in Si–SiO₂ structures, grown on n–type silicon crystal, after the γ –rays irradiation with dose above $5 \cdot 10^5$ rad [32]. According to Parchinskii, et al. [50], the highest density of surface states is observed at $E_c - (0, 32 \pm 0, 04)$ eV. This value coincides with the determined E_x value. Therefore the current at low forward bias for irradiated structures is deals with carriers, which are trapped by P_b –centers. Besides the negative charge accumulation at interface results in both barrier height increase and observed TE current decreasing. But as mentioned above, the main reason of TE current reduction is the n rise, which is induced by RDs generation at silicon near surface region.

Fig. 1,a and Fig. 1,d shown that USTs cause an increase of a space charge limited current. In particular, SCLC exceeds the TE current at the whole used forward voltage interval in the case of $t_{\rm UST}=60$ min. We used Eq. (3) to fit experimental I-V data of irradiated and ultrasonically treated structures. The obtained fitting parameters are summarized in Table 1. According to Eq. (4), the detected increase in I_0 value is evident of AI decrease in P_b —center concentration. The P_b —center annealing is known [51, 52] to deal with the passivation of dangling bonds at the oxide–silicon interface by hydrogen atoms. Thus the obtained results indicate about the AI diffusion of hydrogen. Similar process has been reported early [20, 53, 54], but the RDs acoustically–induced annealing was observed in our case.

The AI increase in $m_{\rm F}$ value (or T_c rising — see Eq. (5)) testify to the narrowing of the trap level energy distribution. So it is known [42] that $m_{\rm F}=2$ is observed in the case of single–energy trap. The detected narrowing of the energy distribution is evident of a AI passivation selectivity, that is, UST leads to atomic hydrogen capture by dangling bonds, which correspond to certain levels only. In our opinion, the key parameter of the bond ultrasound passivation is a mechanical stress, which are generally non–uniform at the interface. The impurity diffusivity is known [55] to depend on mechanical stress. On the one hand, it can be a reason of a hydrogen displacement under acoustic loading condition. On the other hand, the effectiveness of AI passivation is determined by a mechanical deformation level and UST assists to the structure uniformity.

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