

Effect of ultrasonic treatment on the defect structure of the Si-SiO₂ system

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The effect of ultrasonic treatment (UST) on the defect structure of the Si-SiO₂ system by means of electron spin resonance (ESR), metallography, MOS capacitance technique and secondary ions mass-spectroscopy (SIMS) is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and structure and may be

caused by vibrational energy dissipation which are a functions of defect's centers type. The influence of the UST on the Si-SiO₂ interface properties depends on the oxide thickness and crystallographic orientation. The density of point defects and absorbed impurities at the Si-SiO₂ interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation conditions.

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1 Introduction In the course of the integrated circuit (IC) manufacturing process, silicon wafers are repeatedly subjected to various treatments: mechanical, chemical, thermal etc. resulting in the creation of defects and surface contamination. Ultrasonic treatment (UST) is widely used in IC technology for cleaning and, more recently, for the improvement of various parameters of IC elements and semiconductor devices. A decrease of point defect (PD) density in Si-SiO₂, structure revealed by electron spin resonance (ESR), and an improvement of its electrical and structural parameters by a low intensity 100 kHz UST has been observed [1, 2]. A marked enhancement of the homogeneity of polycrystalline silicon films can be achieved by UST [3]. The improvement of the Si-SiO₂ interface properties by means of UST can be explained by the dissociation of PD and PD-impurity complexes due to the dissipation of US vibration energy at the defect site and PD gettering during the subsequent thermal treatment (oxidation) [1]. The nature and identity of the defects within the well prepared Si-SiO₂ interface, giving rise to trapping sites and a

fixed charge, continue to be of considerable interest. A number of models of the defects at the Si-SiO₂ interface and in SiO₂, have been proposed but, with the exception of a relatively few cases, even the precise ESR measurements have not allowed for their unambiguous identification. The oxygen vacancies (E'centres) [4] are the major identified PD in SiO₂. E'centres were observed in the crystalline and amorphous modifications of SiO₂ submitted to γ - and electron irradiation [5]. A number of different defects have been observed by ESR in the Si-SiO₂ system. The most frequently observed ESR signal is that at $g = 2.0055$ produced by simple physical damage: grinding, heavy particle irradiation etc. Even the best quality Si-SiO₂ interfaces manifest the ESR signal designated P_b [6], which has been later assigned to the unbound orbitals on trivalent silicon at the unavoidably lattice mismatched crystal boundary [7]. A common ESR signal with $g = 1.999$ (P_a centres) is observed near the interface in phosphorous doped wafers and, as has been proposed, presumably arises from donor electrons [7]. However, it has been found that there is no

strong correlation between the number of P_a centres and the intensity of the low-temperature ESR signal that belongs to the electrons localized on the donor phosphorus centres and, hence, the connection of P_a centres either with donor centres or conduction electrons seems doubtful [2]. In [8] it has been established that the dependence of the ESR signal of P_a centres on the oxidation temperature follows an Arrhenius-type temperature dependence with the activation energy ~3.5 eV which is nearly equal to the formation energy of divacancies in silicon and of oxygen vacancies (E' centres) in SiO₂. This allows for a suggestion that the ESR signal of P_a centres is associated with vacancy complexes (presumably divacancies) in silicon and oxygen vacancies in SiO₂ near the Si-SiO₂ interface [9, 10]. If the influence of UST on the evolution of defect structure at the Si-SiO₂ interface, as it was supposed, is connected with the dissociation of PD complexes and their subsequent annihilation with PD of the opposite type, UST can provide us with some additional information about the nature of the PD within the Si-SiO₂ interface. The purpose of the present work is to investigate the influence of UST on the defect structure of the Si-SiO₂ system using ESR, MOS capacitance technique and SIMS.

2 Experimental An n-type silicon, phosphorous doped to $3 \times 10^{14} \text{ cm}^{-3}$ with mechanically or chemically polished (111) and (100) orientated surfaces was used. An oxide layer was thermally grown in ambient atmosphere containing HCl vapour at 1150 °C. The thickness of the oxide layers varied (0.4 and 0.7 μm). UST was carried out by means of a LiNbO₃ transformer at frequency ~10² kHz. The amplitude of the US vibration was varied by changing the voltage of the generator. The samples for UST (60 mm) were coupled with the transducer mechanically. Each sample was treated individually (20 min). UST was made at room temperature, but taking into account the interior friction at the defect site, temperature grow cannot be excluded. ESR spectra were taken at 115 K by an X-band ERS 231 spectrometer with an Oxford Instruments ESR 900A continuous flow helium cryostat. The samples for the ESR measurements were cut from silicon slices with dimensions 12×3×0.3 mm³ and placed into a suprasil ESR sample tube. Before sealing the tube, it was evacuated and filled with He gas. The number of measured centres was taken as proportional to $I\Delta^2$, where I is the intensity and Δ is the width of the ESR line first derivative. The absolute numbers of the centres were determined by means of a ZnS:Mn standard. The structural defects in silicon were brought out by selective etching in Sirtle reagent. The electrical properties of Si-SiO₂ interface were studied by means of the MOS capacitance technique. Al contacts were evaporated on the SiO₂ through a mask and on the back side of the Si wafer. MOS structure was annealed at 510 °C in N₂ ambient (15 min). The surface state density can be reduced by this treatment. Minority carrier generation lifetime was determined by means of non-equilibrium capacitance relaxation time measurements. 3 samples were

measured from each wafers and mean value are shown in Figs. 4, 5, 7. The contamination of Si and SiO₂ by Na⁺ was investigated using SIMS. The profile of Na ions in Si and SiO₂ was measured with Cameca spectrometer. SiO₂ and Si sputtering were performed using Ar ion bombardment.

3 Results and discussion In Fig. 1, typical ESR spectra of Si samples before and after UST are shown. Before UST a signal with $g = 1.9996$ (P_a centres) connected with vacancy complexes is observed. After UST another signal with $g = 2.0055$ (broken bonds of Si atoms) can be seen. The ESR signals of the majority of the paramagnetic centres observed increase after UST in the samples with a mechanically polished surface and decrease in the samples with a chemically polished surface. In samples with mechanically polished surface the damage layer is not completely removed and the generation of defects and their redistribution by US can be enhanced, while in the samples with a chemically and mechanically polished surface the annihilation of the defects in volume prevails.

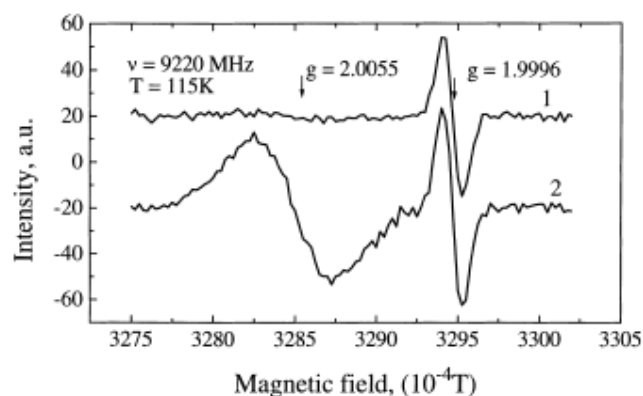


Figure 1 ESR spectra of the Si samples before (1) and after UST treatment (2).

Table 1 Absolute numbers of spins for the centres in the Si-SiO₂ structure, subjected before oxidation to UST with different US wave intensities.

centre	g	T (K)	number of centres, 10 ¹² absolute units		
			control sample	UST amplitude, arb. units	
				5	10
broken bonds	2.0055	20	2.5	1.3	2.3
P _a	1.9995	115	1.0	0.6	0.8
P atoms	1.9986	20	0.8	0.7	0.8
thermal donors	1.9986	20	0.3	0.5	2.3

Table 1 displays the absolute numbers of spins for the centres in the Si-SiO₂ structure, subjected before oxidation to

UST with different US wave intensities. A new signal with $g = 1.9986$ appears in Si-SiO₂ samples. This signal can be associated with point defect-impurity complexes, for example, with silicon-oxygen complexes-thermal donors. Some of the known thermal donors are paramagnetic and have nearly the same g -factor [11]. The number of these centres increases monotonously with US wave intensity. A non-monotonous dependence of the number of the centres with $g = 1.9996$ and 2.0055 on the US wave intensity has been observed. This may be attributed to the competition between the defect creation and their annihilation. The activation energy of the creation of Si interstitial atoms and vacancies is 1.09 and 2.3 eV, respectively [12], and, hence, the creation of Si interstitials by a low intensity UST is more likely than the creation of vacancies. According to [13] the energy of PD generation at volume defects is considerably lower than the energy of PD creation on a surface. Thus, if the vacancies are generated in volume by voids, their density grows larger than the equilibrium value and the surface acts as a sink for the vacancies. It is possible that during UST internal voids are created in Si wafers. This assumption is confirmed by a slight (~2%) increase of wafer thickness detected after UST. If the US wave intensity is sufficiently high for the void formation and oxidation time is long enough, it leads to a decrease of the activation energy of vacancy formation and their flow to the surface. The observed increase of the ESR signal intensity $g = 1.9996$ (Table 1) along with an increase of the US wave amplitude is in good correlation with the above suggestion.

The dependence of the spin density on the US frequency of the US treated Si-SiO₂ samples with (111) and (100) orientation shows that the influence of the US frequency and the sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with $g = 1.9996$ and the lack of this dependence for the centres with $g = 2.0055$ show that the vibrational energy dissipation depends on defect centres and their crystallographic orientation.

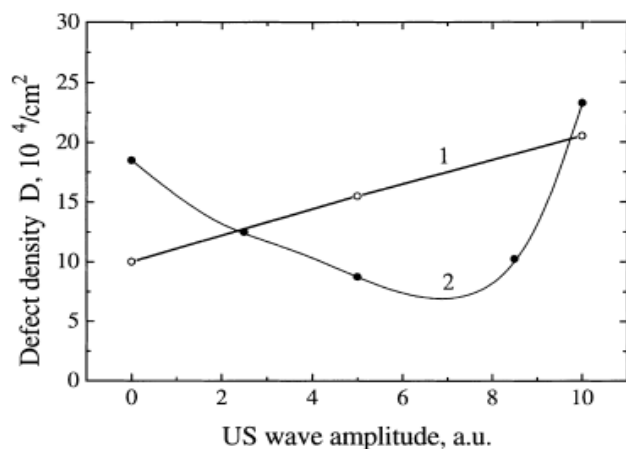


Figure 2 Dependence of the density of the structural defects at Si-SiO₂ interface on the US wave amplitude. SiO₂ film thickness 0.4 μm (1) and 0.7 μm (2).

The dependence of the density of the defects revealed by selective etching on the US wave amplitude for samples with different oxide thickness (Fig. 2) shows that the defect density, the so-called ‘etch pits’, connected with SiO inclusions in Si surface region, in samples with ‘thin’ oxides (0.4 μm) grows with the increase of the US wave amplitude, and changes non-monotonously with a minimum at an intermediate US intensity in samples with ‘thick’ oxides (0.7 μm). In these samples an interaction between Si interstitials and vacancies at an intermediate US wave intensity can occur. This brings about the annihilation of PD and the decrease of the density of PD-impurity complexes. A comparison of these results with results in Table 1 allows a conclusion that the increase of the defect density in the samples with ‘thin’ oxides film is accompanied by an increase of the ESR signal with $g = 1.9996$ connected presumably with SiO complexes (thermal donors). The minimum of the defect density in the samples with ‘thick’ oxides and the minimum of the ESR signal with $g = 1.9996$ connected with vacancy complexes appear at the same US wave intensity. This allows one to suggest that the creation of thermal donors is due to different point defects. Despite of a large number of articles published on the formation of thermal donors there is not yet a general agreement on their exact nature. While the original models relate the thermal donors to pure oxygen complexes, more recent models involving also vacancies and silicon self-interstitials have proposed [14]. The obtained results allow to suggest that both types of the point defects - self-interstitials and vacancies may be responsible for the formation of thermal donors. Two different types of thermal donors have been observed in numerous works [14].

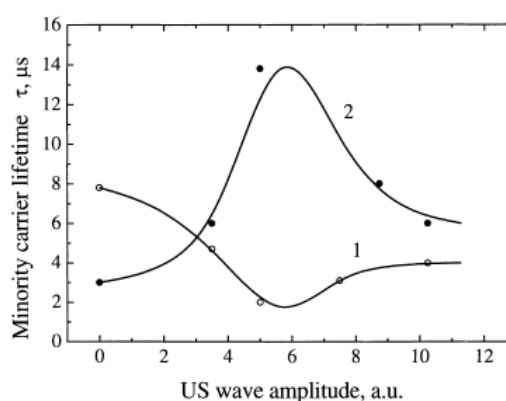


Figure 3 Dependence of the minority charge carrier lifetime on the US wave amplitude. Oxides thickness 0.4 μm (1) and 0.7 μm (2).

In Fig. 3, the dependence of the minority charge carrier generation lifetime (τ) on the US wave amplitude for the samples with different oxide thickness is shown. In the samples with thick oxide there is a maximum in the dependence of the τ on the US wave amplitude and in the samples with thin oxides, a minimum. An interdependence

between τ and the defect density shows that the structural defects form electrically active centres and their density can be varied by UST.

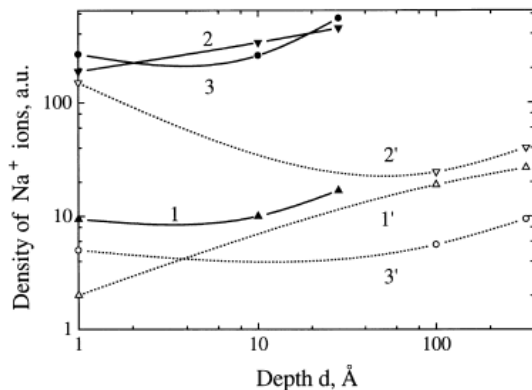


Figure 4 Influence of the UST on the surface contamination. The distribution of the density of Na⁺ ions in Si and SiO₂ surface layers. (1, 2, 3) Distribution of Na⁺ ions in Si; (1', 2', 3') distribution of Na⁺ ions in SiO₂, (1, 1') US wave amplitude 5 units, (2, 2') 10 units, (3, 3') control samples.

In Fig. 4, the density distribution of Na⁺ ions in the Si and SiO₂ surface region for the samples, subjected to UST before oxidation, and control samples is shown. It follows from the results presented that UST with US wave amplitude 5 units reduces the Na density in the Si surface region (curves 1,3), and leads to a Na redistribution and a slight increase of the density in SiO₂. The UST with the wave amplitude 10 units reveals the independence of the Na concentration from the US treatment in the Si surface region and its increase in SiO₂. The observed influence of the US treatment on the surface contamination can be explained by the dependence of the efficiency of the impurity adsorption on the density of the surface defects. Surface defects may act as effective adsorption sites. The UST with wave intensity 5 units lowers the density of defects at the surface (see Fig. 2) and, subsequently, lowers the density of Na atoms. The influence of the UST on the density of Na in SiO₂ observed in the samples treated by US with wave intensity 10 units, can be explained by the creation of defects on the surface and the enhanced adsorption efficiency of the Na atoms. The adsorption of impurities on the defect-sites can render their removal difficult. This leads to an increase of the density of Na atoms in SiO₂. The Si-SiO₂ system can be in a non-equilibrium state. A long-time relaxation of the defect structure is possible (Fig. 5). UST reduces weak Si valence bond density and improves the interface reliability (Fig. 6).

Comparison of the results in Fig. 5 and Fig. 6 enable to conclude that interstitial Si atoms are responsible for minority charge carriers lifetime diminishing and UST depending on the oxides thickness reducing or enhancing its density.

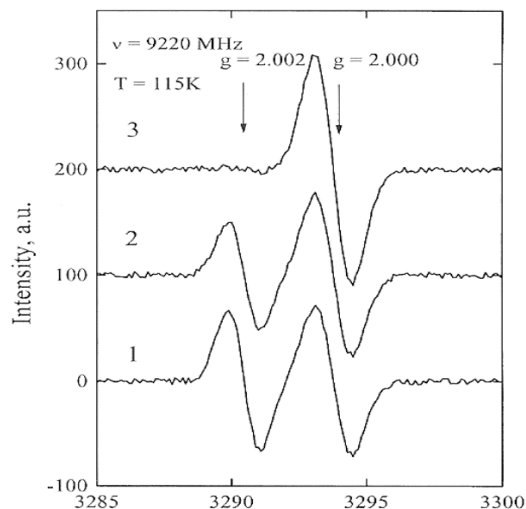


Figure 5 ESR spectra of the Si-SiO₂ system: 1 day (1), 15 days (2) and 30 days (3) after the preparation of samples.

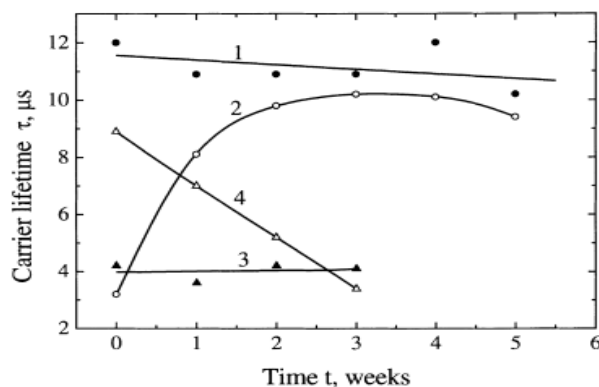


Figure 6 UST influence on the Si-SiO₂ interface reliability. (2, 4) Control samples. SiO₂ film thickness 0.7 (1, 2) and 0.4 (3, 4) μm.

ESR spectra of the Si and Si-SiO₂ samples prepared from wafers with diameter 150 mm and thickness 350 μm subjected to the UST show that UST slightly increases the vacancies ESR signal intensity in initial wafers and in Si-SiO₂ structures treated before oxidation and does not influence on the ESR signal connected with unsaturated bonds indicating higher degree of purity of these wafers received from Wacker Siltronic AG. It must be noted that contrary to the results obtained by UST samples treatment before oxidation, Si-SiO₂ samples treatment does not influence on the interface defects structure. This may be connected with differences in Si-Si and Si-O atoms binding energy: 1.84 eV and 2.9 eV, respectively. After Si-SiO₂ samples US treatments slightly increase samples thickness connected with voids formation.

4 Conclusion It follows from the presented results that the density of point defects and their complexes can be varied by UST. The non-monotonous dependence of the defect density on the US wave intensity can be explained by the competition between the defect generation and their annihilation. The dependence of the evolution of the defect structure on the UST frequency and crystallographic orientation of the sample varies for the different defect centers. This can be explained by the dependence of vibrational energy dissipation mechanisms on the defects centers type and structure. It has been shown that the density of contamination (Na) can be varied by UST. UST influences predominantly the nonequilibrium defects and allows one to improve the stability of the Si-SiO₂ system and IC. Ultrasound is widely used not only for defects in engineering but in medicine as well (cancer treatment).

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