HYDROGEN SEPARATION IN THE Si-SiO_2 STRUCTURES AND ITS INFLUENCE ON THE INTERFACE PROPERTIES

D.Kropman[1*], E.Mellikov[1], T.Kärner[2], Ü.Ugaste[3], T.Laas,[3] I.Heinmaa,[4] A.Medvid[5], P.Onufrievs[5]

[1]Tallinn University of Technology, Ehitajate tee 5,19086
[2]Department of Physics,Tartu University,Tartu,Estonia.
[3]Department of Natural Sciences, Tallinn University,Tallinn,Estonia.
[4]Institute of Chemical Physics and Biophysics, Tallinn,Estonia.
[5]Riga Technical University,Riga,Latvia
*Tallinn,Estonia.daniel.kropman@mail.ee

Abstract

The type and density of the point defects that are generated in the Si surface layer during thermal oxidation depend on the oxidation conditions: temperature, cooling rate, oxidation time, impurity content. The interaction between point defects with extended defects and impurities affect the SiO_2 structure and Si-SiO_2 interface properties. The influence of point defects and impurities may be diminished and the interface properties improved by an appropriate choice of oxidation conditions and postoxidation treatment of the samples.

Key words: EPR,NMR,point defects,Si-SiO2,hydrogen,Laser irradiation

Introduction

The decrease of the size of integrated circuit elements and increase of the silicon wafer diameter result in an increasing influence of point defects on their electrical parameters, reliability and yield. It has been suggested by Tan and Gösele that vacancies and self-interstitials are in local dynamical equilibrium and their densities follow the mass action law [1]. If it is reached in the Si surface layer at sufficiently high oxidation temperature and long oxidation time, this brings about a supersaturation of vacancies and undersaturation with self-interstitials, while at lower oxidation temperature or shorter time a saturation of interstitials and undersaturation with vacancies take place. It has been shown in [2] that there exist an oxidation time (temperature) where vacancies and interstitials coexist in a nearly equal density and interaction between them during the cooling at the interface is possible. This may lead to the depletion of both interstitials and vacancies. The investigation of the point defects interaction with impurities and its dependence on the oxidation condition offers new possibilities for the improvement of the properties of the Si-SiO_2 interface

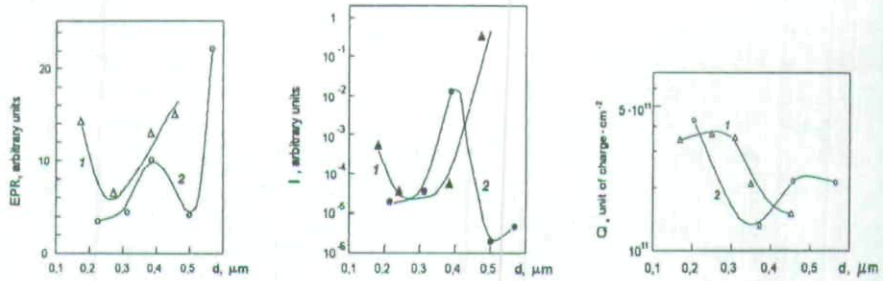
and devices. The purpose of the present work is to investigate the dependence of point defects generation kinetics on the oxidation condition, its interaction with impurities (hydrogen) and influence on some structural and electrophysical properties of the Si-SiO_2 interface by means of EPR, surface photovoltage spectra (SPV), MOS capacitance technique and nuclear magnetic resonance (NMR). An attempt to improve interface properties by laser irradiation was also made .

Experimental

Si (n and p-type) of 15 Ωcm resistivity (111) orientation was used. The oxides were thermally grown in dry oxygen at 1050- 1200 °C. The density of point defects was varied by varying the cooling rate of the samples. The thickness of the oxide layers varied from 0.2 to 0.6 μm. EPR spectra were taken at 115 and 300 K. To evaluate the influence of grown-in defects densities on the interaction between point defects and impurities Si-SiO_2 structure on n- and p-type wafers CZ and FZ grown respectively was investigated. The content of impurity in the oxidation ambient was varied by an additional oxygen drying (dew point -90 and -65°C) and by SiH_4 decomposition in NH_3 ambient up to Si_3N_4 formation of SiO_2. Hydrogen does not penetrate through Si_3N_4 and this provides its separation. To evaluate the interdependence between different defects in Si surface region, surface photovoltage spectra and MOS capasitance measurements were performed. To evaluate the content of impurities (hydrogen) in the Si-SiO_2 system and its interaction with point defects the chemical shift of hydrogen by ^1H NMR spectra was measured on n- and p-type wafers. The Si-SiO_2 laser irradiatin (λ=520μm, 10Mw/cm^2) were performed after oxidation before Al evaporation.

Results and discussion

In Fig. 1 the EPR signal intensity (a), SPV signal maximum at 0.49 eV (b) and the charge value in SiO_2 (Q) (c) dependence on the oxides thickness for samples oxidized in different oxidation ambient are shown. It follows from the presented results that the EPR and SPV signals dependence on the oxides thickness revealed a minimum or a maximum, depending on the oxidation ambient. Surface states E_c - 0.49 eV are identified as interstitials Si atoms [3].This allows us to suggest that the simultaneous decrease of the EPR and SPV signals is connected with an interaction between the vacancies and interstitials Si atoms at the interface, while the simultaneous increase of these signals indicated that the interstitial atoms and vacancies are separated and there is no interaction between them.The generation of the point defects at the interface has an effect on the effective charge value in SiO_2. If an interaction between point defects at the interface occurs, the charge is independent of the oxide thickness, while if it is absent, the value of charge diminishes with the oxide thickness (Fig.1,c).



a b c

Fig.1. EPR, SPV signal (0,49 eV) intensity and value of charge (Q) in SiO_2 dependence on the oxide thickness (dew point -90° and –65° C, curves 1 and 2, respectively)

To evaluate the point defect interaction with impurities on the interface the EPR signal and the charge value in SiO_2 dependence on the oxide thickness for n- and p-type CZ and FZ sampless were investigated. The maximum of the I(d) dependence coincide with the minimum of the Q(d) dependence, showing the influence of point defects generation at the interface on the charge value in SiO_2. The Q(d) dependence of the p-type samples is shifted relative to the n-type samples in correlation with the shift of the I(d) dependence in n-type samples with different impurity content. This allows to suggest that impurity adsorbtion on n- and p-type wafers is different.To check this assumption the ^1H NMR spectra of the n- and p-type samples were measured (Fig.2). The ^1H NMR line width of the n-type samples is remarkably broader than that of the p-type samples. The extent of this effect goes up with the extent to which the movement of adsorbed molecules is hindered. One possible reason for that can be the strength of the magnetic interaction with the paramagnetic impurities of the adsorbent. These results confirmed that the content of adsorbed hydrogen on n- and p-type samples is different After Si_3N_4 deposition the difference in hydrogen content between n- and p-type wafers increases. To evaluate the contribution of different hydrogen species, its distribution in SiO_2 on n- and p-type samples and content of bonded and not bonded (weak bonded) hydrogen, the influence of the ion drift in SiO_2 in electrical field (+100 V) at elevated temperature (130°C) on the charge value in SiO_2 in samples with different hydrogen content was investigated. It has been established that in MOS structure on p-type Si the above mentioned treatment brings about increase of the charge value, that is greater than in MOS structure on n-type samples and, hence the content of weak bonded hydrogen in these samples is different.
After Si- SiO_2 structure laser irradiation the influence of BT treatment on the Q value decreases.

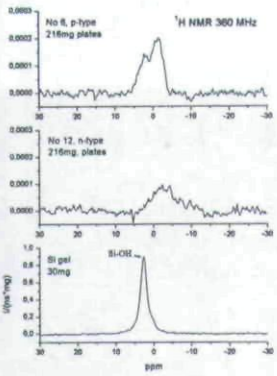


Fig.2. ^{1}H NMR spectra of the samples with SiO_2 film prepared on n- and p-type CZ and FZ grown wafers.

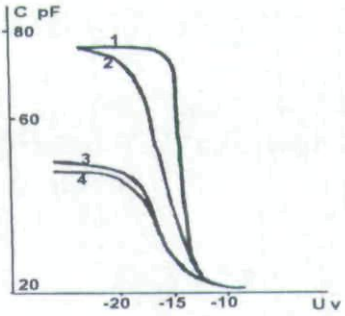


Fig. 3. C-V plots for MOS structure of p-type samples irradiated by laser.
1, 2 – initial plots; 3, 4 – after laser irradiation; 2, 4 – after bias-temperature treatments 130°C, +100V, 20 min.

Conclusions

The presented results confirm the model of point defect generation kinetics in Si-SiO2 system proposed by Tan and Gösele. The type and density of the point defects that are generated in the Si surface layer during thermal oxidation depend on the oxidation condition: temperature, cooling rate, oxidation time, impurity content. The interaction between point defects with extended defects and impurities affect the SiO_2 structure and Si-SiO_2 interface. The influence of point defects may be diminished and the interface properties improved by an appropriate choice of oxidation conditions.

References

1. Tan T.Y.,Gösele U., Appl. Phys., A37, 1985, 1 p.
2. Kropman D.,Dolgov S.,Kärner T., Appl. Phys. A62, 1996, 469p..
3. Lefevre H., Appl.Phys., 22, 1980, 15p.