RD50 funding request  
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Structure Investigations of  
Radiation Induced Defects in Silicon by EPR and HRTEM

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Project abstract: This proposal is focused on structure investigations of Oxygen related defects by using Electron Paramagnetic Resonance (EPR) and High Resolution Transmission Electron Microscopy (HRTEM) methods on O-17 enriched Si-FZ samples. Both methods have not been used so far and will offer deeper insights in point and cluster related defects. This effort is supplementing a larger project funded by the Romanian Ministry for Research and at the same time can be regarded as a follow up of the WODEAN project, where only standard methods (diode characteristic, TSC, DLTS, TCT) had been employed.

Project description

1. Motivation and summary:  
Presently, the understanding in the detailed relation between the microscopic reasons of particle damage effects in silicon sensors as based on defect analysis and their macroscopic consequences on the device performance is still limited. Although many electrically active defects, induced by irradiation, were already detected, investigated and identified (VO, V₂, C₁, C₂O₂, C₃C₆, IO₂, V₂O, V₃O) [1-15] there are still many other yet un-identified defects proved to have a strong impact on the electrical performance of Si sensors operating at ambient temperatures. These defects were detected and characterized from electrical point of view in the last 10 years. They are labeled in the literature as Iₚ, BD, E(30K) and
H(116K), H(140K), H(152K), E4, E5 and E6 defects [16-28]. The identification of the main defects responsible for radiation tolerance of silicon mentioned above as well as their formation kinetics (depending not only on the irradiation fluence but also on the particle type and impurity content) is of crucial importance for further developments of ultra radiation hard silicon material using defect engineering. It is thought that the understanding of the defect generation and kinetics related to the presence of different kinds of impurities inside the silicon bulk represents the key strategy for this purpose.

The proposed project aims at a specific solution of this problem, initiating systematic studies regarding the identification of the chemical structure of the main defects responsible for the changes in the electrical properties of the irradiated silicon: (i) acceptor like (e.g. I_p, type H and E4-E6) and (ii) of the donor like (e.g. BD and E(30K)) centers in defect engineered silicon.

Three kinds of investigations will be performed during the project:

1) *Analysis of electrically active defects* by means of DLTS and TSC methods;

2) *Studies for identification of oxygen related defects* by Electron Paramagnetic Resonance (EPR, ENDOR) methods. EPR is a technique of spectroscopic analysis used to identify paramagnetic centers and investigate the nature of the bonding within molecules by identifying unpaired electrons and their interaction with their immediate surroundings. A novel approach in this context is referring to the identification of Oxygen related defects. Impurities like Oxygen need special attention since in atomic form they do not have a hyperfine structure and a clear identification of related defects cannot be done by EPR. Therefore doping with ^17O isotopes are foreseen. Having non zero nuclear spins, the EPR and ODMR analyses of the resulting hyperfine structure one expects reliable information concerning the localization and structure of the oxygen related defects.

3) *Micro-structural investigation of the extended and clustered defects* by High Resolution-Transmission Electron Microscopy (HRTEM). This technique allows the visualization, at atomic scale, of the extended and clustered defects in solids. The microstructural characterization will be performed in FZ and DOFZ materials irradiated with 1 MeV neutrons and 2 fluences above 10^{16} cm^{-2} (distance between defect clusters < 200 nm) as well as on similar samples irradiated with electrons of energy >15 MeV and, monitor the clusters transformations at 80 C in order to identify the type of clustered defects with large influence on the electrical properties of the diodes (the H and E4-E6 defects).

The EPR and HRTEM studies will be performed on specific prepared material samples for structural and chemical identification of the radiation induced defects (including annealing studies like those performed on Si test diodes). The correlation of these investigations with the defects energy levels detected by DLTS and TSC on irradiated diodes will be correctly achieved by following the annealing effects in the three types of studies (electrical, chemical and structural).

### 2. Pretests and outline for sample preparation with O-17 enrichment:

The above outlined broad scope is the subject of a national project approved by the Romanian Ministry for Research [29]. The special problems associated with the preparation and characterization of O-17 enriched silicon samples needed for the EPR
studies had however been drastically underestimated. A standard oxidation process and diffusion as in DOFZ is impossible because of skyrocketing finances needed for O-17. The first idea was therefore to achieve the O-17 enrichment via ion implantation. It turned out that even this approach was extremely costly and could not completely be covered by the national project. Still available leftover WODEAN funds had been used too and some valuable experience was gained. We achieved an enrichment of about 1e18/cm³ O-17 within roughly 2 to 6 µm depth (implantation energies between 1 and 5 MeV). The activation annealing and characterization by spreading resistance (SR) and secondary ion mass spectroscopy (SIMS) is presently under way. However the overall dose of 4.5e14 O-17/cm² is extremely low for meeting the sensitivity of EPR. Finally a completely different approach is planned, using diffusion of O-17 in small silicon samples encapsulated in quartz ampules filled with 90% O-17 enriched Oxygen. The whole process can be done at ITE. RTA, SR and FTIR will be performed at ITME and the SIMS measurements be carried out at ITE. Calculations (like those done years ago for DOFZ) have shown that for a diffusion process at 1150C/72h an almost homogeneous concentration profile of 5e17 O-17/cm² may be achieved throughout the 300 µm thickness of the samples, leading to a dose of at least 1e16/cm², i.e. 20 times larger than reached for ion implantation.

3. Irradiations:
For EPR studies electron irradiations with energies between 1 and 6 MeV are foreseen. For HRTEM investigation of extended defects irradiations with 15 MeV electrons and reactor neutrons (1 MeV eq.) are planned. The electron irradiations can be performed at University of Minsk, PTB Braunschweig and Rossendorf, neutron damage will be done at JSI Ljubljana. All facilities had already been used in previous experiments and have shown very good results, especially also regarding the reliable dosimetry.

4. Structure studies at NIMP:
Electron Paramagnetic Resonance (EPR, ENDOR) measurements will be employed for structural identification of oxygen related point defects. For these investigations irradiations generating mainly point defects are needed. In this respect irradiations with electrons of energies between 1 and 6 MeV are foreseen. Equipment for multifrequency and multiresonance EPR investigations:
(a) Spectrometers models EMX-plus and ELEXSYS 500Q for X- and Q-band CW EPR, ENDOR (Electron Nuclear DOuble Resonance) /ODMR (Optically Detected Magnetic Resonance) measurements, respectively, in the 3.2–300K temperature range.
(b) Pulsed FT EPR spectrometer ELEXSYS E580 with E560 DICE II pulse ENDOR and E580-400 pulse ELDOR accessories operating in the X-band.
HRTEM studies: A holder for studying annealing of clusters in irradiated silicon will be especially bought for this purpose. The idea is to follow the evolution of the same clustered region during annealing at 80 C and this way to identify the structure of the H-type acceptor like defects responsible for the reverse annealing. Equipment for microstructural investigations: (a) JEM ARM 200F analytical high resolution electron microscope with field emission gun (FEG) operating at maximum 200 kV in the high resolution transmission/scanning microscopy (HRTEM/HRSTEM) modes, with corresponding resolution of 0.19 /0.08 nm. Analytical accessories for EDS (Energy Dispersive X-ray Spectroscopy), EELS (Electron Energy Loss Spectroscopy) and energy filtered TEM
5. Timescale:
Start of pre-tests for O-17 implantation: May 2012
Implantations with 1-5 MeV O-17 (9 steps, total dose 4.5e14/cm²): December 2012
Activation annealing and characterization of implanted samples: January 2013
O-17 (90% enriched) diffusion in encapsulated samples, total: 1e16/cm²: Jan. 2013
Characterization of diffused samples after RTA: SR, SIMS, FTIR: February 2013
Electron irradiations at 1-6 MeV (mainly for EPR investigations): March 2013
Additional irradiations with 15 MeV electrons and 1 MeV equiv. neutrons: April 2013
EPR studies starting March 2013, first results expected June 2013
HRTEM studies starting April 2013 (estimated), results expected till end 2013

6. Breakdown of project costs (preliminary):
(assumed currency relation between € and CHF: 1.00 € = 1.20 CHF)
FZ silicon wafers 1.000,- € 1.200 CHF
Implantation tests including 60% O-17 enriched gas 6.500,- € 7.800 CHF
Annealing and characterization of implanted samples 2.000,- € 2.400 CHF
Purchase of 250 ml 90% O-17 enriched gas 2.500,- € 3.000 CHF
Diffusion process in Quartz encapsulated samples 2.500,- € 3.000 CHF
Characterization of diffused samples (RTA, SR, SIMS, FTIR) 2.500,- € 3.000 CHF
Electron irradiations (only external cost) 500,- € 600 CHF
Neutron irradiations (only external cost) 500,- € 600 CHF
EPR+HRTEM studies 9.000,- € 10.800 CHF
Total cost: 27.000,- € 32.400 CHF

Total 32.400,- CHF
Request to RD50: 12.000,- CHF
Contributions from participating institutes: 20.400,- CHF

7. References
[29] Project PCE 72/05.10.2011 financed by the Romanian Authority for Scientific Research