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Dedicated to Professor Valentin I. Vlad's 70th Anniversary

PARAMAGNETIC POINT DEFECTS IN PURE AND ^{13}C AND ^{17}O IMPLANTED SILICON FOR HIGH ENERGY PARTICLE DETECTORS

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Abstract. The presence and structure of paramagnetic point defects in ^{13}C and ^{17}O implanted ultrapure Si single-crystal material, two impurities which seem to play a major role in the detectors performance degradation and radiation resistance enhancement, respectively, are reported before and after irradiation with 6 MeV electrons. The investigation, performed by Q-band electron spin resonance spectroscopy in the 300 – 10 K temperature range, included also reference ultrapure and ^{16}O doped single-crystal Si-platelets. It resulted in the observation of points defects associated with lattice defects as dangling bonds and impurities.

Key words: silicon, radiation detectors, defects, electron spin resonance.

1. INTRODUCTION

Crystalline silicon microstrip and pixel detectors, which are the key devices for measuring the particles trajectories in elementary particles collisions experiments, are subjected in the high luminosity experiments to extremely intense hadronic fields. The main reason for the extended use of these detectors is the unique flexibility of their structural design for extreme high spatial and time resolution with high signal to noise ratio, the possibility for electronic integration on the same chip and the large experience in semiconductor process technology. However the impact of the high particle intensity by charged hadrons leads to radiation damage effects in the silicon material and hence to degradation in the detector performance limiting their practical use [1]. To improve the radiation hardness of the single crystalline Si material one needs to understand the radiation damage mechanism at high radiation doses/fluencies, the structure and properties of the resulting defects with direct impact on the detector performance [2]. According to previous investigations the degradation in the performance of the Si

detectors used in high energy particle experiments has proved to be higher when increasing the amount of carbon impurity in the silicon device [3]. On the other hand, the oxygen was found to play the opposite role of enhancing the radiation resistance of the detectors [3–5].

To understand the role of the carbon and oxygen impurities in the radiation damage process of silicon at high radiation doses, we have embarked on a program of investigations by multifrequency electron spin resonance (ESR) of the radiation induced point defects on high purity single crystalline silicon doped by ion implantation with carbon and oxygen enriched with nonzero nuclear spin isotopes, namely ^{13}C (99 %, $I = 1/2$) and ^{17}O (70 %, $I = 5/2$) respectively. Here we present the results of the ESR investigations on as received and 6 MeV electrons irradiated single crystal Si-samples implanted with ^{13}C and ^{17}O enriched isotopes, as well as on reference samples of undoped and natural abundant ^{16}O doped samples.

2. EXPERIMENT

Platelets of 15 × 15 mm^2 size were cut from high purity silicon single crystal wafers of 100 mm diameter and 0.3 mm thickness produced by the floating zone (FZ) technique at Wacker-Chemtronic GmbH, oriented with the growth axis parallel to an <100> axis. The reported resistivity of the as received Si-wafers was ρ = 3–4 Ωcm. The impurities content of interest in this investigation were: 10^{16} cm^{-3} (for the natural oxygen) and 10^{15} cm^{-3} (for the natural carbon).

The implantation was done at room temperature (RT) with doses of 4 × 10^{13} ions/cm^2 of ^{13}C (99 % abundance) of 3 MeV and ^{17}O (70 % abundance) of 1 MeV. In both cases the implantation was followed by thermal annealing of the samples at 590 ^0C for 7 days, and at 1200 ^0C for 4 hours, respectively.

We have also investigated a reference sample containing an estimated 10^{17} cm^{-3} of natural oxygen atoms (^{16}O of 99.962 % abundance, with $I = 0$) which was cut from a Si-detector. This sample will be further called Si-16O.

The irradiation of all investigated Si-samples was done at RT with electrons accelerated at 6 MeV, for estimated doses of 76 kGy and 380 kGy. To this purpose we used the electron linear accelerator ALIN-10 operating at 6.23 MeV, 164 W output power, 75 mA electron beam peak current and 100 kHz repetition rate, build at the National Institute for Lasers, Plasma and Radiation Physics, in the Electron Accelerator Laboratory. A ring-shaped electron collection monitor and its associated instrumentation were used for monitoring the absorbed dose rate and accumulated absorbed dose during the irradiation process.

The ESR measurements were performed in the 10–295 K temperature range, with a spectrometer model ELEXSYS 500 Q (Bruker) operating in the Q (34.1 GHz)-band microwave frequency, equipped with a probe head-cryostat assembly, which did allow in-situ illumination experiments. The equipment and magnetic field calibration procedures are described in Refs. 6, 7 and on the webpage: http://cetresav.infim.ro/. The samples for the ESR measurements, of 0.3 × 2 × 5 mm^3

were cleaved form 15 × 15 mm^2 platelets, with the long axis parallel to an <100> axis. By mounting the sample probes in the microwave cavity of the ESR spectrometer with the long axis perpendicular to the magnetic dc field it has been possible to record the ESR spectra for all orientations of the magnetic field in the (100) plane. One should also mention that the orientation of the main crystal axes was checked by X-rays Laue backscattering and found to be correct inside an estimated +/– 1.5 degree accuracy.

3. RESULTS

As will be further shown all investigated Si samples did exhibit only single lines, isotropic EPR spectra characterized by different g-values and ΔB linewidth. In the absence of any resolved hyperfine structure (HFS) the observed spectra can be described by the very simple spin Hamiltonian (SH), with usual notations [8]:

$$\mathbf{H} = \mu_B \, g \, \mathrm{SH}.$$

Thus, the as–grown Si-FZ(100) samples cleaved from a highly polished Si-FZ wafer did exhibit at RT a strong symmetrical line centered at $g = 2.0060$, with linewidth $\Delta B = 0.75$ mT, attributed to the so-called A-center. Its parameters did not change significantly by measuring at lower temperatures. As shown in Fig. 1a, the same ESR spectrum, but in a much lower concentration, was found in samples cleaved from the same type of Si-FZ wafer, but with roughly polished surfaces, strongly suggesting that we are dealing with some surface center produced by polishing. The e^--irradiation entirely changes the ESR spectrum (Fig. 1b). It bleaches the A-center and produces two new centers called B and C, characterized by different g and ΔB values. The asymmetrical, broad spectrum of the B center suggests the presence of spin-spin interactions, typical for aggregated paramagnetic centers. Different from the A-center, the B and C centers which are not visible at RT, required lower measuring temperatures. Moreover, their spectrum is less intense than the A center.

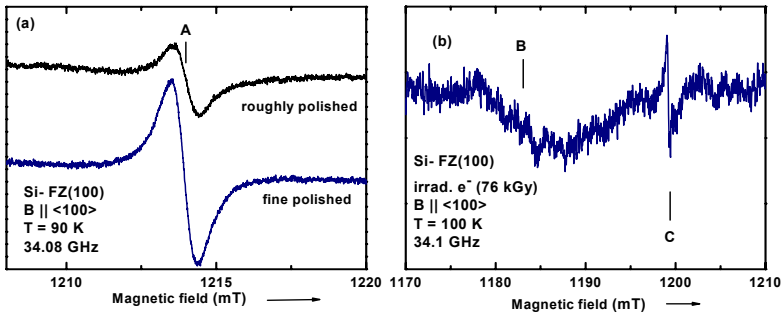

Fig. 1 – The ESR spectra recorded at low temperatures of Si-FZ samples: a) cleaved from two Si-FZ(100) plates with surfaces of different roughness, exhibiting the A-center; b) irradiated with 6 MeV electrons at RT.

The Si-16O sample, doped with natural oxygen, did not exhibit any significant ESR spectrum at RT. However, after e^--irradiation one finds at $T \leq 100$ K (Fig. 2a), an intense, narrow line with $\Delta B = 0.18$ mT, centered at $g = 1.999$. This line was attributed to the so-called D-center.

In the case of both as-received Si-13C and Si-17O samples implanted with the enriched ^{13}C and ^{17}O ions and annealed, the ESR spectra are similar and visible only at $T \leq 140$ K. As shown in Fig. 2b, for the Si-13C sample, the ESR spectrum consists of a narrow line centered at $g = 2.0062$ and linewidth $\Delta B = 0.84$ mT, with parameters close to those of the A-center, and a broad, asymmetrical line at $g = 2.0061$ and linewidth $\Delta B = 1.3$ mT, with parameters close to those of the B-centers.

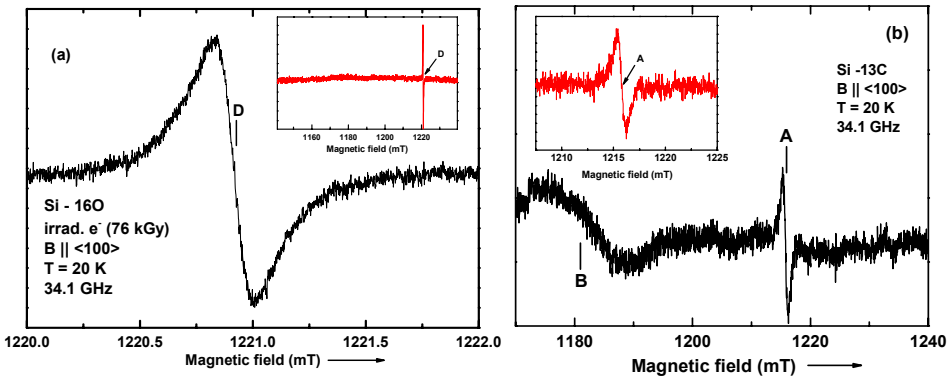

Fig. 2 – The ESR spectra recorded at low temperatures: a) of a Si-16O sample irradiated with 6 MeV electrons at RT. Inset: The ESR spectrum recorded for a large magnetic field sweep range; b) of a Si-13C sample (implanted with ^{13}C), as received. Inset: the ESR spectrum recorded for a smaller magnetic field sweep.

According to Figs. 3a,b, the ESR spectra of the implanted samples exhibit after irradiation similar features. They consist of the narrow line centered at $g = 2.0061$ and linewidth $\Delta B = 1.15$ mT, parameters very close to those of the A center. In the case of the broad line one finds parameters close to those of the B center, but slightly different, namely: $g = 2.059$ and linewidth $\Delta B = 11.3$ mT in the case of the irradiated Si-13C sample, and $g = 2.057$ and linewidth $\Delta B = 13.4$ mT in the case of the irradiated Si-17O sample.

All resulting ESR spectra parameters are presented in Table 1. The parameters of other paramagnetic centers in crystalline silicon, previously reported in the literature, with comparable values are also presented and will be used in our discussion.

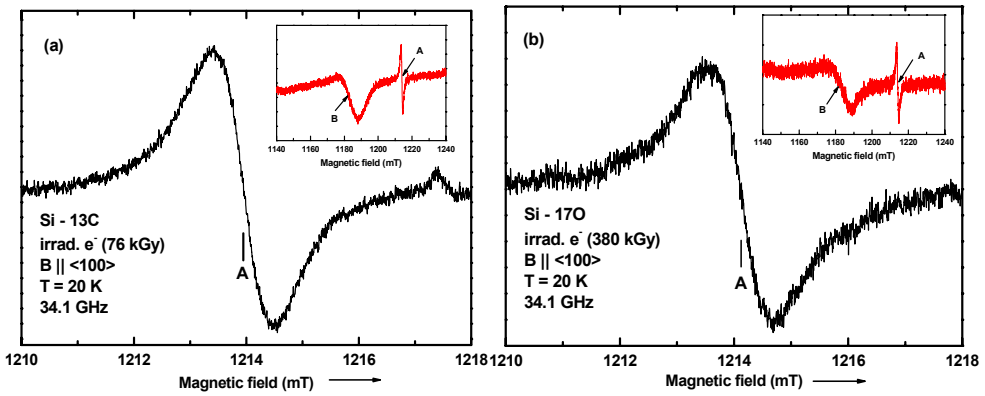

Fig. 3 – The ESR spectra recorded at low temperatures of Si-samples irradiated with 6 MeV electrons at RT: a) of a Si-13C sample; b) the Si-17O sample. Insets: The ESR spectra recorded for a larger magnetic field sweep range.

Table 1

The SH parameters of undoped and doped Si-FZ single-crystal samples, before and after irradiation at RT with 6 MeV electrons. Similar spectra parameters of other paramagnetic centers observed in crystalline Si are also presented for comparison

Center / Sample	g	ΔB (mT)	T_{meas} (K)	Ref.	Obs.
A/Si-FZ	2.0060 ± 0.0002	0.75 ± 0.05	90 - 295	This work	Cleaved from a Si-FZ(100) ingot
A/Si-13C ; A/Si-17O	2.0062	0.84	120	This work	As received
A/Si-13C / 17O (380kGy)	2.0061	1.15	20	This work	e^- (6 MeV)
T2/a	2.0054 ± 0.0003	0.48 ± 0.03	295	[9,10]	O-implanted Si
B / Si-FZ (76kGy)	2.061 ± 0.002	8 ± 1	100	This work	e^- (6 MeV); low conc.
B/Si-13C / 17O	2.061 ± 0.003	13 ± 2	120	This work	As received
B/Si-13C / 17O (380kGy)	2.059 / 2.057	11.3 /13.4	20	This work	e^- (6 MeV)
$(Zn_s)^-$ / Si	2.050			[11]	Subst. $Zn^-(4s^1)$
C / Si-FZ (76 kGy.)	2.032 ± 0.001	0.35 ± 0.05	100	This work	e^- (6 MeV); Unstable at RT
$(Ni_i)^+$ / Si	2.026			[12]	Interstitial $Ni^+(3d^84s^1)$
D / Si-16O	1.999 ± 0.002	0.18 ± 0.15	20 - 100	This work	76kGy
Nl10,NL15, NL18 /Si	1.999 - 1.993			[13,14]	Heat treated
CB/ Si	1.996			[15]	H plasma treated

4. DISCUSSION

In the absence of any resolved HFS, additional information about the structure of the observed paramagnetic centers in the investigated samples can be obtained only by comparing their production properties and referring to existing data from the literature [16]. Examining the data presented in Table 1, one can draw several conclusions.

Thus, the implanted Si-FZ samples exhibit, before and after e^- – irradiation two types of centers called A and B. Inside the experimental error their g-values were found to be the same. Differences were found in the measured linewidth, which can be attributed to variations in the concentration and/or aggregation of the defects, as well as to stability under irradiation. In the absence of any resolved HFS it is hard to conclude that either the carbon or oxygen impurities are involved in the structure of these centers.

Comparing the observed spectra parameters with data available in the literature one finds that a center called T2/a, with slightly different parameters from those of the A center, has been reported in O-implanted silicon [9, 10]. The T2/a center was attributed to an electron trapped at a broken (dangling) Si-bond in the amorphous zones produced by implantation. This model is supported by the presence in the as-grown Si-FZ sample cleaved from Si-FZ(100) plates of the A center, with an increased intensity for the highly polished plates. In this case the amorphization is known to be produced at the surface by polishing. However, in the as grown, polished Si-FZ sample the A-center disappears by irradiation. Meanwhile in the implanted samples its intensity strongly increases. This different behavior under irradiation suggests different trapping mechanisms for the electron/hole pairs produced by irradiation at the dangling bonds in the two cases. They seem to be due to some structural differences, related either with different aggregation states and/or surface vs. volume localization [17].

The B-center has been observed in small amounts in both ^{13}C and ^{17}O implanted Si-samples, its concentration strongly increasing by e^-irradiation. It exhibits a rather large $\Delta g = g - g_e = 0.0587$ deviation from the free electron $g_e = 2.0023$ value, which strongly suggests a defect in which the paramagnetic electron is strongly bound to an impurity ion. A close g value was reported in a brief communication [11] for the substitutional $(Zn_s)^-$ $(4s^1)$ center in silicon. It is very likely that such an ns^1-type center [18] is associated with an unintentional impurity in the as-grown Si-FZ. The large linewidth suggests a possible unresolved hyperfine structure and/or various aggregation states, aspects which remain to be investigated.

The Si-FZ sample did exhibit after irradiation, besides the low intensity line from the B-center, the narrow line spectrum centered at $g = 2.032$, attributed to the C-center. This center, with a very low concentration, is unstable at RT, being bleached out in a few weeks of storing the irradiated sample at RT. Its rather large

$\Delta g = 0.0297$ deviation suggests a structure in which the paramagnetic electron is bound to an impurity. Indeed, the interstitial $(Ni_i)^+$ ($3d^8 4s^1$) center exhibits a close $g = 2.026$ value [12].

Finally, the D center observed in the Si-16O sample exhibits a $g = 1.999$ value, close to the free electron value, suggesting as origin weakly bound electrons. Paramagnetic centers with close *g*-values, also observed only at low temperatures were observed in heat treated Si [13, 14] and in hydrogen plasma treated silicon [15], being attributed in this last case to conduction band electrons.

In-situ illumination experiments were performed on all samples down to 20 K, using the light from a 10 mW He-Ne laser, without observing any light induced effects on any of the four observed paramagnetic centers

5. CONCLUSIONS

ESR spectroscopy at low temperatures has resulted in the observation of four types of paramagnetic centers in the as-received, un-implanted and implanted Si-FZ samples, before and/or after irradiation with 6 MeV electrons at RT. One of them, called the A-center has been demonstrated to consist of electrons trapped at dangling bonds associated with the amorphous zones, either at the surface, produced by polishing, or in the volume of the Si- samples by ion implantation. However, differences in stability and/or production properties under irradiation between the polished and the implanted samples were observed, being attributed to structural differences which remain to be identified.

The B and C paramagnetic centers have been attributed to electrons localized in deep electron traps at some impurity ions. It is not yet clear what is, if any, the role of the amorphization zones in their formation/structure.

The D-center, observed only in the Si sample doped with natural oxygen cut from a Si-detector, has been attributed, based on the small Δg deviation, to weekly bound electrons in the Si lattice.

No isolated paramagnetic centers which could be attributed to electrons localized at the two ^{13}C and ^{17}O isotopically enriched ions have been observed, suggesting that either the impurities were not distributed uniformly in the silicon lattice or much larger radiation doses should be employed, which is not surprising considering that we are dealing with an extremely radiation resistant material.

Further investigations by pulsed ESR and double electron-nuclear resonance (ENDOR) techniques may bring new information about the nature and role of impurities in the structure of the observed paramagnetic centers.

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