2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

DEFECTS IN NTD SILICON STUDIED BY EVAPORATED AND DILUTED ^{111}CD PROBE NUCLEI BY MEANS OF PERTURBED ANGULAR GAMMA-GAMMA CORRELATION TECHNIQUE

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ABSTRACT

In the present work a microscopic investigation of defects in ultra-pure silicon doped with phosphorus was carried out using a nuclear technique in order to identify defects in a very low concentration. The samples were doped by Neutron Transmutation Doping (NTD) process, which produces highly uniform doping concentrations. Perturbed Angular Gamma-Gamma Correlation (PAC) technique using the well-known gamma-gamma cascade of 177-245 keV ($I=5/2^+$, Q=0.83b, $T_{1/2}$=84.5ns) from ^{111}In→^{111}Cd ($T_{1/2}$=2.83d) probe nuclei was used to measure the electric field gradient (EFG) at probe sites in silicon single crystals at different temperatures. Probe nuclei were inserted into the samples by evaporation and dilution methods, and a discussion is made regarding the impact of these two probe nuclei insertion methods on PAC spectra. PAC results points out a probe nuclei migration process which is carefully investigated, as well as an unknown, unreported frequency, which is associated with probe nuclei occupying near-surface sites. The results are then compared, and discussed on the basis of temperature influence in the site occupation of ^{111}In nuclei in NTD silicon.

1. INTRODUCTION

Progress in semiconductor technology is driven by progress in the knowledge and control of defects, these include intrinsic defects, such as vacancies and self-interstitials, and extrinsic defects, such as dopants and impurity atoms. These defects can improve or even degrade the quality of semiconductor materials depending on its electrical properties and environment. As a consequence, strong efforts have been devoted to the investigation of defects in these materials. One of the key points in controlling electrical properties of semiconductor materials resides on the influence of doping process and thermal treatment on the electrical activation level of dopants.

In this context, the use of radioisotope nuclear techniques makes possible to improve our understanding on defects in semiconductor materials, offering higher sensitivities to the presence of small amounts of impurities and the identification of chemical nature of defects. One of these techniques is Perturbed Angular Gamma-Gamma Correlation (PAC) that measures local hyperfine interactions at the site of probe nuclei in semiconductors. This work will mainly focus in the discussion concerning intrinsic defects in ultra-pure silicon doped with phosphorus by means of Perturbed Angular Gamma-Gamma Correlation spectroscopy. For an overview on the study of intrinsic defects in semiconductors with radioactive probes see [1].

2. PERTURBED ANGULAR GAMMA-GAMMA CORRELATION TECHNIQUE

In order to study semiconductor materials, it seems clear that one needs some technique that presents good sensitivity to low defect concentrations. Although we have a great variety of techniques that fill these requirements, many of them are not able to deliver microscopical information about the chemical identity of intrinsic and extrinsic defects. The use of nuclear probe based techniques has proven to be such an interesting method that is capable of delivering information at atomic scale with respect to geometric and electronic structure.

In this context, Perturbed Angular Correlation (PAC) technique has been succesfully applied to the study of local properties of semiconductors as well as solid state physics. For an understanding on the use of radioactive probes in solid state physics see [2].

PAC technique measures the electric field gradient (EFG) acting on a radioactive nucleus by means of the interaction between the EFG tensor and the nuclear quadrupole moment (Q) of probe nucleus. The gamma rays from 177-245keV cascade excited ^{111}Cd, populated from the EC decay of ^{111}In introduced in samples, were detected by 4 BaF_2 detectors. The coincidence counts were registered as function of the time elapsed between the emission of the two radiations (time resolution about 0.6ns). During this time, ^{111}Cd nuclei are in their intermediate spin state ($I=5/2^+$, $T_{1/2}$=84.5ns) and are perturbed by the environmental EFG, which induces transitions between their magnetic sub-states. The coincidence counting rate, without time resolution effects, is given by the perturbed time-differential γ-γ correlation function, which is expressed (neglecting the A_{44} terms) by the following function:

$$\boldsymbol{W}(\boldsymbol{\theta},\boldsymbol{t}) = 1 + \boldsymbol{A}_{22}\boldsymbol{G}_{22}(\boldsymbol{t})\boldsymbol{P}_2(\cos\boldsymbol{\theta}) \quad . \tag{1}$$

where A_{22} are the unperturbed angular correlation coefficients of the γ-γ cascade, $G_{22}(t)$ are the perturbation factors, $P_2(\cos\theta)$ are Legendre polynomials and θ is the angle between the detectors. The perturbation factor is extracted by determining the ratio:

$$\boldsymbol{R}(\boldsymbol{t}) = 2.[\boldsymbol{C}(180°,\boldsymbol{t}) - \boldsymbol{C}(90°,\boldsymbol{t})]/[\boldsymbol{C}(180°,\boldsymbol{t}) + 2\boldsymbol{C}(90°,\boldsymbol{t})] \tag{2}$$

where $C(\theta,t)$ are the geometric mean of the coincidences $W(\theta,t)$ taken from the spectra recorded at angle θ. The measured perturbation function R(t) can be expressed by the following model:

$$\boldsymbol{R}(\boldsymbol{t}) = \boldsymbol{A}_{22}\boldsymbol{G}_{22}(\boldsymbol{t}) = \boldsymbol{A}_{22}\sum_{\boldsymbol{i}} \boldsymbol{f}_{\boldsymbol{i}}\boldsymbol{G}_{22}^{\boldsymbol{i}}(\boldsymbol{t}) \tag{3}$$

where $\boldsymbol{f}_i$ are the fractional site population and $\boldsymbol{G}_{22}^{i}(\boldsymbol{t})$ are the corresponding perturbation factors that in the case of electric quadrupole interaction are given by:

$$\boldsymbol{G}_{22}(\boldsymbol{t}) = \boldsymbol{S}_{20} + \boldsymbol{S}_{2\boldsymbol{n}}\cos(\boldsymbol{\omega}_{\boldsymbol{n}}\boldsymbol{t})\exp(-\boldsymbol{\omega}_{\boldsymbol{n}}^2\boldsymbol{\tau}_{\boldsymbol{R}}^2/2)\exp(-\boldsymbol{\omega}_{\boldsymbol{n}}^2\boldsymbol{\delta}^2\boldsymbol{t}^2/2) \tag{4}$$

where the primary frequencies ω_n and their amplitudes S_{2n} are related to the hyperfine splitting of the intermediate nuclear level and depend on the nuclear quadrupole frequency $\omega_Q = eQV_{ZZ}/4I(2I-1)\hbar$ and the assymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx}, V_{yy} and V_{zz} are the elements of the EFG tensor in its principal-axis system. As usual, V_{zz} is the largest component of the EFG tensor and generally one uses the spin-independent quadrupole frequency defined by $\nu_Q = eQV_{zz}/h$, where Q is the nuclear electric quadrupole moment of the intermediate level. The known quadrupole moment of 0.83b for the $I=5/2^+$ intermediate level of ^{111}Cd has been used to determine V_{zz}. The effects of finite time resolution τ_R of detectors and the distribuition of EFG with a width δ are properly taken into account in equation 4.

The defect properties are directly related to the electric field gradient (EFG) measured by PAC. The EFG in silicon may be produced by a specific defect in the neighborhood of the probe nucleus [3] resulting in a quadrupole hyperfine interaction with a characteristic frequency. Not only a defect but also a non-cubic environment may result in non-zero EFG at probe sites.

Probe Nuclei

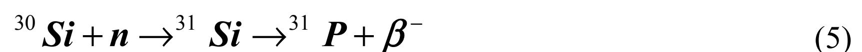
An important feature of a PAC experiment, is the ability to observe time dependent perturbation through the analysis of a γ-γ angular correlation. In order to make it possible, it is required a radioactive isotope that emits a cascade of two γ-rays. In this work, it was used $^{111}In \rightarrow {}^{111}Cd$ as the probe atom.

The ^{111}In probe nuclei used in PAC measurements is obtained from the irradiation of ^{109}Ag nuclei with alpha particles in a cyclotron accelerator. The half-life of ^{111}In is 2.83d and the gamma cascade of interest in the daughter nucleus ^{111}Cd is the one with energies of 171keV and 245keV passing through an intermediate state (E_i=245keV, $I=5/2^+$, $t_{1/2}$=85ns, $\mu=0.7656\mu_N$). Most of the results on defects in semiconductors have been obtained with this kind of probe because of its favorables parameters (adequate lifetime of parent probe and intermediate state).

3. SAMPLE PREPARATION AND MEASUREMENTS

The samples were obtained from commercial ultra pure silicon wafer grown by means of Float Zone (FZ) process. The silicon wafer with 0.5mm thickness was cut in 3mm x 3mm samples. Samples were then doped with phosphorus using Neutron Transmutation Doping (NTD) process, which produces a highly homogeneous doped material.

NTD process consists on silicon single crystal irradiation with thermal neutrons in a nuclear reactor. The method is based on the following nuclear reaction:



$$^{30}Si + n \rightarrow {}^{31}Si \rightarrow {}^{31}P + \beta^- \quad (5)$$

On this process, silicon captures a thermal neutron and subsequently transmute itself on the doping element through the emission of a Beta particle. It is relevant to mention that

microscopic investigations for silicon doped by NTD method have not been reported in literature. The irradiation process was carried out in IPEN IEA-R1 nuclear reactor.

After doping process, PAC probe nuclei ^{111}In inserted on samples through Dilution and Evaporation methods. On diluted samples, probe nuclei ^{111}In were introduced through thermal diffusion of $InCl_3$ in methanol. This procedure was made in order to avoid silicon contamination with hydrogen. On evaporation process, probe nuclei ^{111}In were inserted in samples through "electron-beam" process in an Edwards Auto 306 evaporator machine.

4. RESULTS AND DISCUSSIONS

Silicon samples were first submitted to the evaporation of a thin ^{111}In layer. Next, it was made an evaporation of silicon adding an extra layer in order to assure that probe nuclei remain inside sample material. The sample then was submitted to different annealing procedures as presented in Fig.1.

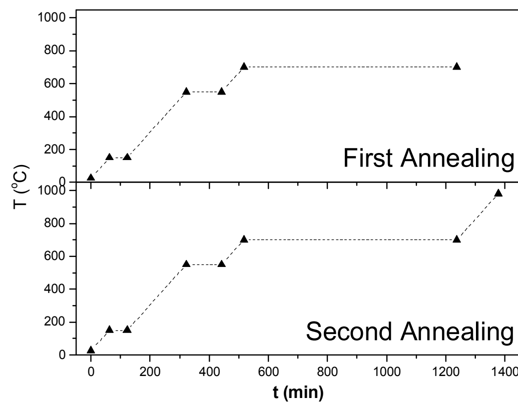


Figure 1. Temperature as function of time for both annealing processes.

Fig.2 shows TDPAC spectra for ultra pure silicon measured at room temperature before and after both annealing procedures.

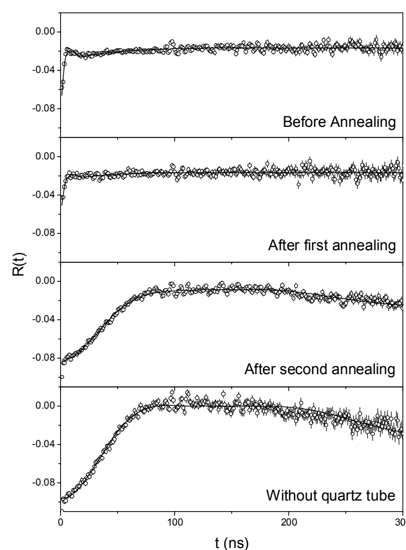


Figure 2. PAC Spectra before and after annealing processes

Results point out to the existence of two different frequencies associated to substitutional sites, as well as an unknown, undefined frequency discussed later in the text. The hyperfine parameters values obtained from spectra are presented on the Table1.

Table 1. Hyperfine parameters (^{111}In evaporated sample)

	ν_Q		fraction (%)	
	Substitutional	**Unknown Site**	**Substitutional**	**Unknown Site**
Before Ann. 1	13.1 (5)	286.9 (1)	18%	82%
After Ann. 1	14.4 (5)	247.2 (1)	17%	83%
After Ann.2	18.1 (1)	-	100%	-
Without tube	18.9 (1)	-	100%	-

Through the table, it can be clearly seen the impact of both annealing procedures. Before first annealing, only 18% of probe nuclei reside in substitutional sites with corresponding 82% of probe nuclei with an unknown, unreported frequency.

In order to explain this frequency, one can first consider possibility of probe nuclei residing on interstitial sites in silicon. Cordeiro and Carbonari [4], in a recent work had associated a highest frequency with interstitial sites, however, Channeling and Mossbauer experiments [5] have shown strong evidences that In inside a silicon matrix mostly occupy substitutional sites. Another relevant point concerning this discussion is that theoretical calculations to possible interstitial sites presented a high frequency (of order of 400MHz) which was not observed in experimental measurements.

The fact that the highest frequency observed in this work has no mention in literature allied to the fact that there are no reports of experiments in silicon with probe nuclei inserted by evaporation method seems to point out the possibility that this frequency is somewhat related to probe nuclei insertion process (evaporation). Once the evaporated layers are very thin, the most possible reason for this higher frequency seems to be the fact that after evaporation process, most probe nuclei occupy sites that are very close to the surface of the sample, experiencing a different frequency which was observed in this work.

Observing Table1, it can be seen that after first annealing sequence no significant changes can be observed. However, after second annealing process significant changes can be observed. The highest frequency, associated to probe nuclei in near surface sites, could not be observed, while almost 100% of probe nuclei reside in substitutional, defect-free, sites. These changes seem to be relevant, once both processes were similar with exception made to the last step in the second annealing (temperature rising from 700°C to 980°C, see Fig.1). This last step seems to point out the occurrence of an ordering process with the migration of probe nuclei to substitutional sites. It was made a last measure without the quartz tube in which the sample was put in order to verify the possibility of contamination of the tube. PAC spectra showed that this possibility was not verified.

It is relevant to say that Wichert [6] mentioned that in an experimental measurement Cd nuclei has diffused outside the sample for temperatures near 950K. In our measurements, one can see an opposite behaviour: Cd occupying sites near the surface of the sample, diffused inside the sample for a similar range of temperatures. This fact lead us to the following conclusion: for this range of temperatures, Cd nuclei become mobile inside silicon matrix, and the behaviour of migration processes might depend on the particularities of probe nuclei insertion methods and annealing temperatures.

It is also relevant to mention that the dopant sites (produced by NTD method) could not be experimentally observed. This fact is well explained by the extremely low doping concentrations (of order of $10^{16}cm^{-3}$) as well as the very uniform concentrations produced by this doping process.

5. CONCLUSIONS AND FINAL REMARKS

PAC Technique was presented in the context of studying defects in semiconductor materials due to its sensitivity to the small amount of impurities and its ability to provide information in atomic scale. In order to study NTD silicon, $^{111}In \rightarrow ^{111}Cd$ was used because of its favorable parameters. Our investigation revealed two different sites associated with substitutional probe nuclei, and an unknown frequency associated to probe nuclei occupying near-surface sites. The behavior of the fractions pointed out to a recovering process with probe nuclei migration to substitutional sites over the temperature range from 780°C to 980°C. It is relevant to mention that due to the very uniform concentrations of dopants produced by NTD method, it could not be observed sites associated with dopants. There are no articles reporting investigations in silicon obtained from NTD method, emphasizing the relevance of the results obtained in this work.

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