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Study of defects in Silicon by means of Perturbed Angular Gamma-Gamma Correlation Spectroscopy

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ABSTRACT

In the present work a microscopic investigation of defects in ultra pure silicon single crystals was carried out using a nuclear technique in order to identify defects in a very low concentration. Perturbed Angular γ-γ Correlation (PAC) technique using the well-known γ-γ cascade of 177-245 keV with an intermediate level of 245 keV ($I = 5/2^+$, Q = 0,83 b, $T_{1/2}$ = 84.5 ns) from ^{111}In-^{111}Cd (T1/2 = 2,83d) probe nuclei was used to measured the electric field gradient (EFG) at the probe sites in silicon single crystals at different temperatures. The PAC results show dynamic interactions and are discussed on the basis of the temperature influence in the site occupation of ^{111}In nuclei in pure silicon without any doping process.

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 in these materials. These defects can improve or even degrade the quality of semiconductor material 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.

The doping process is a fundamental step in the development of a semiconductor material. Properties like energy gap and resistivity highly depend on chemical nature and concentration of doping elements. Commonly used doping techniques like diffusion and ionic implantation produce highly inhomogeneous doping concentrations and a large number of lattice defects. The quality of a semiconductor material critically depends on the nature and concentration of electrically active defects. As an example, the electrical properties in semiconductors are significantly altered if 1 out of 10^9 atoms is replaced by a defect, which corresponds to a defect concentration of about 10^{14} cm^{-3}.

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 γ-γ 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 sillicon by means of Perturbed Angular γ-γ Correlation Spectroscopy. For an overview on the study of intrinsic defects in semiconductors with radioactive probes see [1].

2. PERTURBED ANGULAR γ-γ CORRELATION TECHNIQUE

In order to study semiconductors, it seems clear that we need 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 don't give 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].

The PAC technique can measure the electric field gradient (EFG) acting on a radioactive nucleus by means of the interaction between the EFG tensor with the nuclear quadrupole moment (Q) of the probe nucleus. The gamma rays from the 177-245 keV cascade of excited ^{111}Cd, populated from the EC-decay of ^{111}In diluted in the samples, were detected by 4 BaF_2 detectors. The coincidence counts were registered as a function of the time elapsed between the emissions of the two radiations (time resolution about 0.6 ns). During this time ^{111}Cd nuclei are in their intermediate spin state ($I = 5/2$, $T_{1/2} = 84.5$ ns) 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 angular correlation function, which in polycrystalline samples is expressed (neglecting the A_{44}-terms) by the following function [3]:

$$W(\theta,t) = 1 + A_{22}G_{22}(t)P_2(\cos\theta) \qquad (1)$$

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:

$$R(t) = 2\left[\frac{C(180^\circ,t) - C(90^\circ,t)}{C(180^\circ,t) + 2C(90^\circ,t)}\right] \qquad (2)$$

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:

$$R(t) = A_{22}G_{22}(t) = A_{22}\sum_i f_i G_{22}^i(t) \qquad (3)$$

where f_i are the fractional site population and $G_{22}^i(t)$ are the corresponding perturbation factors that in the case of electric quadrupole interaction is given by:

$$G_{22}(t) = S_{20} + \sum_{n=1}^{3} S_{2n} \cos(\omega_n t) \exp(-\omega_n^2 \tau_R^2 / 2) \exp(-\omega_n^2 \delta^2 t^2 / 2) \qquad (4)$$

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 asymmetry 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 0.83 b 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 distribution of the EFG with a width δ are properly taken into account in equation 3.

The defect properties are 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 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 the probe sites.

2.1. Probe nuclei

An important feature of a PAC experiment, is the ability to observe the time dependent perturbation by 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-^{111}Cd as the probe atom.

The ^{111}In probe nuclei used in the PAC measurements is obtained from the irradiation of ^{109}Ag nuclei with alpha particles in a cyclotron accelerator. The half-life of the ^{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, μ = 0,7656 μ_N). Most of the results on defects in semiconductors have been obtained with the probe ^{111}In because of its favorable 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, which produces a highly homogeneous material. The silicon wafer with 0,5mm thickness was cut in 3mm x 3mm samples.

The samples were first submitted to an annealing at 250°C for 24 hours in vacuum to remove impurities on their surface. Approximately 20–30 μCi of carrier free solution of ^{111}In in the form of $InCl_3$ (in methanol solution) was dropped over the the surface of the sample. The reason to use Indium Chloride in methanol instead to water solution was to avoid contamination of hydrogen due to the presence of water. It's well known that hydrogen promotes passivation of dopants in Silicon, for more information on the effect of hydrogen in silicon see [3]. Afterwards, the samples were sealed in quartz ampoules under vacuum and heated to 600°C for 24 hours in order to dope with ^{111}In probe nuclei.

The PAC measurements were performed with a conventional slow–fast coincidence setup using four BaF_2 detectors in 90^o geometry. The time resolution of the detector system was of the order of 0.7 ns. The measurements were carried out at several temperatures using a small tube furnace where the temperature was controlled to within 0.5 K.

4. RESULTS AND DISCUSSIONS

Figure 1 shows some TDPAC spectra for ultra pure Silicon at different temperatures. The spectrum at room temperature shows a broad distribution that is ascribed to probe nuclei occupying non-substitutional Si sites. Above 600 K the relaxation of the angular correlation increases with temperature to a complete destruction of the anisotropy within a few nanoseconds. This behavior presents the typical features of dynamic interactions. Dynamic interactions are generally caused by time-dependent EFGs. Those time-dependent EFGs arise when the field gradient tensor changes its magnitude or orientation within the time window of the probe nucleus.

One of the possible effects that might be responsible for dynamic interactions in probe atom site is the decay after-effect. It occurs due to the influence of chemical transmutation process in the electronic shell of probe atom. The electron capture (EC) decay, happens via the capture of a K shell electron by ^{111}In, and transforms that isotope into an excited ^{111}Cd nucleus. Then, the decay aftereffect is related to the time required for reaching the ground state of ^{111}Cd. In reference [4], it was verified that aftereffects (^{111}In in Silicon) mostly happens in low temperatures range, which are far below temperatures investigated in this work.
The dynamic effects can also be attributed to a random movement of impurity elements, like hydrogen around the probe or even the movement of the radioactive indium atoms in the crystal lattice [5], which may produce a fluctuating time-dependent EFG in the probe atom site.

In fact, when a probe atom is subjected to dynamic interactions a fluctuating EFG is observed as a relaxation of the perturbation function that can be approximated by:

$$G_{kk}(t) = \Gamma_{kk}(t).\exp(-\lambda_k t) \tag{5}$$

Where Γ_{kk} is dependent on the relative time scale of a given motion as compared to TDPAC time window: in the slow fluctuation regime, $\Gamma_{kk}(t)$ is the same as the static perturbation. In the fast fluctuating regime $\Gamma_{kk}(t)$ is the perturbation function that corresponds to a time average of the fluctuating EFG (see reference [6] for furhter details), within this regime λ_k is proportional to w^{-1} where w is the time rate of EFG fluctuation.

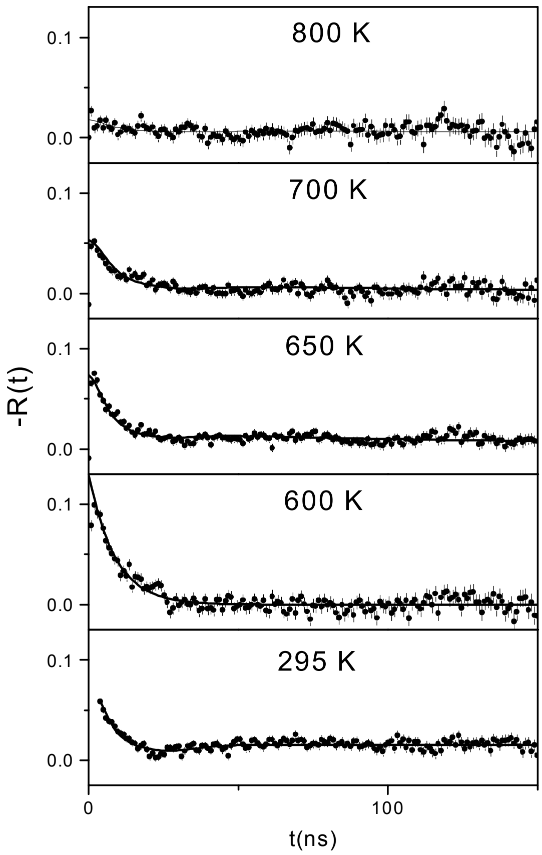

Figure 1. TDPAC Spectra of ultra pure Sillicon: measured at different temperatures.

The intensity of the dinamic interaction is then reflected by λ parameter, which relates to the transition rate beetween different states of an EFG tensor. An increase in that parameter causes an increasing exponential damping of the modulation amplitudes in PAC spectrum. Thus, the sharp-decrease spectra behaviour shown above can, in fact, be ascribed to dinamic, time-dependent interactions. The λ parameter, fitted for each one of the spectra is shown in Figure 2 as function of temperature.

From Figure 2, we can see that dynamic interactions become more intense as temperature increases. In fact, most of the information concerning the effects responsible for generating these dinamic interactions in pure Sillicon is still not known. It's expected that in future investigations our understanding on these effects become more accurate and clear.

Another interesting point concerning our measurements is related to the behavior of silicon sample after annealing process in contrast to measurements made before the annealing sequence. Table 1 shows the parameters obtained for silicon sample before and after annealing.

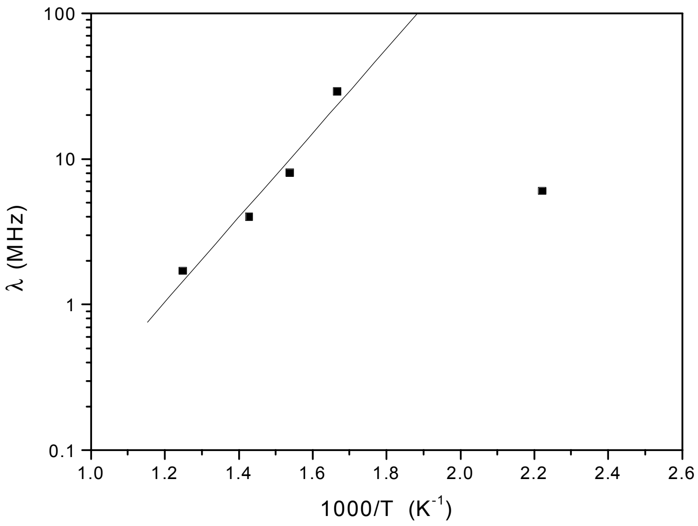

Figure 2. λ parameter as function of temperature in ultra pure Sillicon.

Table 1. Parameters for ultra pure silicon at 295K before and after annealing sequence

	Before annealing		After annealing	
Crystal site	substitutional	interstitial	substitutional	interstitial
ν_Q (MHz)	12.1	120.6	11.6	90.3
Fraction (%)	8.6	91.4	16.1	83.9
δ (%)	50.1	30	50.9	28

From the frequencies obtained, it is known that the smaller frequency obtained in both cases is related to substitutional sites. The highest frequency is then associated with non-substitutional or interstitial sites. The increasing of smaller frequency fraction during annealing (from 8.6 to 16.1%) indicates that some of the interstitial sites became substitutional during this process.

Another interesting point is the high δ parameter values, which indicates broad frequency distributions. The nuclear probe nuclei are probably located near the surface of the sample generating this wide distribution of frequencies. If we had used ion implantation technique for the insertion of ^{111}In in silicon, we would expect smaller values for δ parameters as well as higher fractions of substitutional sites.

5. CONCLUSIONS

PAC technique was presented in the context of studying defects is 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 semiconductors, ^{111}In was used as nuclear probe because of its favorable parameters. Our investigations in ultra pure silicon showed strong dynamic interactions that increased with temperature. The dynamic interaction was analyzed as function of λ parameter that is responsible for spectra attenuation. It could also be noted that the annealing process promoted some changes in the fraction of substitutional sites. As a future work, more investigations on the effects that generate those dynamic interactions can be made.

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