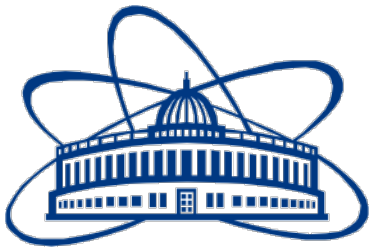

Joint Institute for Nuclear Research

Laboratory of Nuclear Problem

Final Report on the START Program

Study of structural evolution of Si monocrystal after induced defects and hydrogen implantation

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Participation period:
September 04 - October 29
Summer Session 2022

Abstract

The structural evolution of Silicon monocrystals, after hydrogen implantation at different fluences of 10^{14}, 10^{16}, 10^{17}, has been studied. The energies of the protons used for the hydrogen implantation are around 2 MeV.

The chosen structural study method is Positron Annihilation Spectroscopy. The data from the positron spectroscope is processed using the LT10 software from Dr. Jerzy Kansy ad Dawid Giebel. The acquired results from the experiment are more in depth examined using computer modeling of PALS with software Abinit.

Additionally Doppler broadening has been performed and computer studied at different depths. In this way we have done examination of the energies at which the electrons annihilate.

The computer modeled results for the silicon lattice in the presence of vacancy cluster, containing one hydrogen atom is: 229 ps and in the case of four hydrogen atoms is: 219 ps. The results are expected as with higher electron presence we anticipate lower positron lifetime.

Contents

1 Introduction

With the shrinking size of electronic components and transistor sizes new production technologies were needed. When transistor sizes went smaller than 20nm it become evident that the semiconducting properties of the silicon bulk in the devises should be manipulated.

This is when the idea of adding insulator between the bulk silicon and the source and drain in the transistor came up. People called it Silicon on Insulator (SOI) technology [1].

Ion implantation of hydrogen and other light materials into silicon have been used by the industry for producing electronic components with the SOI architecture. The process named Smart Cut (reference) and protected by US patent 5374564 [2] makes this possible. The technology provides power efficiency, lower production costs, higher performance speed and better replication of the chips.

In the development of this process manufacturers faced problems with the defects caused by the ion implantation in the silicon crystal. To ensure that no or minimal defects will be present in the silicon lattice years of science work has taken place. The formation energies of the vacancies had to be studied and the overall geometry and types of these vacancies had to be also known in order false production to be omitted or minimized.

The reason why in this study Positron Annihilation Spectroscopy has been chosen as a study method is because it is of about 4 orders of magnitude better in spatial resolution than TEM. The method is particularly sensitive to defects such as vacancy clusters with sizes from 0.1 to 1 nm and a minimum concentration of up to $10^{-7}cm^{-3}$

2 Positron annihilation spectroscopy

In the following research we have used two positron annihilation spectroscopy methods to determine the defects in the crystal: 1) Positron annihilation lifetime and 2) Doppler broadening

For better understanding we will have a look over the fundamental processes governing these techniques.

2.1 Annihilation process

The existence of the positron as a particle has been predicted by the ingenious physicist Paul Dirac [3]. He yields the existence of particles with the same wave functions but opposite energies.

We can obtain equations for finding the positron or electrons energies by following the Dirac's way of thinking, solving the classical quantum Schrödinger's equation.

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{\mathcal{H}}\psi$$

Linearisation (1) of the Hamiltonian in the above expression allows us to obtain the relativistic energy momentum by substituting α and β with the corresponding Dirac's matrices. Dirac matrices (2) on the other hand consist of Pauli's matrices (σ_k) as two of their arguments or of the identity matrix in the case of β.

$$\hat{\mathcal{H}} = \alpha_1 \hat{p_1} c + \alpha_2 \hat{p_2} c + \alpha_3 \hat{p_3} c + \beta m c^2 \tag{1}$$

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad \alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \tag{2}$$

Pauli's matrices (3) represent an observable describing the spin of a spin 1/2 particle.

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3}$$

The identity matrix I is sometimes referred to as the fourth of the Pauli's matrices and it is denoted as σ_0 (4). Together with the other tree matrices they form a basis describing the real vector space of 2×2 Hermitian matrices.

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4}$$

Solving the Schrödinger's equation with the additions from Dirac's and Pauli's works we obtain the following form of the energies of the positron and electron:

$$E = \pm \sqrt{\overrightarrow{\mathrm{p}}^2 + m^2}$$

The result of this is: we get two particles, one with positive energy and one with negative. Each of these particles own either a spin up or spin down property. They share the same wave function but differ in phase or sign [3].

Why and how the annihilation exactly happens? Reason number one is that as we all know positive and negative charges attract each other. Here in our case the positron possesses a positive charge and the electron has the negative one. This means that we have a present attraction between the particles. But what happens when they meet?

In physics we call it annihilation. What really happens is that since the positron and the electron are each others antiparticles they share the same wave function, but they are oscillating in an antiphase. This means that when they meet a destructive interference happens and the two particles stop existing in the form we know them from quantum physics.

Interesting phenomena is that in this process of annihilation two (three in some cases) γ -rays are emitted from the interacting antimatter pair [4]. In order to preserve the linear momentum of the annihilating pair and its total energy the two photons have energies of 511 keV and are directed in an angle from each other slightly different from

180^o [4](Fig. 1).

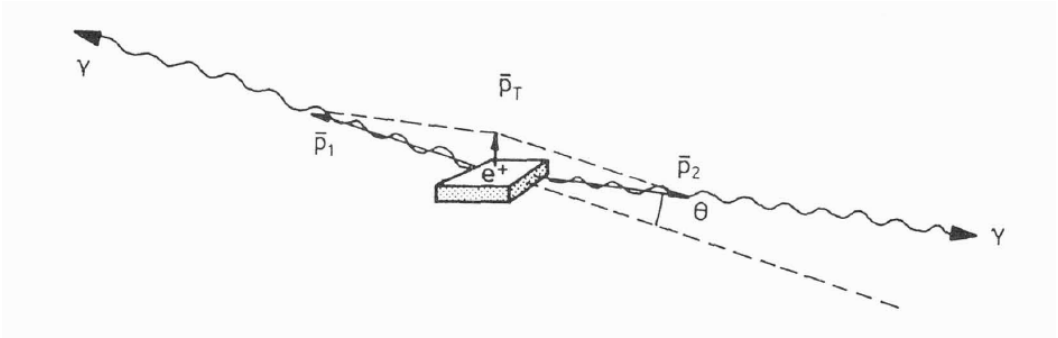

Figure 1: When a positron (antimatter particle) comes to rest, it interacts with an electron, resulting in the annihilation of both particles and the complete conversion of their rest mass to pure energy in the form of two oppositely directed 0.511 MeV photons.

It is exactly this phenomena of the γ -rays emission that allows us to perform Positron annihilation spectroscopy.

2.2 Experimental installation for measuring the lifetime

How do we measure the positron's lifetime? The possibility of measuring the positron's lifetime comes from the fact that almost simultaneously with the emission of the positron from the ^{22}Na source a gamma quant with the energy around 1.27 MeV is also emitted. After that when the positron annihilates in the sample with the electrons we get one more emission of two more quanta with energy around 511 keV. Detecting these quanta, the starting one and the ones from the annihilation site, measuring their energies and the time passed between their appearances gives us the lifetime of the positron responsible for their emergence.

As we see from Fig.1 the probed material is placed between two scintillator photo multipliers which detect the signals from the annihilating positrons. They transform the γ rays into electric signals. The pulses are processed by discriminators. Their output pulses start and stop a time-to-amplitude converter as an "electronic stopwatch". The amplitude of the output pulse is proportional to the time difference between the birth and the annihilation γ-quanta and, thus, represents a measure of the positron lifetime.

The activity of the source is set to be sufficiently low in order to ensure that on average only one positron is in the sample. This avoids the intermixing of start and stop quanta originating from different annihilation events. In order to obtain the complete lifetime spectrum, more than 10^6 annihilation events must be recorded.

Now we are left only with the question how do we produce our positrons? Well we already said that we have a ^{22}Na source (1) (Fig.2). This is a proton rich (neutron

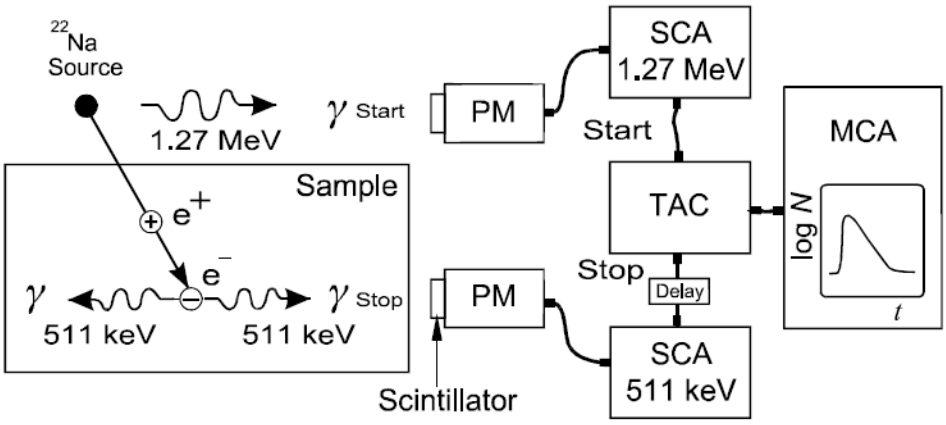

Figure 2: Scheme of the positron lifetime experiment.. The lifetime is measured as the time difference between the appearance of the start and stop g-quanta (PM—photomultiplier, SCA—single-channel analyzer). The amplitude of the time to amplitude converter (TAC) analog output pulse is proportional to this time difference. The whole lifetime spectrum N(t) is stored in a multi-channel analyzer (MCA).

deficient) material which emits positrons naturally experiencing beta decay. These positrons first pass through the diaphragm (2) for selecting their right energies. Then are passed to the transfer channel (3). The Surko trap (4) is for storing the positrons and then the target insertion (5) passes them to the emitter. Vacuum pumps (6) are present to preserve the clean environment in the system [5].

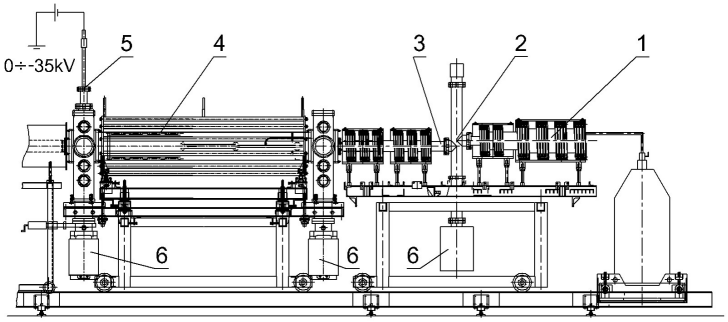

Figure 3: The scheme of positron injector at LEPTA facility: 1- $^{2}2Na$ positron source (+50 V); 2- diaphragm; 3- transfer channel; 4- Surko trap; 5- target insertion; 6- vacuum pumps

2.3 Positron behaviour in the material

Usually the positron enters the medium at energies around 200 keV. After interactions with the material's atoms its energy decreases due to energy exchanges in

ionizing or excitation processes. This happens for times smaller as 1-10 ps. During this time the positron is able to penetrate a distance in the solid of 10-1000 micro meters, depending on the material's density. This is the reason why this method is only suitable for probing bulk materials. Although in recent years low positron annihilation spectroscopy exists.

After slowing down, positrons diffuse around in a delocalized Bloch function [6]. The explanation for this is given by solid state quantum mechanics. Bloch's theorem yields the solution to Schrodinger's equation for a particle subject to a spatially periodic potential. The resulting wave functions of these particles are spread out over the lattice. This spread out we call delocalization. In metals the lifetime is around 100-400ps, and during this time the positron will diffuse around 200nm.

If the probe contains defects such as vacancies, vacancy cluster and dislocations, i.e. regions of less than average electron density, positrons may become trapped, i.e. localized at these defects. This is because the positron is repelled by the positively charged ion cores. Hence, structural defects which represent missing (or a reduced density of) ions will provide attractive potentials for positrons [7].

Trapped in such potential traps with low electron density the positrons experience longer lifetime. Having a record of these lifetimes and some characteristics of the emitted quanta we can determine the types of the defects, their magnitude and from the rates with which the defects trap positrons, defect concentrations can be derived.

2.4 Doppler broadening

If the momentum of the annihilating pair has a component, p_x in the direction of the emitted γ-quanta, the frequencies of these quanta and their energies will be Doppler shifted by the following quantity [3]:

$$\Delta E = \frac{cp_x}{2} \tag{5}$$

One of the emitted quanta will have energy $E_0 + \Delta E$, the other one $E_0 - \Delta E$, where $E_0 = m_0c^2 = 511$ keV.

We can see from equation (5) that the difference in the energy is proportional to p_x. This gives us a very useful tool for measuring one of the components of the moment of the annihilating pair.

Obtaining information from the Doppler broadening spectra happens by characterizing the spectra with two parameters: S and W (Fig.1).

S is parameter defined from the area A under the spectrum in a narrow energy range symmetrical around 511 keV (6). While W is a parameter defined from the sum of the areas under the lateral parts of the spectrum, i.e. in two regions symmetrical around 511 keV (7).

$$S = \frac{A}{C} \tag{6}$$

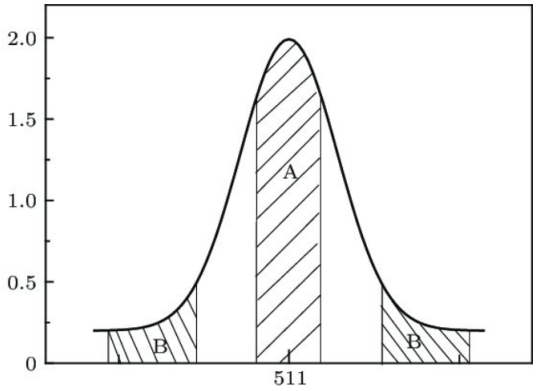

Figure 4: The type parameter definition of Doppler broadening spectral peak [8].

,where C is the whole area beneath the curve.

$$W = \frac{B}{C} \tag{7}$$

The physical meaning of the parameters are: S gives the participation of annihilating pairs with low momentum, such are happening with valence electrons. The bigger the value of S the higher the concentration of defects if this type. W gives the participation of annihilating pair with high momentum, such are happening with core electrons. This gives us information about defects of core electron type.

The Doppler broadening measuring equipment in LEPTA, JINR is shown on the picture below.

Figure 5: Doppler broadening measuring equipment available at the LEPTA project in JINR.

It consists of hyper pure Germanium detector with a resolution of about 1.2 keV to capture precisely the incoming 511 keV gamma qanta [5].

A preamplifier and amplifier make the information readable and possible for processing.

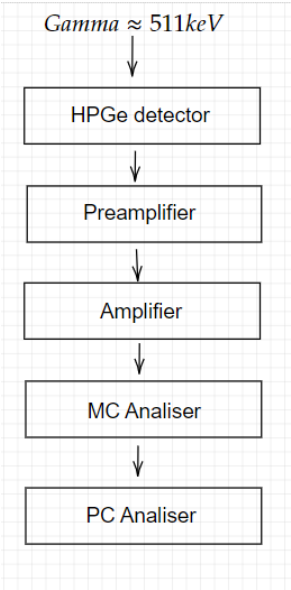

Figure 6: Block diagram of the Doppler broadening equipment at LEPTA.

2.5 Trapping model

The trapping model gives us the so-called rate equations. They describe how the positron annihilates in a specific state or transits to another state [9]. From the solutions of these equations we can derive the probability that the positron will annihilate from a certain state and the corresponding intensities for each type of event.

We will have a look over the simple case where the positron possess two possible states: the first one being a free state (delocalized) and the trapped state (localized). Annihilation is possible from both states, and transitions are only allowed from the free state to the trapped state. The rate equations are:

$$\frac{dn_f}{dt} = -kn_f - \lambda_f n_f$$
$$\frac{dn_t}{dt} = -kn_f - \lambda_t n_t$$

, where n_f and n_t are the the probabilities that the positron will be in respectively free or trapped state at any given time t. λ_f and λ_t are the annihilation rates from the specific states.

Solving these differential equations with initial values for $n_f(0) = 1$ and $n_t(0) = 0$ we get the following results for the annihilation rates:

$$n_f(t) = e^{-(\lambda_f + k)t}$$
$$n_t(t) = \frac{k}{\lambda_f + k - \lambda_t}(e^{-(\lambda_t)t} - e^{-(\lambda_f + k)t})$$

We can easily get that the probability that a positron annihilates from the free or the trapped state is:

$$P_f = \lambda_f \int_0^\infty e^{-(\lambda_t)t}\, dt = \frac{\lambda_f}{\lambda_f + k}$$

$$P_t = 1 - P_f = \frac{k}{\lambda_f + k}$$

The measured lifetime components are $\tau_f = 1/(\lambda_f + k)$ and $\tau_t = 1/\lambda_t$. Rearranging the decay components, the corresponding intensities are:

$$I_t = \frac{\lambda_t k}{\lambda_f + k - \lambda_t} \int_0^\infty e^{-(\lambda_t)t}\, dt = \frac{k}{\lambda_f + k - \lambda_t}$$

$$I_f = 1 - I_t$$

As it was stated above these equations are valid for the specific case when we have defined two state positron system. The equations and the following conclusions could be generalised and derived for more complicated positron state systems, following the same logic. Nevertheless this won't be a subject of our matter here and it won't be done.

3 Computing models

In order to justify our experimental results and explain in a more detailed way the events that we study in our sample we use computer simulating. The Positron Annihilation Lifetime experiment can be studied with the help of the software Abinit. This program uses Two-Component Density-Functional Theory (TCDFT) [10] calculations along with the Projector Augmented-Wave (PAW) [11] method to perform: lifetime calculations in a perfect material and electron-positron momentum distribution calculations.

Abinit uses different approaches when we have a perfect lattice and when we have some defects present in the crystal [12]. In the first case it assumes that when we have no disturbances in the crystal the positron wave function is delocalised and that its density is close to zero. In the second case we have the localised wave function of the positron in the defect. When we look at the density distribution of the positron (Fig. 7) we can see it exactly concentrated in the present defect.

Describing the exact type of crystal defects happens by simulating several types of defects. Comparing the resulting lifetime values from the computer with the real experimental data gives this exact explanation of the form and type of the defects. In this study we have done four simulations of a defects. Each of them containing either one to four hydrogen atoms. The hydrogen atoms are placed in the spot of a missing

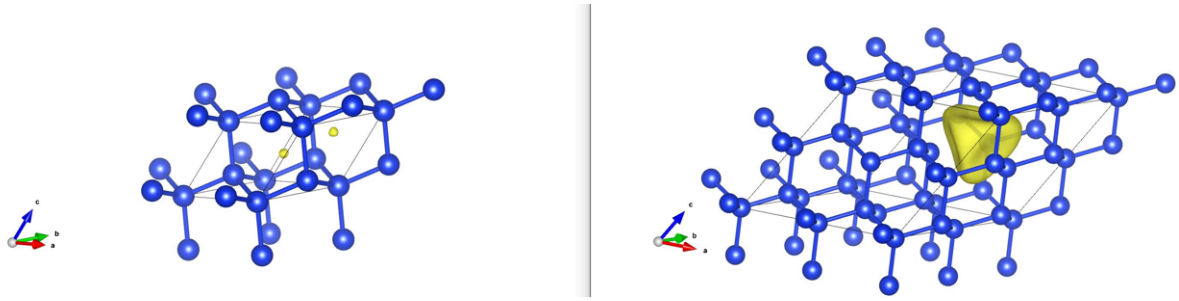

Figure 7: Picture on the left visualises the positron density distribution (yellow) in a perfect Si (blue) lattice. Picture on the right visualises the positron density distribution in Si lattice with a vacancy of one Si atom missing. The visualisation was done using VESTA software.

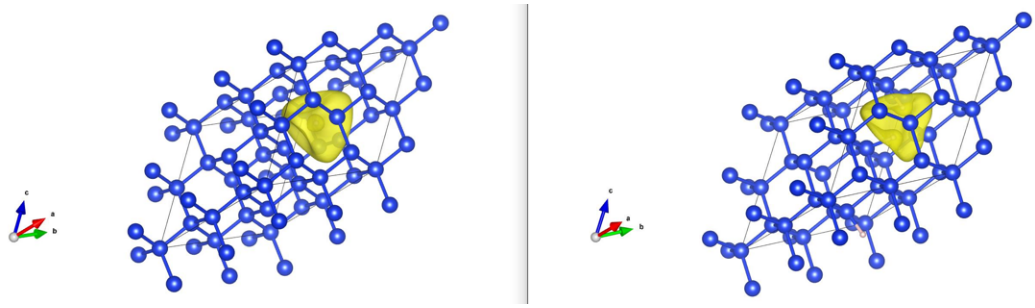

Figure 8: On the picture of the left we have the positron density distribution in the presence of 1 hydrogen atoms in a mono silicon vacancy. On the picture of the right we have the positron density distribution in the presence of 2 hydrogen atoms in a mono silicon vacancy.

Si atom. The positron density distributions are shown on Fig. 8 and Fig. 9.

Analyzing the visualised data it can be seen the positron density behaves just as described in the theory. In the first case of a perfect lattice we have near to zero concentration. In an empty vacancy we have the biggest value of the positron's density. As we introduce more and more hydrogen atoms in the vacancy, meaning larger electron concentration we can see lower volumes of the positron's presence.

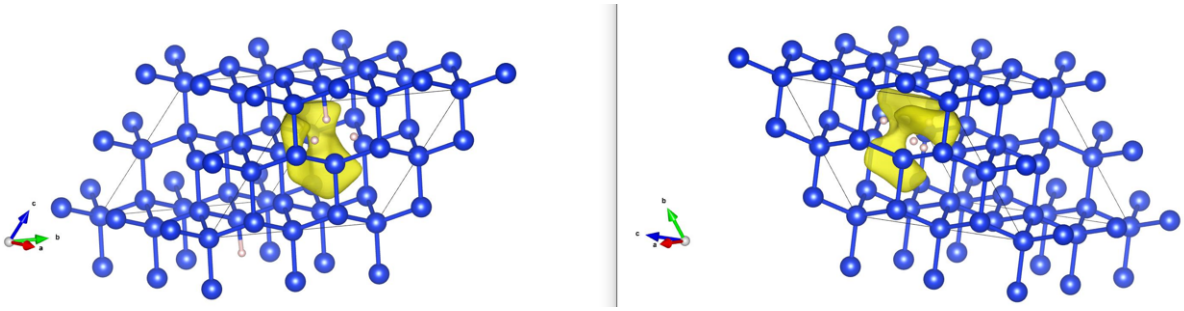

Figure 9: On the picture of the left we have the positron density distribution in the presence of 3 hydrogen atoms in a mono silicon vacancy. On the picture of the right we have the positron density distribution in the presence of 4 hydrogen atoms in a mono silicon vacancy.

4 Experimental results

At the presents moment only results from the computer modeling are available (Table 1).

Results for the positron lifetime in the different defects	
Type of defect	Result for the lifetime (ps)
Si perfect lattice	226 ps
Si with clear mono vacancy	255 ps
Si with one H in the vacancy	229 ps
Si with two H in the vacancy	225 ps
Si with three H in the vacancy	224 ps
Si with four H in the vacancy	219 ps

Table 1: Table of results for the computer modeling of the lifetime values for the different type of defects

The results correspond with the available theory. As expected the positron's lifetime has biggest value in a free electron space. Such low electron density space is when we have one clear Si vacancy in the lattice. Lowest positron lifetime we have in a perfect Si lattice, where the electron density is highest.

5 Conclusion

Positron lifetime is lower where it has a higher electron density. Investigating the calculated positron lifetime in various silicon lattice defects, we found the following dependencies:

- In the presence of point defects of the type of vacations and vacation clusters, an increase in the life of the position is seen to have taken place. This happens when the volume of the cluster increases and is an effect which is within standard limits.
- When hydrogen atoms are implanted to a vacancy cluster in a silicon vacancy, the positron lifetime decreases to values even lower than the perfect lattice. The localization of the positron wave function undergoes strong degeneracy and the positron density forms in areas where hydrogen atoms are not present (4 hydrogen atoms in one silicon vacancy).

After receiving the results from the experiment we will determine the type of defects we have caused from the Hydrogen implantation. Energies of formation are also expected to be examined via Doppler broadening measurements.

References

[1] Bich-Yen Nguyen, George Celler, and Carlos Mazuré. A review of soi technology and its applications. *Journal of Integrated Circuits and Systems*, 4(2):51–54, 2009.

[2] Alex Usenko. c12) united states patent.

[3] I Luka˘cevic. Quantum mechanics lecture 8: Relativistic quantum mechanics. *UJJS, Dept. of Physics, Osijek*, 2013.

[4] M Eldrup. Positron methods for the study of defects in bulk materials. *Le Journal de Physique IV*, 5(C1):C1–93, 1995.

[5] Aleksey A Sidorin, Igor Meshkov, E Ahmanova, M Eseev, A Kobets, V Lokhmatov, V Pavlov, A Rudakov, and S Yakovenko. Positron annihilation spectroscopy at lepta facility. In *Materials Science Forum*, volume 733, pages 322–325. Trans Tech Publ, 2013.

[6] Natasha Proctor and Richard Scalettar. Delocalization of quantum particles in a time-dependent potential.

[7] RM Nieminen and MJ Manninen. Positrons in imperfect solids: theory. In *Positrons in solids*, pages 145–195. Springer, 1979.

[8] Li Yu-Xiao Zhang Peng Jin Shuo-Xue Lu Er-Yang Yu Run-Sheng Wei Long Wang Bao-Yi Hu Yuan-Chao, Cao Xing-Zhong. Applications and progress of slow positron beam technique in the study of metal/alloy microdefects. 2015.

[9] J de Vries. Positron lifetime technique with applications in materials science. 1987.

[10] Robert G Parr. Density functional theory. *Annual Review of Physical Chemistry*, 34(1):631–656, 1983.

[11] Peter E Blöchl. Projector augmented-wave method. *Physical review B*, 50(24):17953, 1994.

[12] Aldo H Romero, Douglas C Allan, Bernard Amadon, Gabriel Antonius, Thomas Applencourt, Lucas Baguet, Jordan Bieder, François Bottin, Johann Bouchet, Eric Bousquet, et al. Abinit: Overview and focus on selected capabilities. *The Journal of chemical physics*, 152(12):124102, 2020.