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Absence of positronium formation in clean buried nanocavities in *p*-type silicon

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Buried nanocavities at about 350 nm depth in Si were produced by thermal treatment of He implanted *p*-type (100) Si. The internal surfaces of the nanocavities were found free of impurity decorations by examining the high-momentum part of the Doppler-broadened positron annihilation spectra. Positron lifetime measurements with a pulsed slow positron beam show neither a short lifetime (125–150 ps) ascribable to parapositronium nor a longer lifetime (2–4 ns) ascribable to pick-off annihilation of orthopositronium. The lifetime of positrons trapped into nanocavities was found to be about 500 ps. The absence of positronium formation could be explained by an insufficient electron density and a lack of electron states in the band gap at the nanocavities internal surfaces produced in the *p*-type silicon.

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Positron annihilation spectroscopy (PAS) is widely used to detect and characterize open volume defects with sizes ranging from single vacancy to nanocavities in both bulk and thin films of conductors, insulators and semiconductors.[1,2] Due to its importance for microelectronic industry, silicon is one among of the most studied materials. In particular the engineering of layer of nanocavities is of great technological interest in microelectronics. The presence of nanocavities can be detected by PAS from (a) a long positron lifetime and (b) a narrowing of the momentum distribution of the positron-electron annihilating pairs and, in some cases, from the formation of positronium (Ps). The possible Ps formation in voids in silicon was not deeply investigated although an answer is important both from a fundamental point of view as for the applied material science. The search of buried cavities in which a high fraction of positrons can form positronium is also of fundamental importance for the proposed Ps Bose condensation experiment.[3] In this paper we present a search of Ps formation in buried cavities in *p*-Si.

Ps, the hydrogenlike atom formed by an electron and a positron bound pair, exists in two different spin states: parapositronium *p*-Ps (singlet state, total spin 0, formation probability 1/4) and orthopositronium *o*-Ps (triplet state, total spin number 1, formation probability 3/4). In vacuum *p*-Ps decay into two gammas with a mean lifetime of 125 ps while *o*-Ps decay into three gammas with a mean lifetime of 140 ns. Bound positron-electron pairs can also form in insulators and at the surface of metals and semiconductors.[4,5] When Ps is formed in a solid its annihilation properties are influenced by the many-body interaction with the electrons of the medium.[6] The *p*-Ps lifetime can increase up to about 150 ps[7] and *o*-Ps can decay by pick-off annihilation into two gammas with a reduced lifetime down to few nanoseconds.[4] These variations can be easily measured by PALS (positron annihilation lifetime spectroscopy). *p*-Ps annihilation also produces a strong narrowing of the momentum distribution of the positron-electron annihilating pairs measured by Doppler broadening spectroscopy (DBS) or by angular correlation of annihilation radiation (ACAR) technique. *Para*-Ps manifests itself with a characteristic narrow peak around zero momentum in ACAR measurements whereas in DBS it would produce an increase in the S parameter (normalized values with respect bulk Si >1.1) calculated as the ratio of the counts in the central area of the 511 keV annihilation peak and the total area of the peak. In dense metals and semiconductors, diffusing thermal positrons at the surface can pick up an electron in the surface state and successively be emitted as Ps having a maximum energy, $\epsilon_{Ps}=-[(\phi_{+}+\phi_{-})-6.8]$ eV, where ϕ_{+} and ϕ_{-} are the positron and the electron work functions, respectively.[8] If $\epsilon_{Ps}>0$ no Ps is formed by thermal positrons but a Ps fraction can still be formed by the epithermal positrons reaching the surface.[9] These positrons are a small fraction of the positrons implanted in the material with an energy below 1.0 keV.[10] Theoretical calculations[8] predict that no escape of Ps from Si surface would be possible ($\epsilon_{Ps}=0.15$ eV) but two experiments[11,12] have shown emission of Ps from clean Si surfaces due to thermalized positrons. It was suggested that the apparent disagreement between experiment and theory can be due to the existence of surface electron states having energy eigenvalues in the band gap.[8,13] In bulk *a*-Si, Ps formation was observed by ACAR only in hydrogenated voids, with an average diameter of about 2 nm.[14] In several positron studies of microvoids in Si, large values of S parameter (>1.11)[15,16] and lifetimes >500 ps[17] were found and explained by the possibility of Ps formation inside the voids. Recently[18,19] ACAR distributions have been measured in *p*-Si samples with empty cavities and with cavities decorated either by implantation of H^{+} or by exposure to a D_2 ambient. After deconvolution, a narrow Gaussian (about 1.60 mrad FWHM) due to thermal *p*-Ps was clearly visible in the samples with hydrogen and deuterium decorated cavities. In sample containing empty cavities after deconvolution a Gaussian with 3.4[18] or 3.92[19] mrad FWHM was observed and attributed to about 10% of hot *p*-Ps formation,[18,19] and no three gammas *o*-Ps annihilations were observed by DBS.

In this deconvolution, the contribution due to positron annihilation at the surface was neglected, moreover the possible influence of a 1.37 T magnetic field, used to focus the positron beam on the sample, on the mixing of *o*-Ps and *p*-Ps spin states was not discussed or considered.[18]

From the experiments on clean Si surface[11,12] also Ps formation in Si clean buried cavities is expected. But, at present, the available data[18,19] do not give an exhaustive answer.

In our experiment for searching the Ps formation, we have employed three different positron annihilation techniques: DBS and coincidence DBS to characterize the internal surfaces of the cavities and PALS to detect short and long lifetimes due to the Ps formation. The characterization of the internal cavity surfaces is required to have a clear correlation between surface conditions and Ps formation. DBS measurements were performed to obtain the parameters needed for the deconvolution of the coincidence-DBS measurements. PALS was chosen because it is the only technique that can give simultaneous evidence of Ps formation decaying as *p*-Ps and *o*-Ps. For DBS and coincidence-DBS a continuous slow energy positron beam tunable from 0.05 to 25 keV was used (details in Ref. 21). For coincidence-DBS we employed two Canberra low-noise high purity germanium detectors 45% efficiency, 1.4 keV resolution at 511 keV, with a peak to Compton ratio of 72:1, in a 180° configuration 3.5 cm from the samples. PALS was performed with a pulsed slow energy positron beam (tunable from 0.5–18 keV) with a total time resolution (pulsing plus detector system) of 230–250 ps (details in Ref. 22).

To obtain buried cavities we proceeded as follows. High purity *p*-type (100) silicon wafers (1.7–2.5 Ω cm), Czochralski-grown, were implanted at room temperature with He^+ ions at 40 keV (He projected range 350 nm) with a dose of 8×10^{16} ions/cm^{-2}. The density of the beam current was about 8 $\mu A\ cm^{-2}$ and the sample holder, kept near room temperature, was tilted by 7° to reduce channeling effects. Successively the samples 1 cm × 1 cm size were heated for 2 h in vacuum at 800 °C. A complex process involving He and vacancies produces He agglomeration (bubbles formation), He out diffusion and finally formation of cavities with the characteristics faceting.[20] Characterization with TEM (transmission electron microscopy) reveals a layer of cavities between 300 nm and 530 nm depth. In this layer the largest cavities have sizes up to 25–30 nm. Few and smaller (3–5 nm) cavities are randomly distributed from the surface up to 300 nm.

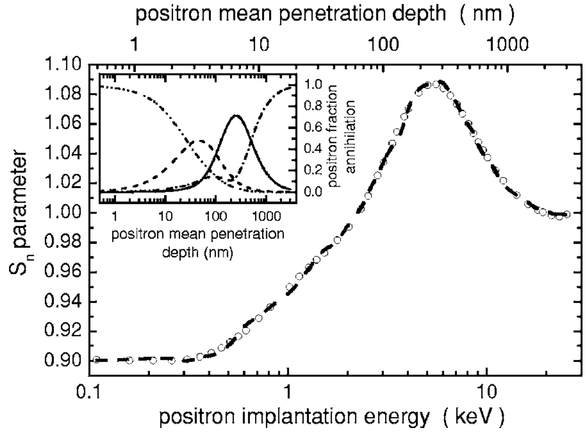

FIG. 1. S_n parameter versus positron implantation energy (lower axis) and mean positron implantation depth (upper axis). The dashed line is the best fit with a model base on the diffusion equation. In the inset the positron annihilation probabilities f extracted by the diffusion model are reported as a function of the mean positron implantation depth: f_s at the surface (dash dot dot); f_{d1} in decorated defect near surface (dash); f_{d2} in cavities (full line); f_b in bulk (dash dot).

In Fig. 1 the depth profile DBS spectrum is shown. The normalized $S_n = S/S_{Si}$ parameter (energy window: $|511\ \text{keV}-E_\gamma| < 0.85$ keV for the central area and $|511\ \text{keV}-E_\gamma| < 4.25$ keV for the total peak area, where E_γ is the energy of the detected gamma ray) is plotted as a function of positron implantation energy. The error on the measured S is 0.001 (more than 2×10^5 counts in the peak). The S_n curve was fitted with a model based on the solution of the stationary diffusion equation.[20,23] In this model the S_n parameter is expressed as a linear combination: $S_n(E) = S_s f_s(E) + S_b f_b(E) + \Sigma S_{di} f_{di}(E)$, where $f_s(E), f_b(E), f_{di}(E)$ are the positron annihilation probabilities at the surface, in the bulk, and in the different defect type i, respectively. S_s, S_b, S_{di} are the characteristic values of S_n for positron annihilating at the surface, in the bulks and in the different defect types i, respectively. The fractions $f_i(E)$ are found by solving the diffusion equation, knowing the positron implantation profile and giving, as an input, the guess functions for the defect distributions. Here, we only report the results of the analysis. Details of the procedure can be found in Refs. 20 and 23. The best fit was obtained assuming two different defect profiles with $S_{d1} = 1.023$ and $S_{d2} = 1.12$. The first defect profile, the derivative of a Gaussian, is centered at $\langle d \rangle = 33$ nm. It describes decorated defects very close to the surface. The second one is a Gaussian centered at $\langle d \rangle = 300$ nm and of a width (four times the standard deviation) of 200 nm, and is mainly due to the buried cavity layer. However, the center of this distribution is shifted towards the top of the cavity layer because it includes also the smaller cavities and vacancy agglomerates present from the surface of the sample down to the cavity layer which are sampled by positrons. TEM resolution does not permit us to observe the decorated defects revealed by positrons, corresponding to the first distribution with $S_{d1} = 1.023$.

The effective diffusion length that takes into account the presence of surface field,[24,25] was found to be 100 nm from fitting a nonimplanted sample. The fractions f, as obtained by the fitting procedure, of positron reaching the surface (f_s), annihilating into the bulk (f_b) and trapped into the first (f_{d1}) and second (f_{d2}) defect profile are reported as a function of the positron implantation energy in the inset of Fig. 1. The effective diffusion length must be evaluated carefully, because it affects the extracted values of the fractions $f_i(E)$ needed to deconvolve the coincidence-DBS measurements. In this case, due to the high trapping rate of the defects, we have checked that increasing the diffusion length by more than 50%, the values of the fractions change less than 5%. This change does not affect the results reported below.

Voids and cavities in silicon could be efficient gettering centers for impurities like heavy metals and oxygen. To

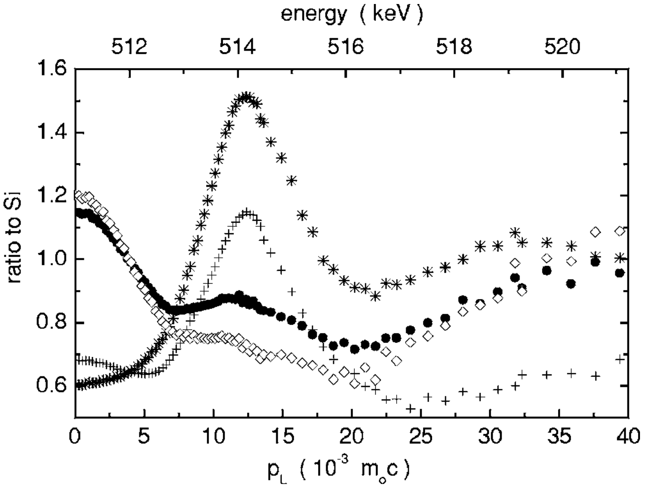

FIG. 2. Ratio curves to bulk Si. Ratio curve of the 511 keV annihilation line as measured at 5.5 keV (full dots). Characteristic ratio curves C_s, C_{d1}, C_{d2} of surface (stars), defect close to the surface (plus), cavity (open diamond), respectively. The curves of the surface (stars) and defect close to the surface (plus) have been reduced by a factor of 1.5.

probe the internal surfaces of the cavities, that usually are believed to be pristine surfaces when produced with the above procedure, we have employed the coincidence-DBS technique. Decoration of open volumes are evidenced by peaks or bumps in ratio curves constructed as the ratio between the 511 keV annihilation line measured in the sample under investigation and a reference 511 keV annihilation line measured in bulk Si.[26,27] In this experiment, the 511 keV annihilation line was measured for several positron implantation energies with two germanium detector in coincidence. For each energy about 1×10^7 counts were acquired.

In the case of depth profiling, a 511 keV annihilation line $C_E(E_\gamma)$ measured at a particular positron implantation energy E (depth) is due to the linear combination of different contribution coming from the different positron annihilation states. In our case, $C_E(E_\gamma)=f_s(E)C_s(E_\gamma)+f_b(E)C_b(E_\gamma)+f_{d1}(E)C_{d1}(E_\gamma)+f_{d2}(E)C_{d2}(E_\gamma)$, where C_s, C_{d1}, C_{d2}, and C_b are the characteristic Doppler lines of positron annihilating at the surface in the two defect types (superficial defects and cavities) and in the bulk. The characteristic Doppler lines are independent from the positron implantation energy and can be used to reconstruct every $C_E(E_\gamma)$ by knowing the $f(E)$. The annihilation probability are known from fitting the S_n vs E curve (Fig. 1 and inset). The characteristic C_s, C_{d1}, C_{d2}, C_b lines are found by measuring C_E at four positron implantation energies and solving the system. In Fig. 2 the ratio curves C_E/C_b for E=5.5 keV (the position of the maximum of S_n curve) is shown (full dots). In the same figure, the characteristic ratio curves of the surface C_s/C_b (SiO_2 layer), of the defects close to the surface C_{d1}/C_b , and of the cavity C_{d2}/C_b, that reconstruct the C_E/C_b curve are reported. A variable average smoothing was applied to the ratio curves starting from E_γ=515 keV. The spectra have been normalized to unity. The characteristic ratio curve for cavity (open diamond in Fig. 2) has a shape typical of a cavity with clean surface, i.e., without any decoration.[26,28] As a by-product we can note that the peak near 514 keV of the C_{d1} curve, indicates that the superficial defects are oxygen decorated.[27]

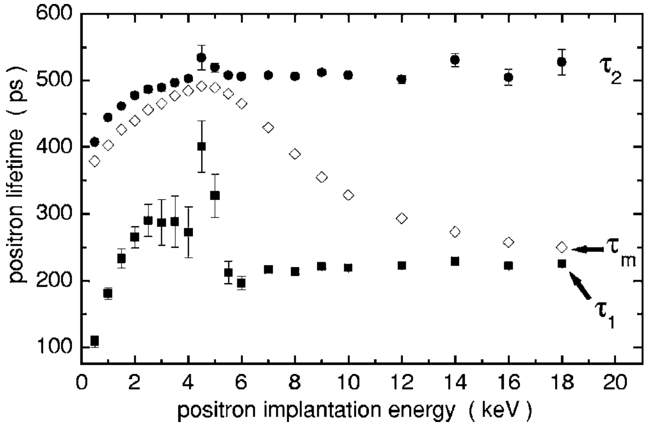

FIG. 3. Positron lifetimes as a function of positron implantation energy.

The results obtained by the analysis of the lifetime spectra are reported in Figs. 3 and 4. As an example, the inset of Fig. 4 shows a lifetime spectrum at 5.5 keV implantation energy. Note the very good peak to background ratio (3000:1) and the absence of disturbing side peaks. The lifetime spectra as a function of positron implantation energy have been analyzed by a modified version of PATFIT.[29] The mean lifetime τ_m increases from 380 ps at 0.5 keV to 500 ps at 4.5 keV, and decreases to 250 ps at 18 keV (Fig. 3) implantation energy. Perfect fits to the lifetime spectra are obtained with only two lifetimes (τ_1, I_1 and τ_2, I_2). No long tails and corresponding long lifetimes due to pick-off of *o*-Ps are observed (Fig. 3 and inset of Fig. 4). At the lowest implantation energies the lifetime τ_1 is very short ($\sim$100 ps, $I_1 \cong 10\%$) corresponding to a positron bulk lifetime reduced by the surface acting as a sink for the freely diffusing positrons. At an implantation energy of 3 keV τ_1 assumes its maximum value of 300 ps characteristic for positrons trapped into open volumes with a divacancy character.[2] At higher implantation energies it decreases to the bulk value of pure Si. τ_2 starts from a surface lifetime value of 400 ps (positrons trapped at the SiO_2 native oxide layer at the surface) and increases up to 500 ps at implantation energies higher than 4 keV.

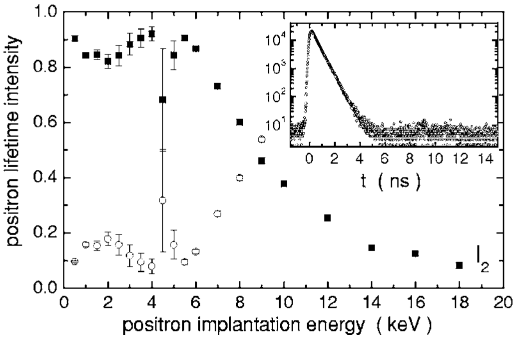

FIG. 4. Intensity of positron lifetimes of Fig. 3. Inset: lifetime spectrum as measured at 5.5 keV. Please note the high peak-to-background ratio and the clear absence of any lifetime beyond 0.5 ns.

Figures 3 and 4 show that, when the fraction of positron annihilating in cavities increases, τ_1 and τ_2 (and I_1 and I_2) are less distinguishable, i.e., mixed, because of the distribution of cavity sizes.

Also the observation of 10% of hot *p*-Ps formation in buried cavities[18,19] is not confirmed by our measurements, because careful tests have imposed an upper limit of 2% for the intensity of the *p*-Ps lifetime of 125 ps, not to mention the three times more of *o*-Ps pick-off annihilation with a lifetime of a few nanoseconds. This was not observed. We underline that with PALS technique, if Ps had be formed, we would have detected it, be it from epithermal as well as from thermal positrons.

Analysis of external clean Si surfaces, examined by scanning tunneling microscopy, direct and inverse photoemission,[30] reveals electronic states in the band gap associated with dangling orbitals occupied by zero, one or two electrons. The different possible reconstructions of the silicon surface can narrow or even remove the band gap.[30] Although there are no detailed experiments and calculations, Ps formation from thermal positrons and surface electrons is expected to be strongly influenced by the external surface states. Clear evidences are reported when the surface is modified by adsorbates: for example the Ps yield increases when hydrogen is adsorbed on clean Si surface.[12]

Electrical properties of buried cavities produced by He implantation in *p*-type and *n*-type Si, were measured by conductivity, capacitance versus voltage, deep-level transient spectroscopy (DLTS) techniques, and the presence of dangling bonds on internal surfaces was supported by electron paramagnetic resonance (EPR).[31] Like at the external surfaces, at the internal surface of cavities the dangling bonds have been found to present an ambipolar character: they can possess positive (donorlike) or negative (acceptorlike) charge states which introduce deep levels in the band gap. Differently from the external surfaces, at the internal surfaces of cavities the charge states can be more limited from the strong Coulomb interaction among dangling bonds. It was found that in *n*-type Si the cavities are negatively charged (trap electrons) while in *p*-type Si both signs of carriers (holes and electrons) are trapped but with a predominance of populated positive states.[31]

From the above consideration we propose that the observed absence of Ps formation in the studied samples could be due to the lack of negative populated states at the surface of the cavities. Boron doping is the probable responsible of the formation of the unoccupied states. Studies on boron adsorbed on Si external surfaces have shown that acceptor boron located underneath the surface extracts the electrons from the dangling bond orbitals.[30]

If the above hypothesis is correct, Ps formation would be more favored in cavities produced in *n*-type materials. In pure Si it would depend on the type of reconstructed internal surface of cavities that probably is also related to their size. Comparative measurements searching Ps formation in *n*-type, *p*-type, and pure Si buried cavities will be interesting and clarifying.

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