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ABSTRACT

Optical (VIS photoluminescence, photoluminescence decay, IR absorption) measurements on Czochralski-grown silicon, subjected to several thermal treatments are presented. These data are supplemented by positron annihilation techniques (lifetime, Doppler broadening). We report also some preliminary positron-annihilation data on these films of Si-related, low-ε materials.
Keywords: positron annihilation, photoluminescence, Czochralski grown silicon, MSSQ

1 INTRODUCTION

Some of many tasks of contemporary semiconductor technology are: i) the search for visible emission from silicon monocrystals; ii) search of material with very low dielectric constant (close to ε=1), in order to increase the speed of processing signals in ultra-high integration-scale circuits. One of the solutions to the latter subjects is to introduce open spaces in the silicon-based material. Therefore, a precise, non-destructive characterization of porosity in microelectronics is required. This task has also applications in biotechnology research, aiming to improve the quality of penetration barriers and selective filtration membranes.

Pure silicon due to its characteristically configuration of electronic bands have very low effective visible photoluminescence at 1.1 eV band. Some silicon based materials have more effective photoluminescence effects, ex. porous silicon [1], polycrystalline films [2] and SiO_2 films [3]. In our previous work [4] a new way of obtaining photoluminescence from silicon monocrystal was presented. The positron annihilation spectroscopy which allows to determine kind of microdefects in monocrystal structure and chemical surrounding of the defects [5] is very useful in studies the physical effects behind these phenomena.

2 EXPERIMENTAL

2.1 Optical studies

Continous photoluminescence spectra were excited with using continous wave 488 nm line of Ar-ion laser with $10 W/cm^2$ power and recorded by a SPEX double spectrometer interfaced with RCS 31034A02 photomultipiler.

Time resolved spectra have been obtained at 80 K using 410 nm line of a frequency-doubled $Ti:Al_2O_3$ laser operating at a repetition rate of 4 MHz yielding 1.5 ps long excitation pulses with a peak power density of 500 Wcm^{-2} . A streak camera model C4334 Hamamatsu was used as a detector. IR absorption was studied using SPECORD 71 IR.

2.2 Positron annihilation

Three positron-annihilation techniques were used for present measurements. Silicon samples, modified in bulk, were studied using lifetime technique and Doppler-coincidence technique in bulk. The low-ε films were studied by depth-resolving Doppler broadening technique using a monoenergetic positron beam [6].

In Doppler techniques the S-parameter (annihilations with electrons of low moment) characterizes the shape of the 511 keV annihilation line. An increase of this parameter shows that positrons annihilate in some, open-volume defects. The V-parameter indicates the fraction of positrons that form o-Ps and annihilate in 3γ; formation of o-Ps is possible in presence of "large" cavities, therefore indicating presence of nano-pores.

In beam measurements the medium implantation depth for positrons with E kinetic energy was calculated with using of the following formula [7]:

$$x = (A/\rho)\,[E(\mathrm{keV})]^n,$$

where ρ is a density in [g/cm^3] and, A = 400 and n=1.6 are constants.

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An improvement of Doppler technique, based on coincidence technique [5] allows reducing the high-energy tail of the γ spectrum and in this way to determine the "chemical environment" of the defect. Our lifetime technique uses a fast-fast coincidence system with Hamamatsu R2083Q photomultipliers and BaF_2 scintillators. ^{22}Na sodium source deposited on kapton foil is used as the positron source. The time resolution of the apparatus is 160 ps (FWHM).

3 SAMPLES

Two kinds of materials has been chosen for present studies

- Czochralski grown silicon containing high amounts of interstitial oxygen (1.1×10^{18} cm^{-3}). The thermal treatment consists of one or two preannealing stages at 450°C and 650°C for 20 h and the annealing step at 950-1150°C with an auxiliary use of a high hydrostatic pressure [8]. This type of annealing leads to a massive oxygen precipitation (up to 85%) and creation of different oxygen-related defects, as seen in IR studies. We studied samples with the whole annealing cycle and some of them, treated only in a single or a double step.
- MSSQ (methylsilsesquioxanes) SiCOH layer (3400 Å) deposited on silicon substrate treated in N_2 (400 °C, 30 min) and then treated in N_2 plasma (450 °C - 900 °C for 30 min in vacuum) in order to seal the pores. The dielectric constants of the dielectric layer is ε =2.9.

4 RESULTS

4.1 Photoluminescence spectra of Cz-silicon

The spectral distribution of photoluminescence at 80 K for three selected samples show some differences due to the specific thermal treatment. Sample No 5 was treated at (650°C/20h + 1050 °C/20h), sample 7 at a single step (725°C/20h) and sample 8 at (725 °C/20 h + 900 °C/5h in 10 kbar hydrostatic pressure) cycle.

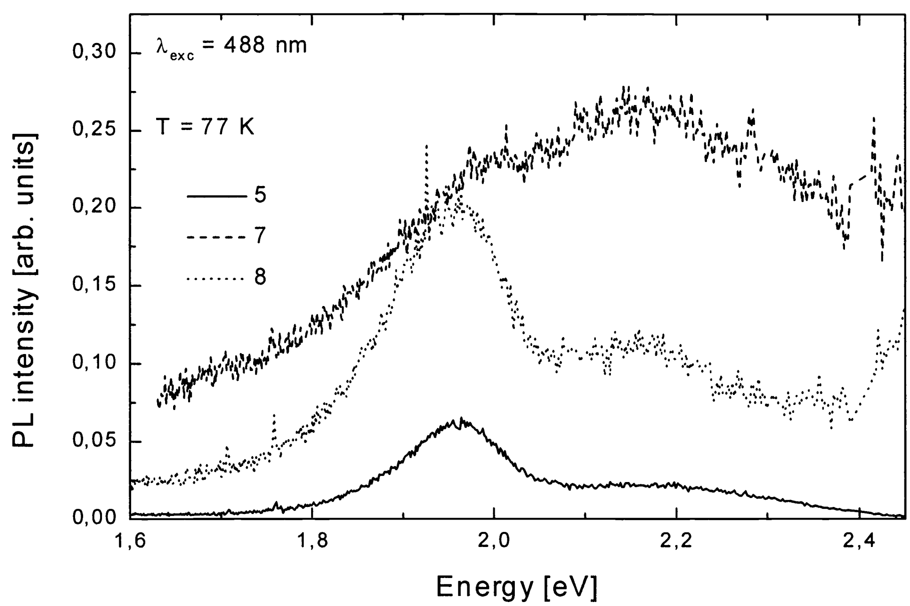

Figure 1: Photoluminescence spectra of the samples excitated by Ar-ion laser at 488 nm vawelenght.

In all samples, two peaks can be distingiushed, one narrower (0.1 eV at FWHM) centered at about 1.95 eV and second, a broad one (0.3 eV at FHWM) centered at about 2.2 eV. In samples No. 7 and No. 8 the intensity of both peaks rises, but the second one becames more visible, overlapping even with the first peak in sample No. 7. This can indicate existence of two kinds of light emitting defects, which are growing with thermal treatment of the samples.

Each sample has its specific decay time and intensity of photoluminescence. Decay of the photoluminescence of the sample No. 5 is the shortest (about 4 µs) in comparison to other samples. Sample No. 7 has the highest intensity of photoluminescence and, seems, two distinct lifetimes of the PL decay. The decay time of sample No. 8 is the longest.

In spite of these differences, rather short decay times in all samples suggest that photoluminescence originates from defects in the Si or SiO_2 phases. Positron data are used to shed some more light on this question.

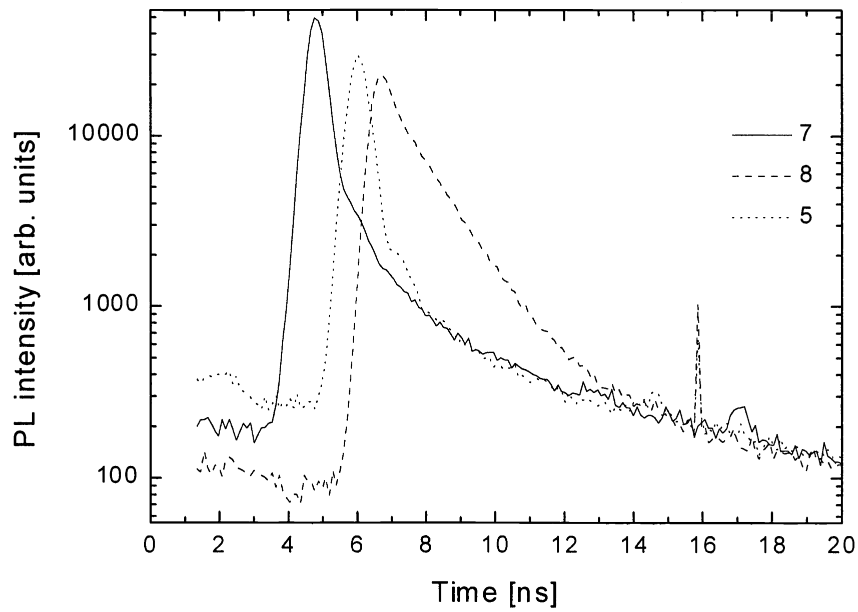

Figure. 2: PL decay spectra for the Cz-Si samples. Note that the position of the start signal is shifted, for clarity reasons.

4.2 Positron lifetimes and coincidence spectra in Cz-silicon

Measurements on almost 50 Cz-Si samples subjected to different treatments showed that these treatments usually cause a rise of the positron lifetime, from 220-221 typical for low O-contents silicon up to 227 ps in some samples, with the whole thermal cycle. Furthermore, in samples treated under high pressure we notice another, longer (about 500 ps) lifetime, indicating large open volumes, like vacancy clusters or extended dislocations.

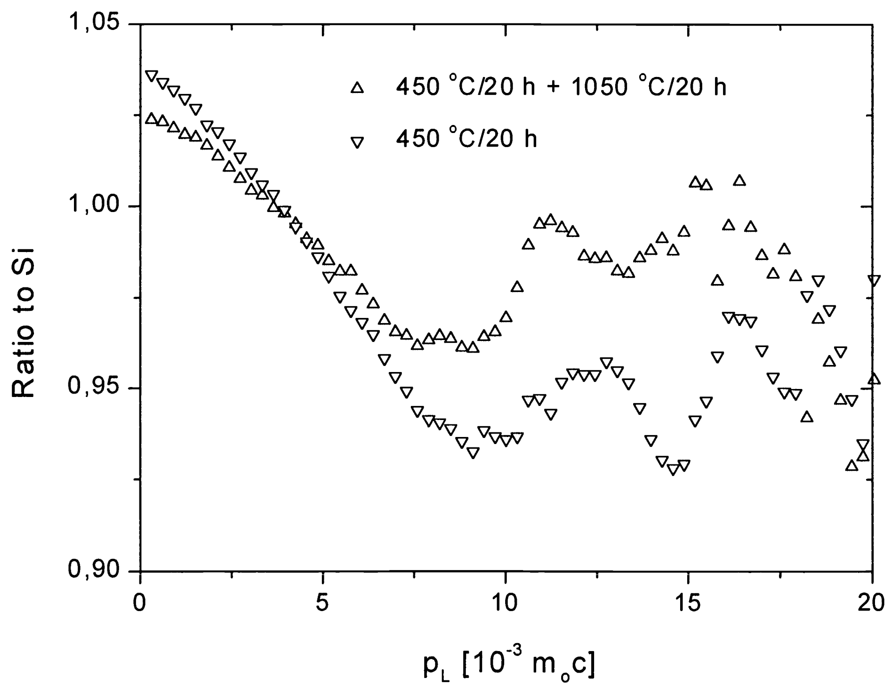

Figure 3: Doppler coincidence curves of Cz-Si. A peak rising at about $12\times10^{-3}m_0c$ units is typical for oxygen near-to-defects.

Positron coincidence measurements show that specific thermal treatment causes increase or dissolution of the oxygen precipitates in Cz-Si monocrystals (Fig. 3): a specific peak, which can be attributed to oxygen at „near-to-defects", appears. Single treating in temperature range 450 °C – 650 °C causes dissolution of the native as grown oxygen precipitates. Further annealing in temperature 1050 °C causes slight increase of precipitated oxygen. This can be visible also in the PL spectra, where intensity is lower for the sample with second annealing in 1050 °C.

4.3 SiCOH film

Beam measurement allow to distinguish clearly three layers in as-deposited films, see Fig. 4a,b:
1° a layer to approximately 20 nm much homogenous one and without cavities,
2° a layer from about 20 nm until to the interface with the silicon that introduces cavity. These cavities are evidenced by the rise of the S parameter value in Fig.4a and by the formation of the o-Ps peak in the V-parameter, see Fig. 4b.
3° a third layer is the substrate silicon (S parameter has been normalized to S=1).
A signal of o-Ps seen at in Fig. 4b is connected to o-Ps formed in surface (interface with the empty one) from the positron dissemination towards the same surface.
Thermal treatments of samples show collapsing of the inner cavities, starting from 450°C. This is evidenced by lowering of the value of S with the heat treatments (Fig. 4a) and the disappearing the signal of the formation of o-Ps (Fig. 4b). A strange reversal of the signal can be noted between the 450 °C and 500 °C; it is not to be excluded that some degassing of the samples takes place in this range of temperatures. At 600 °C we observe a clear decrease of the dimensions of the cavities and they number, the same as at 800°C and 900 °C: the material is collapsing even if some remains of cavities are still visible in Fig. 4b.
In additional studies we checked for ageing of the samples. After approximately 40 days two as-deposited samples have been re-measured. They shown a significant reduction of the positron signal, correlated to filling of the porosity by air gases (probably water vapor and/or nitrogen). After the thermal treatment at 400 °C, 48 h under vacuum the positron signal returns to its initial value demonstrating a desorbtion of the intrapolated gases.

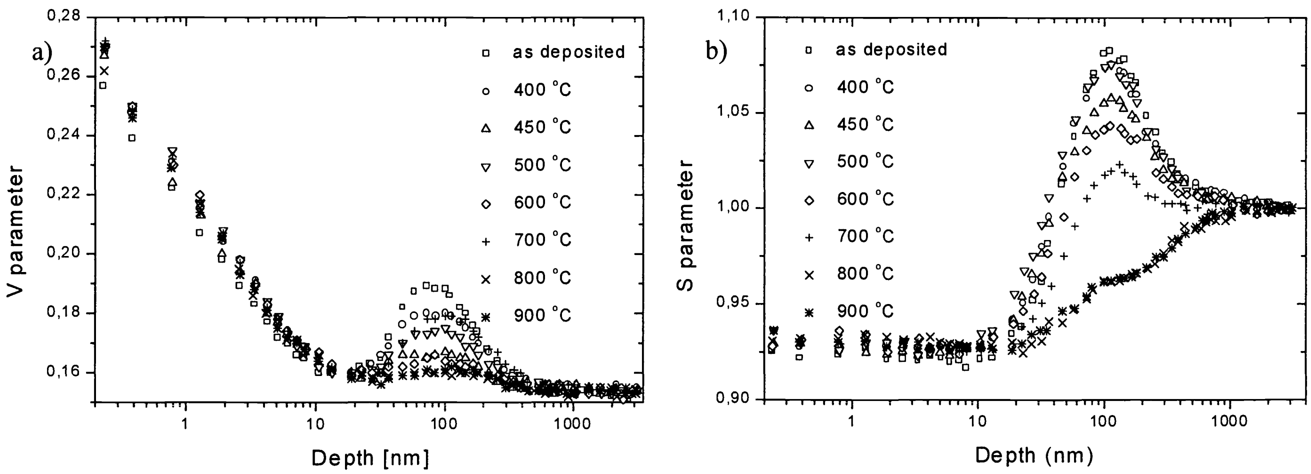

Figure 4: a) S-parameter for different thermal treatments of the samples b) V-parameter vs. thermal treatments of the samples.

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