SILICON HYPERDOPED WITH SELENIUM FOR BROAD BAND INFRARED PHOTODETECTORS AND SOLAR CELLS

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Abstract. In this work, we present the formation of silicon layers hyperdoped with selenium through Se implantation followed by pulsed laser annealing. The concentration depth distribution of Se atoms was investigated by Rutherford backscattering. The crystallinity of the doped silicon layer and the fraction of Se atoms in Si lattice sites were determined using backscattering yield analysis. Experimental and theoretical sub-band properties were compared and discussed. Notably, a significant increase in light absorption across a wide spectral region (0.2–23.0 μm) was observed, demonstrating the potential of selenium hyperdoping for enhancing infrared absorption in silicon.
Key words: silicon, hyperdoping, selenium implantation, laser annealing, impurity sub-band.

СЛОИ КРЕМНИЯ, ГИПЕРДОПИРОВАННЫЕ СЕЛЕНОМ, ДЛЯ ШИРОКОДИАПАЗОННЫХ ИК-ФОТОДЕТЕКТОРОВ И СОЛНЕЧЫХ БАТАРЕЙ

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Аннотация. В этой работе мы представляем формирование слоев кремния, гипердопированных селеном, путем имплантации Se с последующим импульсным лазерным отжигом. Распределение концентрации атомов Se по глубине было исследовано методом обратного Резерфордовского рассеяния. Кристалличность легированного слоя кремния и доля атомов Se в узлах решетки Si были определены с помощью анализа выхода рассеянных ионов гелия в режиме каналирования их. Были сравнены и обсуждены экспериментальные и теоретические характеристики подзоны в запрещенной зоне Si. Примечательно, что наблюдалось значительное увеличение поглощения света в широкой области спектра (0,2–23,0 мкм), демонстрирующее потенциал гипердопирования селеном для усиления поглощения инфракрасного излучения кремнием.
Ключевые слова: кремний, гипердопирование, имплантация селена, лазерный отжиг, примесная подзона.

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Introduction. In recent years, number of the world's leading micro- and optoelectronic laboratories have been working to develop high performance photodetectors and light emitting devices in the near (NIR) and mid-IR(MIR) regions, silicon waveguides and modulators whose fabrication will allow electronic and optoelectronic devices to be integrated in a single integrated circuit. But due to the large band gap of silicon (1.12 eV), for the wavelength longer than 1.1 μm, optical and electrical performance of silicon drops sharply. Extending the sensitivity of silicon-based and silicon technology-compatible photodetectors and solar cells to the IR range is therefore an active area of research.

It has been established that the highest absorption coefficient ($\sim 10^4$ cm^{-1}) in the IR spectral range (up to ~ 3 μm) is registered for single-crystalline silicon hyperdoped with chalcogen atoms (S, Se, Te). The equilibrium chalcogen solubility in silicon is $\sim 10^{16}$–10^{17} cm^{-3}. If the impurity concentration exceeds the equilibrium solubility limit by 3–4 orders of magnitude, the impurity levels form an impurity sub-band. Then, photon absorption through electron transitions "valence band – impurity sub-band" and "impurity sub-band – conduction band" becomes possible. Impurity doping level higher than the equilibrium threshold can be achieved by non-equilibrium

techniques such as ion implantation followed by femto-, pico-, and nanosecond laser pulses.

Experimental. Silicon (111) *p*-type double-side polished wafers were implanted with 140 keV $^{80}Se^+$ ions to the fluences of $3.1 \cdot 10^{15}$ (Se (0.75 %)/Si) and $6.1 \cdot 10^{15}$ (Se (1.5 %)/Si) ions/cm². Pulsed laser irradiation of the implanted samples was initiated by a ruby laser pulse ($\lambda = 694$ nm, FWHM = 70 ns) with a uniform pulse energy distribution along the area with a diameter of 4 mm. The energy density W in the laser pulse was set as 2 J/cm². Se concentration depth distribution profiles, fraction of impurities at lattice sites and Si crystallinity of the implanted and annealed samples were analyzed by Rutherford backscattering spectroscopy in combination with the channeling technique (RBS/C) using 1.4 MeV He⁺ ions. The optical properties in the NIR spectral range were investigated through measurements of the transmittance and specular reflectance spectra using the Lambda 1050 UV/Vis/NIR spectrometer. The specular reflectance spectra were measured at an 8° incident angle using a Universal Reflectance Accessory with an accuracy of 0.1 %. The optical properties in the MIR range were studied by Fourier Transform Infrared Spectroscopy (FTIR) in the transmittance and reflectance mode using a Perkin Elmer Spectrum 3 Optica FTIR spectrophotometer.

Results and discussion. Pulsed laser melting leads to a considerable redistribution of the implanted impurity toward the surface and into the bulk (200–250 nm) with the formation of a decreasing plateau with the average Se concentration nearly $7.5 \cdot 10^{19}$–$1.0 \cdot 10^{20}$ cm⁻³ and $1.1 \cdot 10^{20}$–$1.5 \cdot 10^{20}$ cm⁻³ for the ion fluences of $3.1 \cdot 10^{15}$ and $6.1 \cdot 10^{15}$ ions/cm², respectively and accumulation of impurity in the near-surface layer of around 10–20 nm thickness. As a result, a thin layer of accumulated selenium (~1–3 % of the total number of implanted atoms) formed in the near-surface region of the Si sample (Figure 1).
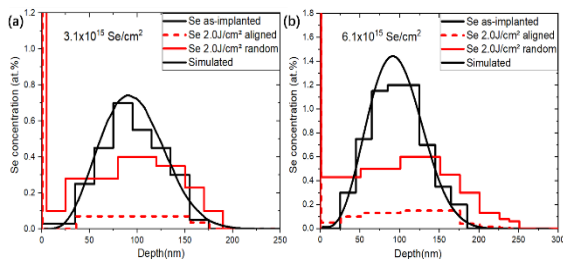

Figure 1 – Depth distribution of Se concentration measured in random and channeling regimes on the samples implanted with the fluence of $3.1 \cdot 10^{15}$ cm⁻² (*a*) and $6.1 \cdot 10^{15}$ cm⁻² (*b*)

The degree of crystallinity f_{cr} of the laser annealed layer was calculated by the formula from Ref. [1]:

$$f_{cr} = \frac{1-\chi^{Si}}{1-\chi_{min}}, \qquad (1)$$

$$f_{cr} = \frac{1-\chi^{Se}}{1-\chi_{min}}. \qquad (2)$$

Table 1. The degree of crystallinity of silicon layer (f_{cr}) and the fraction of impurity at lattice sites after implantation of selenium ions and laser annealing $W = 2$ J/cm²

Se ion fluence (cm⁻²)	$f_{cr} =$ $(1-\chi^{Si})/$ $(1-\chi_{min})$, %	Se yield in random case (Se/cm²)	Se yield in aligned case (Se/cm²)	Se fraction in the lattice sites, %
$3.1 \cdot 10^{15}$	93.6	$3.05 \cdot 10^{15}$	$0.86 \cdot 10^{15}$	72.0
$6.1 \cdot 10^{15}$	91.9	$5.46 \cdot 10^{15}$	$1.66 \cdot 10^{15}$	69.6

For the used ion fluences, the lattice incorporation given in Table 1 is relatively low and stems from the trailing edge of the profiles. This suggests some incorporation of Se at the interface area between the implanted layer and underlying crystalline substrate as well as a higher incorporation of Se atoms at the Si lattice sites in the near-surface region. The sensitivity of the RBS method is about 0.01 at. %. The energy density of $W = 2$ J/cm² was found to be optimal in terms of achieving structural perfection (greater than 91 %) and maximizing the concentration of Se at lattice sites (greater than 69 %).
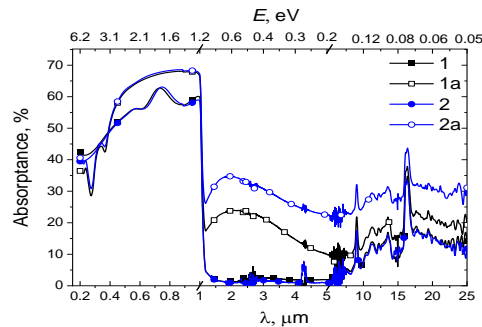

Figure 2 – Absorptance spectra of samples with the Se concentration of 0.75 % (*1*, *1a*) and 1.5 % (*2*, *2a*): before (*1*, *2*) and after PLA (*1a*, *2a*).

Conclusion. The obtained NIR and MIR absorptance spectra (Figure 2) indicate the formation of a sub-band in silicon. The PLA results in an increase of absorption by about 15–17 times in the NIR range. These data also show the increase of absorption after PLA in the MIR range. This indicates the existence of transitions between the formed sub-band and the conduction band of silicon. Before annealing, the implanted layers exhibit a weak absorption after the fundamental absorption edge (1.1 µm). PLA leads to the formation of a wide absorption band in the range of 1–5 µm with a maximum at 2 µm (0.6 eV), which correlates with the activation energy of the Se deep donor level in Si ($E_c - 0.593$ eV) [2].

Referents

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