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Structural and electrical properties of Se-hyperdoped Si via ion implantation and flash lamp annealing

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ABSTRACT

We report on the hyperdoping of silicon with selenium obtained by ion implantation followed by flash lamp annealing. It is shown that the degree of crystalline lattice recovery of the implanted layers and the Se substitutional fraction depend on the pulse duration and energy density of the flash. While the annealing at low energy densities leads to an incomplete recrystallization, annealing at high energy densities results in a decrease of the substitutional fraction of impurities. The electrical properties of the implanted layers are well-correlated with the structural properties resulting from different annealing processing.

1. Introduction

Silicon hyperdoped with chalcogens with the doping concentration far exceeding the solid solubility limits has recently gained much attention due to its unique optical and electrical properties. This new class of materials is obtained by introducing chalcogens into Si at concentrations far above the solid solubility limit, which gives rise to the formation of an impurity band (IB). This fact allows for a strong subband photoresponse [1,2] and an insulator-to-metal transition [3,4]. Such properties can be used for developing intermediate band solar cells [5–7] and infrared photodiodes [8–10]. However, the formation of the IB in Si with chalcogens is very challenging due to the following reasons: (1) The solid solubility of chalcogens such as S and Se in Si are lower than $10^{16}\,cm^{-3}$ [11], which is far below the Mott limit of $\sim 5.9 \times 10^{19}\,cm^{-3}$ [12] and (2) chalcogens have a large diffusion coefficients in Si [13], resulting in the redistribution and segregation of impurities on the sample surface. Ion implantation followed by either pulsed laser annealing (PLA) or flash lamp annealing (FLA) is known as non-equilibrium method to introduce impurity into the semiconductors well above the solubility limit. The resulting hyperdoped materials formed by ion implantation and pulsed laser annealing show an insulator-to-metal transition, which provides a powerful proof for the formation of IB in Si [3,4,14].

In this paper, we present the structural and electrical properties of Si hyperdoped with Se by ion implantation and FLA. The millisecond time duration of FLA induces a solid phase epitaxy of the implanted layer and the incorporation of Se into Si lattice sites. The structural properties of the Se-hyperdoped Si layers are investigated by Raman spectroscopy and Rutherford backscattering spectrometry/channeling (RBS/C). A correlation between the structural and the electrical properties under different annealing processes is established.

2. Experimental

Semi-insulating Si (001) wafers with a thickness of 525 μm, (resistivity larger than $10^4\ \Omega$ cm; single-side polished) were implanted at energy of 60 keV with Se ions at a fluence (Φ) of $5 \times 10^{15}\,cm^{-2}$ at room temperature, which results in a Se peak concentration (c_{pk}) of $1.3 \times 10^{21}\,cm^{-3}$, c_{pk} is calculated by the following equation: $c_{pk} = \frac{\Phi}{\sqrt{2\pi}\Delta R_P}$, where ΔR_P is the longitudinal straggle [4,15]. The depth profile of selenium in Si after FLA or PLA was calculated from RBS spectra [16]. The profile of selenium in FLA samples is in a reasonable agreement with Stopping and Range of Ions in Matter (SRIM) simulation. Subsequent FLA [17,18] was performed to recrystallize the amorphous layers after implantation. The as-implanted samples were annealed with pulse durations of 1.3, 3 or 20 ms. Right prior to the flash, the samples were preheated up to 400 °C for 30 s. The preheating prior the FLA process was used to reduce the temperature gradient in the sample during ms-range pulse annealing. The estimated peak temperatures at the sample surface were in the range from 1100 °C to 1200 °C. The optimized annealing energy densities for 1.3, 3, and 20 ms were 20, 27, and 36 J/cm^2, respectively. We optimized annealing

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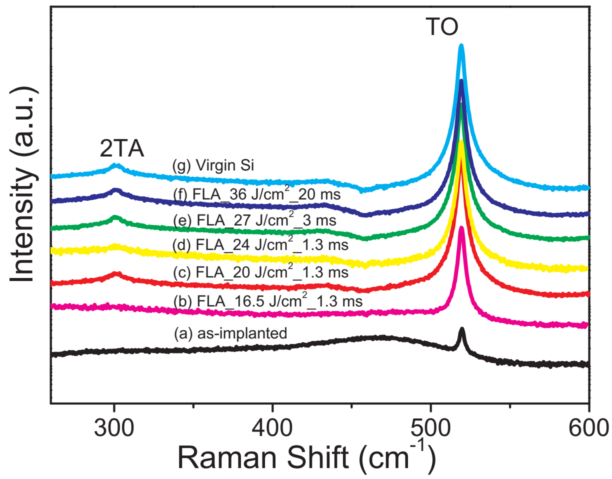

Fig. 1. Room-temperature Raman spectra of virgin Si (g), as-implanted Si (a), and Se-hyperdoped Si samples with a fluence of $5 \times 10^{15}\,cm^{-2}$ annealed at different pulse duration and different energies: (b) 16.5 J/cm^2, 1.3 ms; (c) 20 J/cm^2, 1.3 ms; (d) 24 J/cm^2, 1.3 ms; (e) 27 J/cm^2, 3 ms; (e) 36 J/cm^2, 20 ms. Samples right prior to the flash were preheated to 400 °C for 30 s.

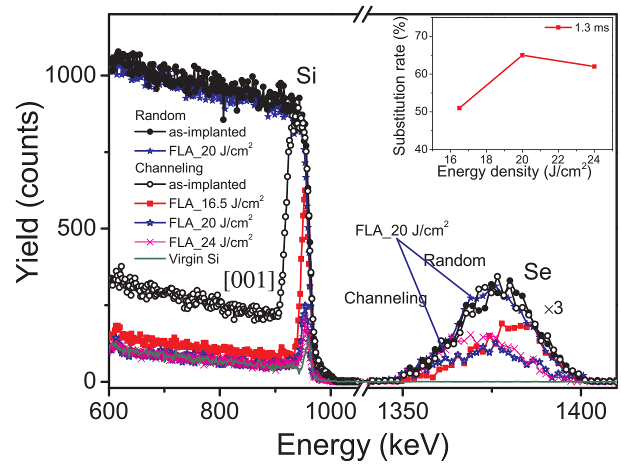

Fig. 2. RBS spectra of Se implanted Si samples with a fluence of $5 \times 10^{15}\,cm^{-2}$ at random and channeling configuration before and after annealing. The RBS spectra for virgin Si are also included for comparison. The inset shows the substitutional fraction of samples annealed at different energy densities.

parameters based on the data obtained by both Raman spectroscopy and RBS/C by considering the best crystalline quality and the largest dopant substitutional fraction.

Raman spectroscopy was carried out to determine the crystallinity degree of the implanted layers using a 532 nm Nd:YAG laser and a charge coupled device camera cooled with liquid nitrogen. RBS/C was performed in order to investigate the degree of lattice reconstruction of the samples and the lattice location of Se in the Si matrix after annealing. For RBS/C measurements a collimated 1.7 MeV He^+ primary beam was used, while the detector was placed at a backscattering angle of 170°. The RBS spectra were measured along random and channeling directions. Electrical properties were investigated by van der Pauw measurements using a commercial Lakeshore Hall System at temperatures ranging from 3 to 300 K.

3. Results

Raman spectra obtained from samples annealed at different energy densities and FLA pulse durations are shown in Fig. 1. A spectrum of a virgin Si wafer is displayed for comparison. The Raman spectrum of virgin Si shows a narrow peak at about 520 cm^{-1} which corresponds to the transverse optical (TO) phonon mode in single-crystalline Si. The spectrum of the as-implanted sample shows a peak at around 520 cm^{-1} with a relatively low intensity, which relates to the TO mode of single crystalline Si substrate beneath the implanted amorphous layer. The observation of a weak band at around 460 cm^{-1} in the as-implanted sample indicates the formation of an amorphous silicon layer during ion implantation process [19]. In Fig. 1(b), the weak band at 460 cm^{-1} is still observed in the sample annealed at 16.5 J/cm^2 for 1.3 ms, suggesting that the used energy density was not enough for the entire solid-phase epitaxial regrowth. However, the weak band vanishes in the spectra of the sample annealed at 20 and 24 J/cm^2. The sample shows a peak at around 520 cm^{-1} which is similar to the single crystalline Si. In addition, another peak located at 303 cm^{-1} corresponds to the two transverse acoustic (2TA) phonon mode of single crystalline Si. From the above-mentioned results, a full lattice reconstruction is obtained by flash pulse duration of 1.3 ms and energy densities of 20 or 24 J/cm^2. From spectra c, e and f shown in Fig. 1, we observe that Se-hyperdoped Si can be recrystallized using any pulse duration if the energy density is properly chosen. The optimized energy density which was selected according to Raman spectroscopy and RBS/C for FLA pulse durations of 3 ms and 20 ms is 27 J/cm^2 and 36 J/cm^2, respectively. The TO and 2TA modes of single crystalline Si are visible in all the samples annealed by different FLA pulse durations, which are similar to the virgin Si in terms of intensity. Raman results indicate that implanted samples can be well-recrystallized by the proper adjustment of FLA pulse duration and energy density.

The crystalline quality and lattice location of the Se implanted Si samples after FLA were determined by RBS/C. Fig. 2 shows the random and channeling spectra of implanted samples after FLA at energy densities of 16.5, 20, and 24 J/cm^2 with the pulse duration of 1.3 ms. A minimum yield χ_{min} is defined as the ratio of the backscattering yield of channeling to that of random spectra, which exhibits the overall level of the lattice quality [20]. If the sample is fully amorphous, χ_{min} is 100%, and then a high-quality single-crystal has a χ_{min} as low as 1–2%. The as-implanted sample shows a χ_{min} of 94.3%, which is indicative of the formation of amorphous Si layers. The yield of the damage peak decreases as the flash lamp energy density increases. In the case of samples annealed for 1.3 ms with energy densities below 16.5 J/cm^2 only partial recrystallization was observed with χ_{min} of around 15%. There is no significant difference in the value of χ_{min} when the energy density rises to 20 J/cm^2 and 24 J/cm^2. The channeling spectra obtained from samples annealed at 20 J/cm^2 and 24 J/cm^2 look very similar to the virgin Si. The χ_{min} values of samples annealed at 20 J/cm^2 and 24 J/cm^2 are around 4%, which indicates a high degree of lattice recovery. The channeling spectra were also measured along the ⟨110⟩ axis for selected samples (not shown) and the Se signal also shows channeling behavior with a similar χ_{min}.

The inset of Fig. 2 shows the substitutional fraction of samples annealed at different energy densities. The substitution of selenium into the Si lattice can be demonstrated by the presence of the channeling behavior. The substitutional fraction f of Se in Si can be calculated by $f = \frac{1-\chi_{min(I)}}{1-\chi_{min(h)}}$, where $\chi_{min\ (I)}$ and $\chi_{min\ (h)}$ are the minimum yield for Se and Si atoms, respectively [21]. Thus the corresponding substitutional fractions of samples annealed at 16.5, 20, and 24 J/cm^2 are 51%, 65% and 62%, respectively. The sample annealed at 20 J/cm^2 exhibits the largest substitutional fraction due to the high degree of lattice recrystallization. Alternatively, for the sample annealed at 24 J/cm^2, the substitutional fraction is slightly lower than that of the sample annealed at 20 J/cm^2. This is attributed to the fact that the sample is overheated and Se atoms start to segregate. When the energy density is below 20 J/cm^2, amorphous Si layers cannot be fully recrystallized, resulting in the lowest substitutional fraction of the Se.

RBS/C spectra of Se implanted Si samples are shown in Fig. 3 for FLA at energy densities of 20, 27, and 36 J/cm^2 with the pulse duration