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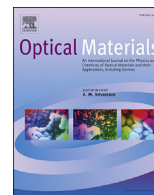
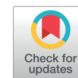


Preparation and characterization of the Si:Co layer for intermediate band solar cell applications



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ABSTRACTS

The Co-implanted silicon layers with rapid thermal process (RTP) have been prepared for intermediate band materials. The characterization of the Si:Co layer has been analyzed and discussed. The results show that the Co concentrations in effective implanted region of the Si layers exceed the Mott limit, satisfying the requirement for the formation of intermediate band in silicon. The Co-implanted samples are well crystallized by RTP treatment. The effective lifetime of the carriers in the samples increases with the Co dose implanted. This indicates that the non-radiative recombination has been suppressed in the post-annealed samples. Furthermore, the optical absorptance of the samples is much enhanced in the wavelength range of above 1100 nm. It can be concluded that the Si:Co layer can be prepared by Co implantation in Si followed by RTP method, and it is a promising material that can be used for intermediate band solar cells.

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1. Introduction

In recent years, many approaches have been proposed to further increase the conversion efficiency of solar cells [1–4]. The intermediate band solar cell (IBSC) is a kind of new concept photovoltaic device [5]. The theoretical efficiency limit of an IBSC can reach 63.2% [6], while that of a conventional solar cell is only 40.7% [7,8]. The IBSC operation is based on the materials with an intermediate band (IB). If an IB is created within the bandgap of a semiconductor material, the photons with energies less than the bandgap would be absorbed which can enhance the cell current and increase the conversion efficiency.

Up to now, there are three approaches to realize the IB materials for the implementation of the IBSC: (1) highly mismatched alloys [9–12]; (2) Quantum dot arrays [13–16]; (3) heavy doping with deep-level impurity [17–21]. The first two approaches are proved to be effective to form an IB in semiconductors. But the host materials are mainly focused on III-V and II-VI semiconductor compounds. For the last method, more appropriate host materials are available especially silicon. Moreover, no complex epitaxy process is needed for the preparation of IB materials. This means that it is easy to realize the large-scale production and reduce the production cost.

For the heavy doping method, the doping element is critical to form IB material. Several reports [19,20,22–25] indicated that the transition elements are attractive for acting as dopant due to their unique partially-filled *d* orbits. In previous work, several transition metals have been investigated as doping element, such as Cr [19], Ti [20], Ni [22], and Mn [23]. But there have been few reports on the Co doping. Moreover, previous reports employed the pulsed laser melting (PLM) to obtain IB materials for the as-implanted samples. However, PLM is just applied to the sample surface only up to about 100 nm deep. And PLM technique is difficult to prepare large-size samples since the pulsed laser is a point-source. Moreover, the laser energy distribution makes the sample surface less uniform. The rapid thermal process (RTP) technique can overcome these problems since it is not limited to the thickness and the area of a sample. Therefore, we propose to prepare IB materials by Co implantation in silicon followed by RTP method. The influence of ion implantation and RTP treatment on the lattice structure, effective carrier lifetime and optical absorptance of the samples has

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been studied. These characterizations are closely related to the performance of IB materials that used for IBSCs.

2. Experimental

2.1. Sample preparation

The samples, 400 μm thick n-Si (111) wafers ($\mu = 1410$ cm^2/Vs, $\rho = 200\ \Omega\cdot$cm, $n = 2.21 \times 10^{13}$ cm^{-3} at room temperature), were cleaned by RCA recipe, followed by HF dipping for 20 s to remove the native oxide layers, and finally dried by N_2. The samples were implanted with Co ions by MEVVA10 ion implanter (Shenyang Huiyu, China) at 35 keV and a background vacuum of 1×10^{-5} Pa. The ion incidence angle was 45°. A thermocouple attached to the substrate was used to measure the average implantation temperature due to the ion beam heating. The value was determined to be about 160 °C. The mean beam current was about 0.5 mA. Co doses of three samples are: 1×10^{15}, 1×10^{16} and 5×10^{16} cm^{-2}, respectively. The annealing process was performed by RTP-500 instrument (Beijing East Star, China) with halogen tungsten lamp heater. The Co-implanted samples were annealed at 1000 °C for 5 s with a temperature ramp rate of 100 °C/second and a post natural cooling step, totally in Ar atmosphere. Before the measurements, the samples were dipped in HF (5 *vol%*) solution for 20 s to remove the oxide layers on the surfaces and dried by N_2.

2.2. Characterization techniques

The samples were analyzed by secondary ion mass spectroscopy (SIMS) instrument (IMS 7f, CAMECA, France) using O^{2+} with energy of 10 keV as the primary ions, at an incidence angle of 38° and an ion intensity of 100 nA. The imaginary part of the dielectric function (ε_2) of the samples was analyzed by spectroscopic ellipsometry (Semilab, GES5-E, Hungary) to show the crystalline state of the implanted region of the samples. The Raman scattering spectra of samples were obtained by HR800 (HORIBA Jobin Yvon, France) with the Ar^+ laser of 532 nm to estimate the crystallinity recovery state of the samples. Effective carrier lifetime measurements were done with WT-2000PV (Semilab, WT-2000PV, Hungary). The test principle of WT-2000PV is based on microwave photoconductivity decay. The optical absorptance of the samples was measured by UV–vis–NIR spectrophotometer (UV-3600, Shimadzu, Japan).

3. Results and discussion

3.1. SIMS analysis

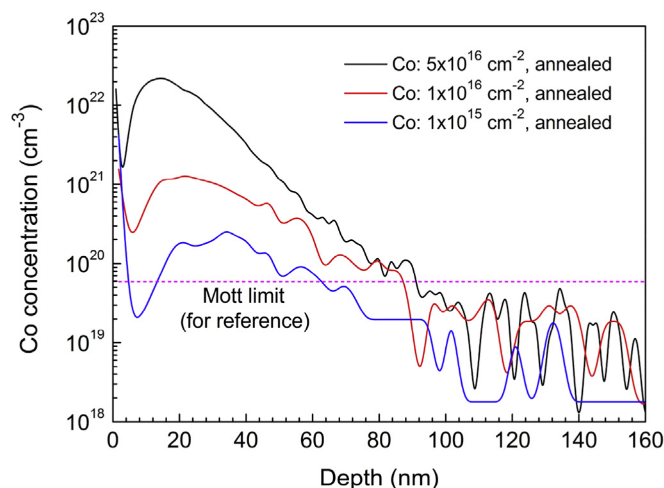

Fig. 1. Co concentration profile of the post-annealed samples implanted with the doses of 1×10^{15}, 1×10^{16}, and 5×10^{16} cm^{-2} from SIMS measurements.

Fig. 1 shows the Co depth distribution measured by SIMS after the RTP process for samples implanted with the doses of 1×10^{15}, 1×10^{16}, and 5×10^{16} cm^{-2}. It can be seen that the Co concentrations in most effective implanted regions of the three samples exceed the Mott limit (~6×10^{19} cm^{-3} at 300 K, for reference) [26–28]. This is important since it satisfies the necessary requirement for forming an IB. According to the IB theory [29], the Mott limit is the threshold value of impurity concentration for the formation of an IB. In practice, the Mott limit is usually above the solid solubility of the impurity element in the host semiconductor. As a result, non-equilibrium preparation techniques, such as ion implantation and RTP, can be used to ensure the very high concentration of impurities that introduced into the host material.

3.2. Spectra of imaginary part of the dielectric function

In order to investigate the influence of ion implantation and RTP on the samples, we plotted the imaginary part of the dielectric function ε_2 versus photon energy. The ε_2 spectrum can provide a clear indication of the crystalline growth and allows the qualitative analysis of crystallinity degree [30]. Fig. 2a shows ε_2 spectra of the as-implanted samples implanted with the doses of 1×10^{15}, 1×10^{16} and 5×10^{16} cm^{-2}. That of the naked Si wafer (non-implantation Co) is plotted as a reference. Two sharp characteristic peaks of the naked Si wafer are at about 3.4 eV and 4.3 eV, but they disappeared for the implanted samples. The ε_2 spectra of the three implanted samples exhibit a "big bulge" at about 3.6 eV, which corresponds to the typical characteristic peak of amorphous silicon. This should come from the fact that after very high dose Co ions are implanted into the crystal silicon samples, the lattices in effective implanted regions of the as-implanted samples are almost destroyed. Then, the Co-implanted layer of samples will appear unordered structure.

The as-implanted samples must be appropriately annealed to obtain high-performance IB materials. After the RTP treatment, the ε_2 spectra of the samples are shown in Fig. 2b. It is found that the sharp characteristic peak at around 3.4 eV can be obviously observed for the annealed samples. For the sharp characteristic peak at around 4.3 eV, it can be found but the peak intensity is weak. Also, the peak intensity of the sample implanted with the doses of 1×10^{15} cm^{-2} is greater than that of the samples implanted with the doses of 1×10^{16} and 5×10^{16} cm^{-2}. The changes of the sharp characteristic peaks of samples should be related with the lattice recovery due to the RTP process. But, from the sharp characteristic peak of samples at around 4.3 eV we can conclude that the Co-implanted layer does not attain a perfect degree of crystallinity recovery, and the sample implanted at lower dose has a better situation than the one implanted at higher dose. As a consequence, the RTP process should be further optimized to obtain a complete lattice recovery. The optimized factors include the value of the annealing temperature and the annealing time in the RTP process, and different implanted doses for samples will require different annealing recipe.

3.3. Raman scattering spectra

To further estimate the crystallinity recovery of the samples, Raman scattering spectra for Co-implanted Si samples after RTP treatment are measured and shown in Fig. 3. We can see that both the spectra of the three samples exhibit a sharp peak at about 520 cm^{-1}, which comes from the Si–Si TO mode of the crystal

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