Solar Energy Materials & Solar Cells 104 (2012) 159–164

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Insulator to metallic transition due to intermediate band formation in Ti-implanted silicon

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ARTICLE INFO

Article history:
Received 9 January 2012
Received in revised form
12 April 2012
Accepted 30 April 2012
Available online 7 June 2012

Keywords:
Metallic transition
Intermediate band
Silicon
Titanium
Ion implantation

ABSTRACT

We have analyzed by means of electrical transport measurements, the insulator to metallic transition due to intermediate band (IB) formation (insulator to metallic-IB) in silicon layers. The samples were implanted with titanium concentrations well above the solid solubility limit and subsequently pulsed laser melted (PLM). Whereas the doping of silicon with Ti impurity concentrations below the Mott limit is known to produce deep levels which act as non radiative recombination centers, the introduction of a high concentration of deep impurities above this limit could form an IB. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements show the remaining titanium concentration profile after PLM, indicating whether this concentration is above or below the theoretical limit for IB formation in the different implanted samples. Sheet resistance and Hall effect measurements performed in the temperature range (100–300 K) show that insulator to metallic-IB transition takes place for concentrations above $\sim 10^{20}$ cm^{-3}. This transition becomes apparent in a rectifying behavior observed in van der Pauw and transversal *I–V* electrical measurements at low temperatures. Contacts exhibit Schottky or ohmic behavior for samples with Ti concentrations below or above the transition, respectively. All these results point out to the metallic behavior of the IB and provide a powerful tool to determine the IB formation in a semiconductor.

1. Introduction

To increase the efficiency of solar cells a great technological effort has been devoted over the last years. The intermediate band solar cell (IBSC) is a promising device based on the intermediate band (IB) concept that has been proposed within the third generation of photovoltaics to exceed the efficiency of conventional solar cells [1]. An IB material is characterized by the existence of an electronic energy band of allowed states within the conventional band gap that enables the absorption of sub-band gap photons. In this process, one photon pumps an electron from the valence band (VB) to the IB and a second photon pumps an electron from the IB to the conduction band (CB). To ensure the occurrence of both processes, the IB must be a semi-filled or “metallic” band. Since the process described occurs in addition to the ordinary pumping of electrons from the VB to the CB, the solar cell photocurrent could be higher than in the case of a conventional design.

In the ideal IBSCs, the IB material has to be placed between an n-type and a p-type layer to increase the photocurrent generated without voltage reduction. Therefore the IBSC could significantly exceed [1] the Shockley–Queisser efficiency limit calculated for single gap solar cells [2]. Experimental results of IB material formation, based on quantum dots [3] and highly-mismatched alloys [4] have been reported. Additionally, a new interest on deep level centers has arisen related to the development of the IBSC concept. In this context, it has been recently proposed that the introduction of ultrahigh concentrations of deep centers can give rise to the formation of an IB, with suppression of non-radiative recombination. This is due to the delocalization of the impurity electron wavefunctions and the consequent suppression of the multiple phonon emission process [5]. In this way, chalcogenides supersaturated silicon materials have been investigated [6,7]. The deep level impurity concentration required to form an IB is denominated Mott limit and has been theoretically calculated ($\sim 6 \times 10^{19}$ cm^{-3}) [5]. The experimental determination of the delocalization transition is an essential point to investigate the IB formation.

Recently, we have proposed deep-level atoms impurified semiconductors as promising candidates to form an IB material [8,9] by means of Ti ion implantation in silicon at the high concentrations required to exceed the IB formation limit [5]. The behavior of transition metal atoms in silicon has been deeply studied in the past, mainly because the deep levels associated to them are known to increase the amount of non-radiative recombination and thus to reduce the carrier lifetime. However, we have achieved evidences of carrier lifetime recovery in these

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http://dx.doi.org/10.1016/j.solmat.2012.04.049

ultrahighly Ti impurified silicon layers, conversely to the classic understanding of the deep level impurity effect in semiconductors and supporting the predictions of a non-radiative recombination suppression when an IB is formed [10].

We have reported that silicon implanted with very high Ti concentrations and subsequently pulsed laser melted (PLM) forms an IB material [8,9]. In these studies, we remarked an important aspect: the electrical decoupling behavior observed at low temperatures between the IB material and the n-Si substrate that is under the implanted layer. This electrical decoupling behavior of the sheet resistance at low temperatures results on a resistivity higher than the Si substrate. This is not possible if a simple conduction model with two parallel layers is considered, since the total sheet resistance could never be higher than the sheet resistance of one of the layers. This indicates that an electrical decoupling effect of the layers is produced at low temperatures. We have proposed a two-layer analytical model based on the van der Pauw setup that explains satisfactorily both sheet resistance and Hall effect measurements of Ti-implanted Si assuming the IB formation. The model takes into account the current limitation in the junction between the IB layer and the substrate that has as a consequence the rectifying behavior. The analytical model fully agrees with the electrical measurements obtained from the Ti impurified layers. The details dealing with this junction were previously reported in Ref. [11].

Additionally to these electrical measurements we have reported recently a strong sub-band gap absorption in these samples that cannot be explained in terms of conventional absorption processes, such as defects or free carrier absorption and that has been suggested that could be produced by the IB formation [12].

In this work, we show an insulator to metallic-IB transition in ultraheavily Ti impurified crystalline silicon. We have measured the electrical behavior of silicon layers implanted with a very high Ti concentration by means of sheet resistance and Hall effect in the (100–300 K) range, in order to evaluate the critical concentration to obtain an IB material. We have investigated the insulator to metallic-IB transition by measuring the electrical rectifying behavior associated to IB formation and the type of electrical contact formed. The analyzed samples show the transition for Ti concentrations between 10^{20} and 8.5×10^{20} cm^{-3}.

2. Experimental

Single crystal n-type Si (111) wafers with a thickness of 300 μm ($\rho=200$ Ωcm; $\mu=1500$ cm^2/Vs; $n=2.2\times10^{13}$ cm^{-3} at room temperature) were implanted in an IBS refurbished VARIAN CF3000 Ion Implanter with ^{48}Ti$^+$ at different doses (10^{13}, 10^{14}, 10^{15} and 10^{16} cm^{-2}) at 33 keV using a 7° tilt angle. After implantation, all the samples were PLM annealed at 0.8 J/cm^2 with a single 20 ns pulse using a KrF excimer laser (248 nm) at J.P. Sercel Associates Inc. (New Hampshire, USA). We have analyzed a non implanted sample but PLM annealed sample for comparative purposes.

Depth profiles of Ti concentration in the Si lattice were obtained by time-of-flight secondary ion mass spectrometry (ToF-SIMS) characterizations. These were carried out with a TOF_SIMS IV system manufactured by ION-TOF, using a 25 keV positive primary ion pulsed Bi^{3+} beam at 45° incidence that scanned an area of 250 × 250 μm^2. The secondary ions generated were extracted with a 10 keV voltage and their time of flight from the sample to the detector was measured in a reflection mass spectrometer. The Ti concentration profiles were calibrated using the non saturated signal of Si^{28}.

The samples were electrically characterized by means of sheet resistance and Hall effect measurements with the van der Pauw configuration at variable temperature (100–300 K) using a Keithley SCS 4200 model with four Source and Measure Units. Samples were 1 × 1 cm^2 pieces of silicon wafers with four aluminum electrodes in the corners. The magnetic field used in Hall effect measurements was 0.88 T. The samples were placed inside a homemade liquid nitrogen cryostat attached to a vacuum pump to avoid moisture condensation. Measurements were performed in the four van der Pauw configurations. For each configuration the polarity of the current source and the direction of the magnetic field were changed, (for a total of 16 measurements), in order to minimize spurious thermo-galvanomagnetic effects.

The electrical characterization was complemented with transversal *I–V* measurements, to further investigate the influence of the Ti implanted dose on the electrical rectifying effect. Prior to Ti implantation, the back side of these samples was superficially implanted with phosphorus at 80 keV with a 10^{15} cm^{-2} dose followed by RTA process at 900 °C during 20 s in an Ar atmosphere to obtain a n$^+$ layer and optimum ohmic back contacts. To carry out these measurements, frontal guard ring contacts with a 1.5 mm of dot diameter and a dot-ring separation of 50 μm, were deposited on the top of the Ti implanted layer to avoid surface current leakages. These contacts were made with a pattern defined by photolithography and subsequently evaporating 200 nm of Al metallic electrodes by e-beam. No additional treatment was done in the Ti implanted layer to improve the contact.

3. Results

In previous papers we have analyzed Ti implanted Si samples with concentrations well above the Mott limit [8,11]. In this work, we extend the study with samples with Ti concentrations below the Mott limit to explore the insulator to metallic transition.

Fig. 1 shows the Ti concentration depth profiles obtained from ToF-SIMS measurements of samples implanted with different Ti doses (10^{13}, 10^{14}, 10^{15} and 10^{16} cm^{-2}) and PLM annealed at 0.8 J/cm^2 [13]. A push effect of the Ti impurities towards the surface with respect to the characteristic Gaussian profile of an as-implanted sample is observed as a consequence of the PLM annealing process, which tends to expel the impurities. However, the PLM permits to obtain Ti impurity concentrations above the solid solubility limit, even for the sample implanted with the lowest Ti dose. The theoretical Mott insulator-metallic limit is only clearly surpassed in the samples implanted with doses above

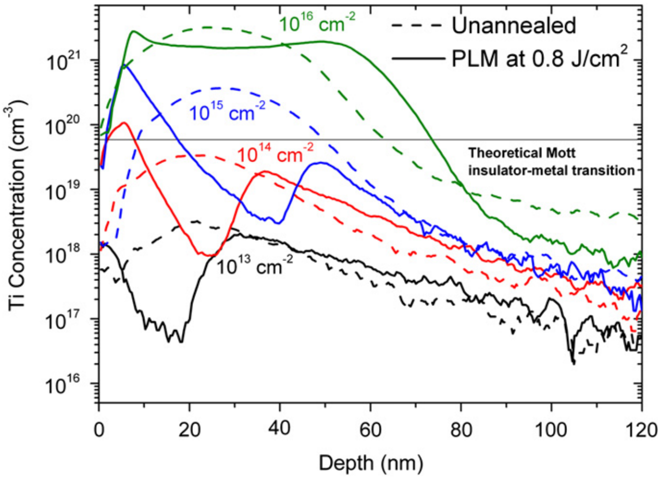

Fig. 1. ToF-SIMS profiles of Ti implanted Si samples with doses of 10^{13}, 10^{14}, 10^{15} and 10^{16} cm^{-2} before and after PLM at 0.8 J/cm^2.