Study of the Electrical Behavior in Intermediate Band-Si Junctions

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Study of the electrical behavior in Intermediate Band-Si junctions

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ABSTRACT

In this study we analyze the electrical behavior of a junction formed by an ultraheavily Ti implanted Si layer processed by a Pulsed Laser Melting (PLM) and the non implanted Si substrate. This electrical behavior exhibits an electrical decoupling effect in this bilayer that we have associated to an Intermediate Band (IB) formation in the Ti supersaturated Si layer. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements show a Ti depth profile with concentrations well above the theoretical limit required to the IB formation. Sheet resistance and Hall mobility measurements in the van der Pauw configuration of these bilayers exhibit a clear dependence with the different measurement currents introduced (1µA-1mA). We find that the electrical transport properties measured present an electrical decoupling effect in the bilayer as function of the temperature. The dependence of this effect with the injected current could be explained in terms of an additional current flow in the junction from the substrate to the IB layer and in terms of the voltage dependence in the junction with the measurement current.

INTRODUCTION

In the last few years, an increasing effort has been made to improve the efficiency of the solar cell technology. The intermediate band solar cell (IBSC) has been proposed as one of the most promising candidates to increase the photovoltaic efficiency in the third generation of solar cells [1]. An intermediate band (IB) semiconductor presents a new electronic energy band of allowed states between the conventional conduction band and valence band. This IB could permit sub-band gap photon absorption by means of valence-to-IB and IB-to-conduction band transitions. This mechanism could overcome the Schockley-Queisser thermodynamical efficiency limit (30-40%) for single junction solar cells [2].

Deep-level impurities are known to act generally as a non-radiative recombination centers that reduce carrier lifetime and the efficiency of the solar cell. However, the introduction of an impurity concentration above the Mott limit ($5.9x10^{19}$ cm^{-3}) could form an IB, which would reduce this non radiative recombination [3]. Commonly, the Mott limit is several orders of magnitude above the solid solubility limit of deep level impurities in semiconductors. Therefore, the combination of two non equilibrium fabrication processes: ion implantation followed by pulsed laser melting (PLM) has been used to achieve these concentrations with high crystal quality [4]. Deep-level Ti impurity is being investigated as candidate to form an intermediate band (IB) material in Si [5]. The fabricated bilayers with this deep-level impurity are formed by the Ti-supersaturated Si layer on the top of a Si substrate. The electrical transport measurements in the van der Pauw configuration have revealed an electrical decoupling effect in the junction of this bilayer [5]. This electrical decoupling effect has been satisfactorily explained and modeled assuming the formation of the IB in the Ti supersaturated Si. For the measurements at very low temperatures the decoupling electrical effect between the layers allows to measure only the electrical transport properties in the Ti supersaturated Si layer where the IB is formed [6].

In this work, we have investigated the effect of the measurement current (1μA-1mA) over the transport electrical properties measured in the van der Pauw configuration in the 14-300 K temperature range. We have analyzed the measurement current effect in the electrical decoupling behavior in the junction between the Ti supersaturated Si layers and the Si substrate.

EXPERIMENTAL

Single crystal n-Si (111) samples with a thickness of 300 μm (μ=1450 cm^2/Vs; n=2.2×10^{13} cm^3 (at room temperature), were doubly implanted with $^{48}Ti^+$ at 35 and 150 keV, with doses of 10^{15} cm^2 and 4×10^{15} cm^2, respectively, in an IBS refurbished VARIAN CF3000 ion implanter. The samples were tilted 7° with respect to the incident beam axis to minimize channeling effects. All these implantation parameters have been selected in order to obtain a homogeneous impurity implanted profile. The PLM was performed with a KrF excimer laser (one pulse, 248 nm, 20 ns total duration) at J.P. Sercel Associates, Inc. (New Hampshire, USA) with an energy density of 1.8 J/cm^2

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 45º 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 with a Keithley SCS 4200 model with four Source and Measure Units. The sheet resistance and Hall effect measurements were carried out using the van der Pauw configuration at variable temperature in the 14-300 K range in a closed-cycle Janis cryostat. Samples were 1×1cm^2 pieces with four Ti/Al metallic electrodes evaporated in the corners. The magnetic field used in the Hall effect measurements was 0.88 T. 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 in order to minimize spurious thermo-galvanomagnetic effects. OFHC cooper sample holder coated with Au was used to minimize the temperature differences between the thermocouple measurement and the sample. Electrical currents in the range of (1 μA-1mA) were injected to analyze the effect in the electrical decoupling behavior of the transport properties measured.

RESULTS

Figure 1 shows the Ti concentration depth profile obtained by means of ToF-SIMS measurements of the sample double implanted with the doses of 10^{15} and 4×10^{15} cm^2, the SRIM simulation for this profile and the profile for the sample after PLM process at 1.8 J/cm^2. The as-implanted sample displays the Ti concentration with the expected double Gaussian-like profile as corroborates the Ti profile simulation obtained with the SRIM software [7]. However the as-implanted sample presents a tail for the deeper region that is not reproduced by the simulation. That is because although the sample was tilted 7° during the implantation to minimize the channeling effects, this channeling is not completely avoided. On the other hand the SRIM program only simulates ion implantation processes in amorphous layers where the channeling effects are not possible. After the PLM process the sample shows a Ti concentration profile clearly above the theoretical Mott limit for the IB formation in a thickness of about 130 nm. The PLM process produce a strong push out effect of the Ti impurities toward the surface producing a redistribution of the Ti concentration profile. TEM images and the electron diffraction (ED) patterns of this sample show an excellent single Si crystal recovery without any kind of silicide secondary phase formation, Ti clustering or Ti precipitates [8].

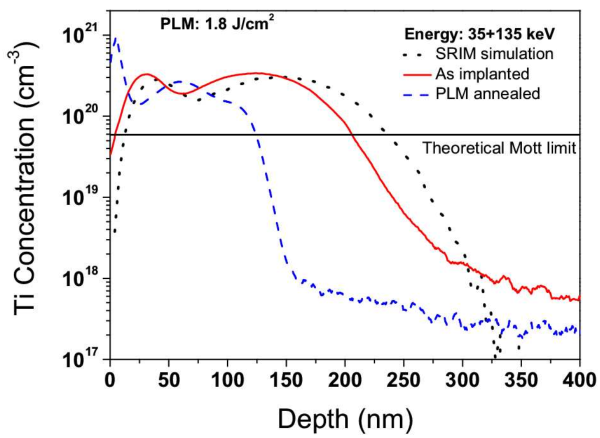

Figure 1. ToF-SIMS profiles of the double implanted sample with the doses of 10^{15} and 4×10^{15} cm^2 at 32 and 135 keV respectively, the SRIM simulation for this implanted doses and energies, and the profile for the Ti implanted Si sample after PLM process at 1.8 J/cm^2

Figure 2a displays the sheet resistance measured in the 14-300 K range for the Ti supersaturated Si samples with different currents (1 μA-1mA). A scheme of the bilayer in the van der Pauw configuration is detailed in the inset of this figure. Figure 2b shows the sheet resistance of the sample measured with the lowest current compared with the unimplanted Si substrate. The sheet resistance of this unimplanted reference sample shows from 300 to 50 K the expected decrease as the temperature is reduced due to the decrease of the phonon scattering [9] and from 50 to 14 K the increase of the sheet resistance due to the increase of the freeze out. The sheet resistance of the Ti supersaturated Si samples exhibit an interesting rectifying effect due to the electrical decoupling in the bilayer. This electrical decoupling effect has been observed previously and has been satisfactorily explained in terms of the IB formation in Ti supersaturated Si layers [10]. The sheet resistance of a sample implanted with a Si dose comparable to the dose of the Ti implanted sample followed by a PLM process and a sample unimplanted but PLM processed, show the same behavior of the Si reference substrate (not shown here). This rules out the attribution of this unusual electrical effect to defects produced during the implantation or PLM process. The sheet resistance in figure 2a of the Ti supersaturated Si sample measured in the van der Pauw configuration shows a clear dependence in the electrical decoupling effect with the current introduced. As it can be observed the sheet resistance minimum located around 225 K is progressively displaced at higher temperatures for the higher measurement current. However, the sheet resistance for the higher measurement currents exhibits a more gradual electrical decoupling effect for temperatures below 200 K.

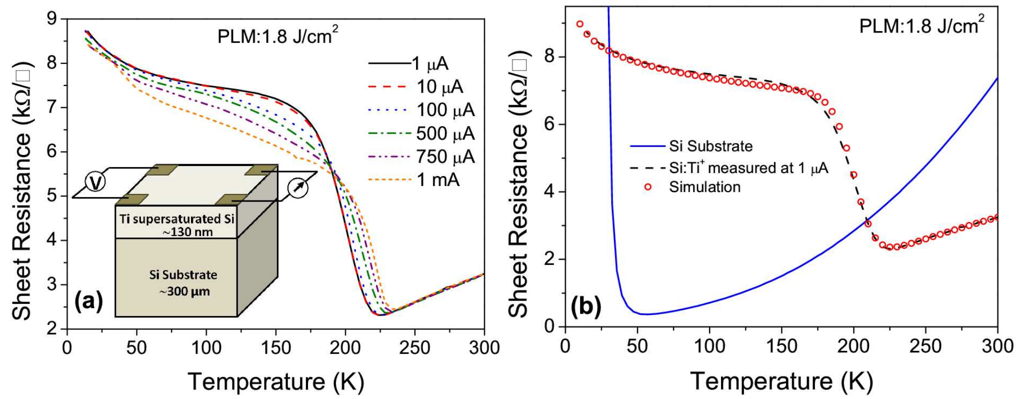

Figure 2. Sheet resistance measured in the 14-300 K range for the Ti supersaturated Si sample with the double implantation at different currents: a) For measurement currents in the range of 1 μA-1mA. Inset: Scheme of the van der Pauw set up and the bilayer.b) For1 μA and a Si reference sample. The fitting obtained from the two-analytical model has been also plotted.

Recently we have developed an analytical two layer model that takes into account the IB formation in the Ti supersaturated Si region with concentrations above the Mott limit [11]. In figure 2b also it has been plotted the simulation obtained with this analytical two layer model for the double implanted layer that have been used to fit the electrical measurements. To take into account the increase of the sheet resistance at very low temperatures a potential dependence of the mobility in the IB has been introduced. As it can be observed in the figure 2b, this fitting is in good agreement with the sheet resistance measured with the lowest currents. This could indicate that a new phenomenon that has not been completely attached in the model has been detected in the measurements performed with the higher currents. Additionally, the differences in the sheet resistance between the analytical model and the measurements carried out with the highest currents cannot been attributed to the tail in the Ti profile with concentrations below the Mott limit since for the lower currents there are no appreciable differences with the model. This gradual electrical decoupling observed at temperatures below 200 K could be explained in terms of an additional current flow in the junction. On the other hand, the displacement of the sheet resistance minimum is associated to the non linear behavior of the IB-substrate junction. This junction has been modeled as a diode but to be introduced in the linear model a resistor is assumed. Consequently this resistor should depend on the measurement current.

Figure 3 shows the Hall mobility measured in the 14-300 K range for the Ti supersaturated Si samples with different currents (1 μA-1mA) and also for the unimplanted Si substrate. While the Si reference substrate, barely visible at the right of the corner, shows the expected Hall mobility tendency as the temperature is decreased due to the reduction of the optical phonon scattering, the Hall mobility for the Ti supersaturated sample shows again an unusual dependence with the temperature that has been associated also with the electrical decoupling effect in the bilayer. This electrical behavior has been also successfully reproduced by the analytical two layer model, which assumes the IB formation in the Ti supersaturated Si. The analytical model reproduces faithfully, with the same fitting parameters, the sheet resistance and Hall mobility electrical behavior observed experimentally. The Hall mobility measurements as function of the temperature for the Ti supersaturated Si sample carried out with different measurement currents shows an analogous behavior to the sheet resistance behavior: a downshift with the temperature in the maximum of the mobility for the lowest measurement currents about 250 K and a more gradual electrical decoupling effect for the samples measured with the highest currents at temperatures below 200K. The electrical behavior of the Hall mobility for the case of the lower current of measurements is correctly reproduced by the analytical two layer model.

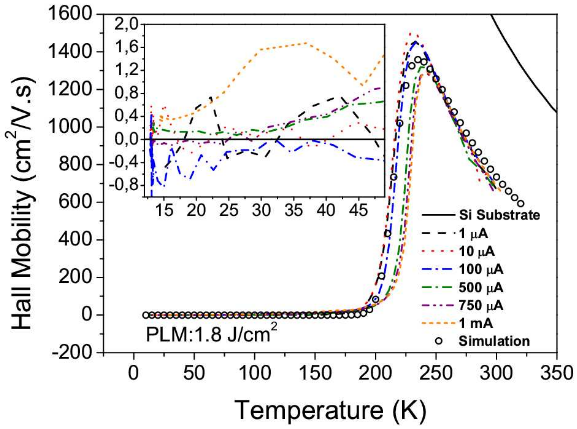

Figure 3. Hall mobility measured in the 14-300 K range for the Ti supersaturated Si sample with the double implantation at different currents (1 μA-1mA). Inset: Hall mobility in the range of 14-50 K to appreciate the change in the carrier type.

In the inset of the figure 3 it can be observed the Hall mobility of the Ti supersaturated Si sample for the different currents of measurement in the 14-50 K temperature range. As it can be observed the carrier type changes clearly from n-type to p-type only for some of the measurements. This change in the carrier type has been associated to the measurement of the carriers in the IB [6]. For the case of the measurements with the high current of measurement, the change in carrier type is not produced. This is due to the gradual electrical decoupling effect observed that suggests the existence of a contribution to the electrical behavior from the Si substrate. In the case of the lowest current of measurements the carrier change type is not clearly observed and an oscillation in the sign change can be appreciated. This could be due to the low current used in the measurement produces a Hall potential (V_H) that has been measured with low accuracy. In any case, for the medium current of measurement employed can be clearly appreciated the change in the carrier type that we attribute to the electrical behavior in the IB.

CONCLUSIONS

In this work, we have investigated the transport electrical properties in the van der Pauw configuration in the junction between the Ti supersaturated Si layers and Si substrate in the 14-300 K temperature range. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements determine that Ti concentration after PLM process is above the theoretical Mott limit, which is a required condition to form an IB material. Sheet resistance and Hall mobility measurements in the van der Pauw configuration of these bilayers exhibit a clear dependence with the different currents introduced (1 μA-1mA). We find that the electrical transport properties measured for the different measurement currents present a gradual electrical decoupling effect as function of the temperature. Whereas electrical decoupling behavior observed for the lowest measurement currents is in full agreement with an analytical two layer model based on the IB formation, an increase in the measurement currents employed produce a progressive deviation from the model. To explain the electrical characteristics observed as function of the measurement current two mechanisms are suggested. First, the gradual electrical decoupling measurements observed at temperatures below 200 K could be explained in terms of an additional current flow in the junction from the substrate to the IB. Secondly, the downshift in the minimum of the sheet resistance and in the maximum of the mobility about 250 K is attributed to a voltage dependence with the injected current in the junction between the IB material and the Si substrate.

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