Electrical properties of silicon supersaturated with titanium or vanadium for intermediate band material

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Abstract— **We have fabricated titanium and vanadium supersaturated silicon layers on top of a silicon substrate by means of ion implantation and pulsed laser melting processes. This procedure has proven to be suitable to fabricate an intermediate band (IB) material, i.e. a semiconductor material with a band of allowed states within the bandgap. Sheet resistance and Hall mobility measurements as a function of the temperature show an unusual behavior that has been well explained in the framework of the IB material theory, supposing that we are dealing with a junction formed by the IB material top layer and the n-Si substrate. Using an analytical model that fits with accuracy the experimental sheet resistance and mobility curves, we have obtained the values of the exponential factor for the thermically activated junction resistance of the bilayer, showing important differences as a function of the implanted element. These results could allow us to engineer the IB properties selecting the implanted element depending on the required properties for a specific application.**

Keywords—Titanium, vanadium, silicon, ion implantation, pulsed laser melting, intermediate band, solar cells.

I. INTRODUCTION

Silicon has been over decades the major material for the use in the microelectronic industry. However, as the demand of better performance or very specific applications increases, silicon has to yields its prominence to other more specific materials. For example, specific materials such as HgCdTe are more suitable than Si for infrared radiation detection [1]. Even so, the scientific community is devoting an enormous effort in the development of Si based materials for this application. The advantages are clear: any silicon based material would be easily integrated in the very mature silicon microelectronics industry and the use of exotic or contaminant materials would be avoided. In this context, novel silicon based materials that show promising optical and electrical properties are being obtained using the combination of deep centers ion implantation and pulsed laser melting (PLM) processes. Specifically silicon supersaturated with Ti or chalchogenides have shown a remarkably infrared absorption [2, 3] and an increase of the photo response for sub-bandgap illumination [4, 5]. One hypothesis to explain these properties is based on the formation of an intermediate band (IB) of allowed states within the silicon bandgap. This IB would permit the infrared photogeneration of extra charge carriers since it would allow optical transitions from the valence band to the intermediate band (VB-IB) or from the intermediate band to the conduction band (IB-CB). The theory of IB materials states that if a great amount of deep centers is introduced in a host semiconductor material the wavefunctions of the impurities would overlap due to the spatial proximities between them. The concentration limit beyond which the IB would be formed is known as the Mott limit [6]. This process would lead to the splitting of the impurity levels forming a band of allowed states within the silicon bandgap and a carrier delocalization [7]. The fabrication of an IB material is a key goal to be achieved by the photovoltaic community since this IB would lead to an increase in the photo-generated current and higher conversion efficiencies [8]. The electrical transport properties of Si supersaturated with Ti have been deeply analyzed in previous works [9-12], associating the unusual transport properties with the formation of an IB within the Si bandgap. Theoretical work has been also done in the field of IB by means of Si supersaturated with Ti [13], confirming some of the experimental results obtained.

In this paper we will deal also with vanadium which is another well-known deep center in silicon. We present electrical characterization of V supersaturated Si comparing this result with those obtained with Ti.

II. EXPERIMENTAL

Samples 1x1 cm^2 in size of n-type Si (111) with a thickness of 300 μm ($\rho \approx 200$ Ωcm; $\mu \approx 1500$ cm^{2}V^{-1}s^{-1}, $n \approx 2.2 \times 10^{13}$ cm^{-3} at room temperature) were implanted at 32 keV with Ti or V at a dose of 10^{16} cm^{-2}. Subsequently the implanted samples were PLM processed at 0.8 J/cm^2 with a KrF excimer laser (248 nm) at IPG Photonics. Also, some Si samples were implanted with Si at 170 keV and 10^{16} cm^{-2} subsequently processed by PLM at 1 J/cm^{-2} for comparatives purposes. Electrical characterization was made at variable temperature (10 – 300 K) placing the samples inside a closed-cycle Janis cryostat. In order to avoid moisture condensation, the cryostat was attached to a vacuum pump. A Keithley SCS 4200 model with four source and measure units was used to perform the sheet resistance measurement and Hall effect measurements with the van der Pauw configuration. A Kepco bipolar current source was used to feed an electromagnet and perform the Hall mobility measurements.

Inset of Fig. 1 represents a non-scaled schematic of the van der Pauw set up that we have used for sheet resistance measurements. As we implant the impurities and we made the PLM process on the top layer, our final processed samples have a parallel structure (implanted top layer / n-Si substrate). We introduce the current by two adjacent terminals and measure the potential difference by the opposite two contacts on the implanted layer. With this structure we expect a parallel conduction scheme i.e. the current will flow from two adjacent contact through the two layers. For the Hall effect measurements, we introduce the current by two nonconsecutive contacts and measure the Hall voltage by the other two contacts.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the sheet resistance as a function of the temperature for the Ti implanted Si sample, for the V implanted Si sample and for the Si implanted sample. Also a reference n-Si unimplanted substrate has been measured. We can observe the expected behavior for the Si unimplanted substrate, i.e. a decrease of the sheet resistance as the temperature decrease due to the reduction of the phonon scattering and an abrupt increase of the sheet resistance at low temperatures due to the freeze-out effect. However for the samples processed with Ti or V we observe a completely different behavior. As the temperature is decreased from room temperature, we measure a sheet resistance with the same tendency of the silicon unimplanted substrate but with lower values, suggesting a parallel conduction mechanism through the bilayer [9]. But at a given temperature ,220 K for the Ti sample and 170 K for the V sample, respectively, the sheet resistance begins to increase as the temperature decreases. The sheet resistance of these samples becomes even higher than the unimplanted silicon substrate. This fact cannot be explained by parallel conduction since the total equivalent resistance of the bilayer cannot be higher than the resistance of one of its conduction branches (silicon substrate). Then, an electrical decoupling seems to have taken place at low temperatures and the electrical conduction is carried out foremost by the processed top layer.

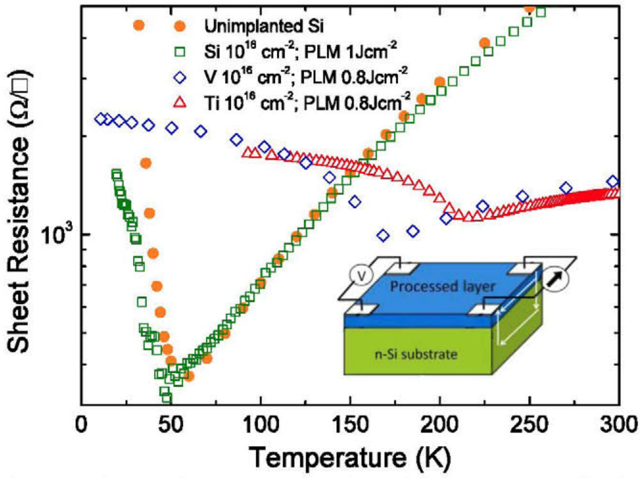

Figure 1 Sheet resistance as a function of the temperature for the unimplanted Si sample, the Si sample implanted with Si at 10^{16} cm^{-2} dose, the Ti implanted sample at 10^{16} cm^{-2} dose and the V implanted sample at 10^{16} cm^{-2} dose subsequently PLM processed at 1, 0.8 and 0.8 Jcm^{-2} respectively. Inset shows a schematic 3D view of the van der Pauw set-up.

Fig. 2 shows in a logarithmic scale the dependence of the Hall mobility absolute value as a function of the temperature for the same samples as in Fig. 1. All the samples present negative values of the Hall mobility, i.e. the majority charge carriers are electrons. We can observe the expected behavior for the Si unimplanted substrate, i.e. an increase of the carrier mobility as the temperature decrease due to the reduction of the phonon scattering. However, for the Ti and V implanted samples we observe also an unusual behavior. The mobility of the Ti and V implanted samples begins to increase as the temperature decreases, as expected, but at a given temperature the mobility suddenly decreases to a very low value. This can be explained by the bilayer decoupling process. In the inset of Fig. 2 we represent in a linear scale the carrier mobility for the V samples focusing in the low temperature range of measurements. We observe that the mobility type changes from n-type (negative values) for temperatures higher than 60 K to p-type (positive values) for temperatures lower than 60 K. This change of sign has been observed previously in Ti implanted Si samples [12] and can be explained in terms of the electrical bilayer decoupling. In this case only are measured the transport properties of the implanted and PLM top layer where the majority charge carriers must be holes.

The Si sample implanted with Si and subsequently PLM

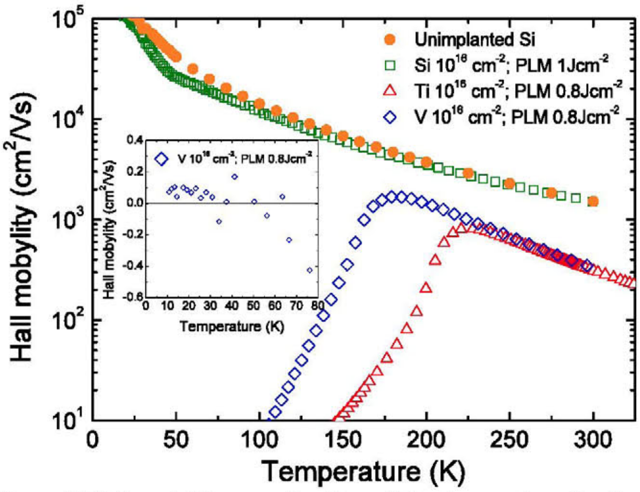

Figure 2 Hall mobility as a function of the temperature for the unimplanted Si sample, the Si sample implanted with Si at 10^{16} cm^{-2} dose, the Ti implanted sample at 10^{16} cm^{-2} dose and the V implanted sample at 10^{16} cm^{-2} dose subsequently PLM processed at1, 0.8 and 0.8 Jcm^{-2} respectively. The inset shows the change of sign in the Hall mobility values of the vanadium implanted sample at low temperatures.

processed shows the same transport properties as the Si unimplanted sample concluding that the unusual behavior observed in the V or Ti implanted sample are due to the impurities and not to the fabrication processes.

In order to explain the physical nature of this electrical decoupling in the framework of the IB theory we have schematized in Fig. 3 the band diagrams corresponding to our bilayer junction at 300 K and at 100 K. In this diagram we assume the IB formation in the implanted layer.

It is expected that the Fermi level should be pinned at the IB energy in the implanted layer since the IB would have a high density of states. Then, the carrier concentration at the CB and VB of the implanted layer should be determined by the Maxwell-Boltzmann statistics and their densities are going to be strongly dependent of the temperature. At 300 K, the thermal energy is enough to promote charge carriers from the IB to the CB in the implanted layer, while at the Si substrate we have the extrinsic electron concentration as it is expected for n-Si with a shallow donor dopant. In this situation the current flow is possible in both ways, from the implanted layer to the n-Si substrate and from the n-Si substrate to the implanted layer. That is, the bilayer is electrically coupled. We have to keep in mind that the carriers at the IB are confined in the implanted region due to the IB has not continuity in the Si substrate and there is not possibility for them to flow towards the substrate.

However, as the temperature decreases and depending on the IB energetic distance from the CB, the Maxwell-Boltzmann statistic will give us a negligibly electron concentration in the CB of the implanted layer. In this situation electron flow from the implanted layer to the n-Si substrate is not possible. Besides this, as the substrate is n-type conduction by the VB is not possible. Therefore the IB material is totally isolated. The temperature for this decoupling, which is the temperature where the sheet resistance starts to increase, is consequently an indirect measure of the IB position. As the temperature decrease, the junction resistance of the implanted layer – Si substrate begins to increase. At very low temperatures, when the electron concentration in the CB of the implanted layer is negligible we would be only measuring the transport properties of the IB. This fact justifies the mobility behavior observed as well as the change of sign of the majority charge carriers meaning that the IB carriers behave as holes.

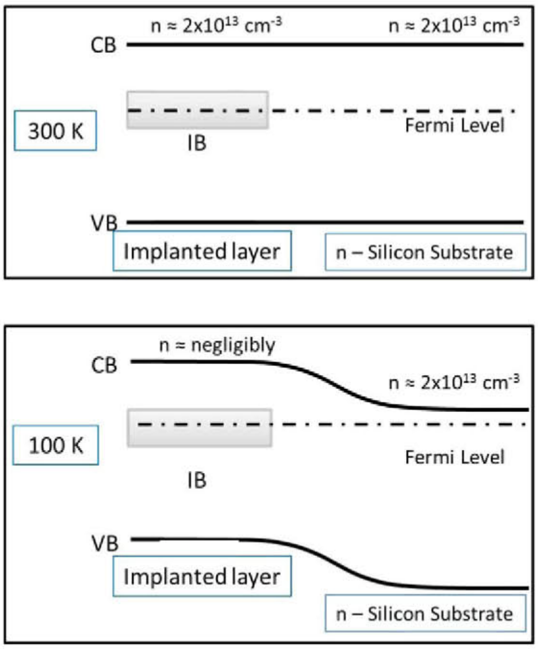

Figure 3 Band diagrams of the implanted layer/n-Si substrate structure at 300 K and 100 K.

We have developed recently an analytical model to fit the experimental sheet resistance and mobility data [12]. Fig. 4 and 5 show the experimental data and the model results for the sheet resistance and the mobility for the Ti and V samples. The fitting is excellent from RT to 155 K for V and to 190 K for Ti, which is the onset of the decoupling. The error between the model and the experimental data in this region is below 1.5%. Nevertheless the experimental resistance increase during the decoupling runs slower than the model prediction. This indicates the possibility of having an additional conduction mechanism on the implanted layer substrate junction extra to the ideal limitation and we are working on it.

The model fitting concludes a junction resistance thermically activated with an activation energy ΔE=0.205 eV. This value is clearly different than the ΔE=0.445 eV found for the Ti samples. This magnitude determines the different temperatures found for the sheet resistance minimum suggesting that the IB-CB energy distance is lower in the V sample than in the Ti sample. It is important to note that these values for the exponential factor are valid just for the 0.8 J/cm^2 annealing and for the 10^{16} cm^{-2} doses.

At room temperature we cannot measure directly the transport properties of the IB. However, using the analytical model we can extract a value of the IB sheet resistance that could be defined as 1/qpμt where q is the electron charge, p and μ are the carrier concentration and mobility of carriers at the IB and t is the implanted thickness with impurity concentration

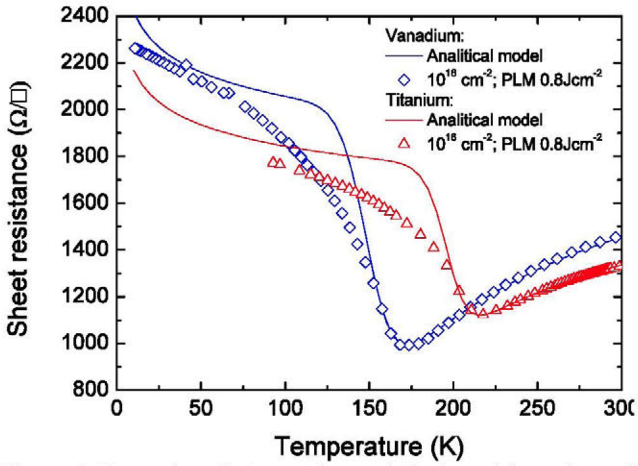

Figure 4 Comparison between the analytical model results and the measured values for the sheet resistance as a function of the temperature in the Ti implanted sample at 10^{16} cm^{-2} dose and the V implanted sample at 10^{16} cm^{-2} dose subsequently PLM processed at 0.8 Jcm^{-2}.

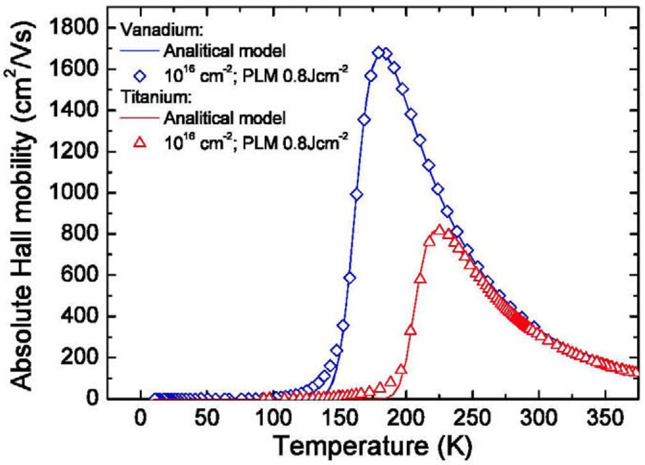

Figure 5 Comparison between the analytical model results and the measured values for the mobility as a function of the temperature in the Ti implanted sample at 10^{16} cm^{-2} dose and the V implanted sample at 10^{16} cm^{-2} dose subsequently PLM processed at 0.8 Jcm^{-2}.

over the Mott limit. The values obtained using this analytical model at room temperature is of 1.7kΩ/□ for the Ti sample and 1.9kΩ/□ for the V one at room temperature. These values suggest that the IB formed with V has very similar transport properties than the Ti one but to determine each parameter of the previous formula we need to know t using SIMS, which is under process.

In conclusion, Ti and V supersaturated Si has been obtained by means of ion implantation and PLM processing. The sheet resistance and hall mobility as a function of the temperature measurements show an unusual behavior that has been attributed to an electrical decoupling in the bilayer structure obtained. This electrical decoupling has been well explained in the framework of the IB theory, assuming that our bilayer structure is composed by a junction formed by an IB material on top of a n-Si substrate. By means of an analytical model we have fitting with accuracy the experimental curves of the sheet resistance and mobility, proving that this model explain the physics of the decoupling process. Important differences, as the IB-CB energy distance have been observed as a function of the implanted element, showing that the vanadium implanted sample presents an IB-CB energy distance lower than the Ti implanted sample. These results are very interesting since imply that we are able to engineer this Si based IB material.

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