Low temperature intermediate band metallic behavior in Ti implanted Si

Javier Olea*, David Pastor, Eric García-Hemme, Rodrigo García-Hernansanz, Álvaro del Prado, Ignacio Mártíl, Germán González-Díaz

Dpto. Física Aplicada III (Electricidad y Electrónica), Facultad de Ciencias Físicas, Univ. Complutense, 28040 Madrid, Spain

1. Introduction

The Intermediate Band (IB) concept has attracted much attention in the photovoltaics field because of its capacity to substantially improve the efficiency of solar cells [1]. An IB located within the bandgap of a traditional semiconductor could take part in the photogenerated current acting as an intermediary step for electrons absorbing low energy photons. This IB should be semi-filled in order to accept transitions from the valence band to the IB and from the IB to the conduction band. The preservation of the open-circuit voltage is also a cause of concern since a direct connection of the IB to the external contacts would reduce the effective bandgap of the structure and obviously the maximum efficiency of the IB device [2]. To avoid this situation, the IB material has to be sandwiched between two emitters, n-type and p-type. In this way the efficiency of an IB solar cell could be maximized up to values well above the Shockley–Queisser limit [3].

There are several possibilities to fabricate IB materials, being the deep level approach one of the most promising. To fabricate an IB material using deep levels we need to introduce a high concentration of impurities in a host semiconductor [4]. If the Mott limit is surpassed, the wavefunctions of the electrons associated with the impurities should overlap, and a band inside the bandgap would be formed. This task might be achieved with the use of techniques out of thermodynamical equilibrium, such as the combination of ion implantation and Pulsed-Laser Melting (PLM), as it has been proposed recently [5]. Remarkable results have been obtained by implanting chalcogenide elements in Si and subsequently annealing with the PLM technique [6,7]. However, bulk IB materials might be fabricated using other procedures such as molecular beam epitaxy [8].

Ti implanted Si has been thoroughly analyzed in the last years as a promising candidate for IB solar cells [9]. Measurements by means of the quasi-steady-state photoconductance technique on Si:Ti samples concluded the reduction of the non-radiative recombination processes, showing the increase of lifetime as Ti concentration is increased [10]. Moreover, optical measurements probed the appearance of a strong sub-bandgap absorption related to the Ti presence [11].

Recently, we have studied Si implanted with extremely high Ti doses, showing that the electronic transport properties of this material are well explained on the basis of an IB formation [12]. From the Hall effect measurements we have deduced that carriers at the IB in these Ti implanted Si samples behave as holes and therefore conduction at the IB has been modeled as p-type [13]. However, the nature of the carriers at a semi-filled IB is a matter of concern and should be deeply studied. In this work we progress in the IB theory by analyzing the conductivity and Hall effect at low temperature of Si samples implanted with very high Ti doses.

2. Experimental

Si n-type (111) 1×1 cm² square samples (μ≈1450 cm²/Vs, n≈2.2×10¹³ cm⁻³, at room temperature) 300 μm thick were implanted with ⁴⁸Ti⁺ in a VARIAN CF3000 ion implanter refurbished by Ion Beam Services Ltd. (France). Implantations were performed at 32 keV with doses in the 10¹⁴–10¹⁶ cm⁻² range. Subsequently, samples were annealed with the PLM technique with a 20 ns long pulse at JPSA Inc. (New Hampshire, USA). After PLM Si:Ti layers with a thickness in the order of 100 nm
are produced [14]. Triangular Al contacts were evaporated in the sample corners to obtain ohmic contacts. Finally, samples were characterized with a Keithley SCS 4200 model by means of conductivity and Hall effect measurements using the van der Pauw set-up and varying the temperature in the 7–300 K range in a closed-cycle Janis cryostat. In order to minimize the differences between the temperature measured and the actual sample temperature, an OFHC copper sample holder Au coated was used, and the thermocouple was placed close to the sample. Fig. 1 shows a diagram of the samples and the measurement set-up for the characterization of the resistivity.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurements were also carried out in order to obtain the Ti depth profile. The complete experimental set-up for this characterization can be found in Ref. [15].

3. Results and discussion

3.1. Bilayer model

Recently, we have developed a two-layer model to study Ti implanted Si with extremely high doses and subsequently PLM annealed samples [13]. Previous experimental results analyzed in the scope of this model, showed that in this material a p-type IB is formed out of the Ti deep levels in the implanted layer. In order to understand the electronic transport properties of the bilayer (implanted layer and n-type substrate), we have to take into account conduction by electrons in the conduction band of the substrate, conduction by electrons in the conduction band of the implanted layer and conduction at the IB in the implanted layer. Following the previous results, conduction at the IB will be considered as carried by holes [13]. Nevertheless, the main conclusions extracted from the present study could be applied to any IB material, independent of the type of carriers at the IB. Hole density in the valence band is considered negligible in the n-type substrate. Since the Fermi level would be pinned deep in the bandgap, at the IB (at about 0.36 eV from the conduction band according to the results reported in Ref. [13]), the hole density is also neglected in the valence band of the implanted layer. Moreover, a strong temperature dependent rectifying behavior is found at the IB/n-Si substrate junction that is modeled with a decoupling function F [12,13]. This function models the temperature dependent resistance of the junction in inverse polarization. At temperatures over 200 K the resistance of the junction is low, and the IB material and the substrate can be analyzed in parallel. At temperatures below 200 K the resistance of the junction is high enough to progressively decouple the substrate from the implanted layer and therefore rule it out from the measurement in the van der Pauw set-up.

Having a bilayer in which conduction takes place by electrons in the conduction band and holes in the IB in layer 1, and by electrons in the conduction band in layer 2 (see Fig. 2), the sheet resistance can be expressed as follows [13]:

\[ R_s = \frac{G_{s1} + G_{set} + G_{s2}F^2}{(G_{s1} + G_{set} + G_{s2}F)} \]  

(1)

Where \( G_{s1} \) is the sheet conductance associated with holes in the IB, \( G_{set} \) is the sheet conductance associated with electrons in conduction band of layer 1, and \( G_{s2} \) is the sheet conductance associated with electrons in conduction band of layer 2. \( F \) is the decoupling function quoted above. The effective mobility of the bilayer can be expressed as follows [13]:

\[ \mu_{eff} = \frac{\mu_{h1} G_{s1} - \mu_{h2} G_{s2} - \mu_{e} G_{s2} F^2}{G_{s1} + G_{set} + G_{s2} F^2} \]  

(2)

Where \( \mu_{h1} \) is the mobility of holes in the IB, \( \mu_{h2} \) is the mobility of electrons in the conduction band of layer 1, and \( \mu_{e} \) is the mobility of electrons in the conduction band of layer 2. These expressions model the sheet resistance and effective mobility of a bilayer, respectively, measured by the van der Pauw technique.

Using Eqs. (1) and (2), we can calculate the effective Hall sheet carrier concentration of the bilayer:

\[ n_{eff} = \frac{1}{qR_s \mu_{eff}} = \frac{1}{q} \frac{(G_{s1} + G_{set} + G_{s2}F)^2}{\mu_{h1} G_{s1} - \mu_{h2} G_{s2} - \mu_{e} G_{s2} F^2} \]  

(3)

\( R_s, \mu_{eff} \) and \( n_{eff} \) depend on the electronic transport properties of the IB material and the substrate, and therefore it is not intuitive to obtain useful conclusions from Eqs. (1)–(3). Nevertheless, we can perform some plausible simplifications.

First of all, it has been reported that at low temperatures \( F \) tends to zero due to the rectifying behavior of the junction, and consequently, \( R_s, \mu_{eff} \) and \( n_{eff} \) would depend less and less on the substrate properties [12,13]. As a consequence, measurements at low temperatures could throw light upon the actual transport properties of the IB.

Moreover, at temperatures low enough, depending on the energy difference between the IB and the conduction band in layer 1, the electron concentration in this conduction band would tend to vanish, according to a freezing out process. We have to take into account that as a result of the extremely high impurity concentration needed to form the IB, the Fermi level is pinned in this IB in layer 1 [13]. Eventually, the condition \( \mu_{h1} p_1 >> \mu_{e} n_1 \) could be satisfied, where \( n_1 \) is the electron concentration at the conduction band in layer 1 and \( p_1 \) is the hole concentration at the IB in layer 1. This condition expresses that the conductivity associated with the IB dominates the electrical transport properties in layer 1. In this case, making the assumption that the IB is a metallic semi-filled band with \( p_1 \) a very high hole concentration, at low temperatures the effective Hall sheet carrier concentration would tend to \( n_{eff} = p_1 t_1 \), where \( t_1 \) is the thickness of the
IB material. Similarly, the effective Hall mobility would tend to $\mu_{\text{eff}} = \mu_1$ at low temperature.

For an IB material in which the IB is located deep enough in the band gap, the electron concentration in the conduction band in layer 1 in equilibrium, which depends ultimately on the thermal generation from the IB, would be very low at temperatures well below 300 K. Moreover, if the IB material has been fabricated introducing a very high concentration of deep impurities [4], the mobility of electrons at the conduction band in layer 1 would be much lower than the mobility of a perfect non-impurified semiconductor. In this situation, the condition $\mu_{\text{eff}} \mu_2 \gg \mu_1 t_1$ is always satisfied in the range of temperatures analyzed here, and the simplifications of Eqs. (1)–(3) can be applied.

However, at low temperature, where the decoupling function $F$ tends to zero, the influence of the substrate on Eqs. (1)–(3) has to be discussed. The condition $\mu_{\text{eff}} \mu_2 t_1 \gg \mu_1 t_2 F$, where $t_2$ is the thickness of the substrate, shall be only satisfied for very low values of $F$, since $t_2 \gg t_1$ (about three orders of magnitude higher in this work). If we take for the IB material properties, the values quoted in Ref. [13] ($\mu_1 \approx 0.5 \text{ cm}^2/\text{Vs}$; $n_1 = 1.7 \times 10^{20} \text{ cm}^{-3}$; $t_1 = 80 \text{ nm}$), and for the substrate the values in the experimental section ($\mu_2 = 1450 \text{ cm}^2/\text{Vs}$; $n_2 = 2.2 \times 10^{13} \text{ cm}^{-3}$; $t_2 = 300 \mu\text{m}$), the previous inequality would be satisfied only for values of $F$ below $10^{-3}$. This result means that in the IB/ n-Si substrate junction, the direct polarization current would be at least $10^3$ times higher than the inverse polarization current for the same polarization voltage. For values of $F$ over $10^{-3}$ an incomplete decoupling would be shown and the bilayer electronic transport properties would still be dependent on the substrate properties making the analysis more complicated.

In the case of the Ti implanted Si samples analyzed here, in which a p-type IB is formed and an n-type substrate has been used, there should be a critical temperature low enough at which both the conditions quoted above become true. Below that critical temperature, $\mu_{\text{eff}}$ would tend to $\mu_2$, and $n_{\text{eff}}$ would tend to $n_1$. Since the sign of the IB Hall mobility $\mu_1$ (p-type) is different from the sign of the IB (n-type), at the critical temperature $\mu_1$ would cross zero and $n_{\text{eff}}$ would go to infinity. Obviously, experimentally one would measure a very low Hall mobility and a very high Hall sheet carrier concentration at that temperature. However, the point of zero effective mobility would mark the proximity of a complete decoupling. Below this temperature one could measure directly the IB transport properties. In the following section we will discuss deeply the experimental results in order to confirm the theoretical model shown above.

3.2. Experimental findings

Fig. 3 shows the Hall mobility as a function of temperature measured for an unimplanted Si substrate and for two implanted samples. The inset shows the Hall mobility at low temperatures of the sample implanted with the highest dose ($10^{14}$ cm$^{-2}$). Except for the values in the inset below 45 K, Hall effect experiments result in n-type conduction for the three samples. To distinguish between p-type and n-type conduction, the sign of the Hall factor has been used to represent the mobility in the inset, and therefore p-type and n-type mobility are shown with positive and negative values, respectively.

The mobility of the unimplanted sample follows the usual trend, showing the phonon scattering from room temperature down to approximately 20 K. The mobility of the sample implanted with the lowest dose has a behavior almost equal to the Si reference sample, except for the low temperature range. On the contrary, the mobility of the sample implanted with the highest dose, has the IB behavior reported previously [12,13]. Below 225 K the mobility decreases as the temperature is reduced, which indicates the drop of the decoupling function $F$ and the trend to $\mu_{\text{eff}} = \mu_1$.

Regarding the low temperature range behavior, the resulting Hall mobility of the sample implanted with a dose of $10^{14}$ cm$^{-2}$ does not reflect the IB rectifying behavior reported previously [12,13]. This IB behavior is characterized, as the sample implanted with the highest dose shows, by a very abrupt decrease of the mobility around 200 K and by very low Hall mobilities at low temperatures. As a consequence, it cannot be stated that in the sample implanted with the lowest dose the IB has been formed. However, the differences between this sample and the reference substrate seem to point out that the Ti impurities are beginning to interact due to the proximity and the onset of a well-formed IB might be close.

On the other hand, the sample implanted with the highest dose has a completely different behavior that has been recently explained by the IB theory [12,13]. Values of Hall mobility in the inset show that for low temperature the effective mobility still decreases when the temperature is reduced. At about 45 K, it crosses zero and tends to a constant value of approximately 0.5 cm$^2$/Vs corresponding to p-type conduction. Although Hall effect in samples with very low mobility is difficult to be measured with reliability, special care have been taken in this temperature range. This result is repeatable and similar mobility values have been obtained for different samples [12,13].

This result can be explained by the model developed above, showing that below 45 K the decoupling function $F$ is low enough to neglect conduction by the substrate. In this situation, Eq. (2) would be simplified to $\mu_{\text{eff}} = \mu_1$. Consequently, the mobility measured below 45 K would be just the IB mobility. Moreover, the positive sign of the Hall effect would point out that carriers in the IB behave as holes. The different behaviors observed for the samples implanted with different doses could point out that the minimum Ti dose necessary to form an IB in Si with the processing conditions used in this work would be between $10^{14}$ and $10^{15}$ cm$^{-2}$ [16]. New experiments are under way in order to specify the IB formation limit in Ti implanted Si.

In a previous work the authors reported (Ref. [13]) that samples implanted with doses over $10^{15}$ cm$^{-2}$ and PLM annealed with energy density of 0.8 J/cm$^2$ did not reach a perfect crystalline structure. Samples processed in such way had a recovered lattice but presented a rather high concentration of defects. However, the electrical behavior of these samples followed the trend predicted by the IB model, in the same way as the samples perfectly recrystallized. We therefore assume that the main conduction mechanism associated with the IB formation is still present in the defective samples, and the main consequence of the defects is to reduce the mobility. Since the mobility in the IB is expected to be very low, as corresponds to a narrow band, conduction by the IB would not be dramatically affected by the presence of defects. This hypothesis is consistent with the similarity of the
effective Hall carrier concentration of the sample increases when the temperature of the sample implanted with the highest dose is almost constant in the range measured down to 45 K, showing a smooth freeze-out process below 50 K (see inset). This result is in agreement with the proposed scenario of interaction of impurities due to proximity. This interaction would reduce the activation energy of carriers and therefore the freeze out effect would begin at lower temperatures. The high concentration of Ti in this sample would also reduce the mobility as it can be observed in Fig. 3.

On the other hand, the sample implanted with the highest dose shows a striking behavior between room temperature and 45 K. The effective Hall carrier concentration of this sample increases when the temperature is decreased due to the decoupling of the substrate (the $F$ function tends to zero), until it reaches a maximum at about 45 K. This maximum is related to the zero effective Hall mobility feature located at the same temperature (see Fig. 3). At temperatures below 45 K a complete decoupling of the substrate would have taken place, and according to the model proposed in the previous section the effective Hall carrier concentration of the sample would be just the hole concentration at the IB. Fig. 4 shows that below 45 K the effective Hall carrier concentration measured is constant down to about 7 K. For this sample no freeze out effect is shown, and therefore a metallic behavior is displayed, corresponding to a semi-filled IB. This result is consistent with the model proposed, and means that the Fermi level would be inside the IB for all the temperature range down to 7 K. This shows that it is not necessary to co-dope Ti implanted Si to form a semi-filled IB, as it seems to occur in the chalcogen implanted Si case [9,17].

To display the volumetric Hall carrier concentration of the three samples in Fig. 4 the thickness of the substrate has been used as reference, i.e. 300 μm. However, below 45 K a complete decoupling of the substrate takes place in the sample implanted with the highest dose due to the temperature dependent substrate decoupling effect inherent to the structure depicted in Fig. 2[12,13]. To show the actual carrier concentration of this sample below 45 K we should take into account only the thickness of the implanted layer, which is about 80 nm (see inset in Fig. 5). This would result in a constant Hall carrier concentration of about $2 \times 10^{21}$ cm$^{-3}$.

Surprisingly, an increase of only two orders of magnitude in the implantation dose results in an increase of more than four orders of magnitude in the low temperature volumetric carrier concentration. Similar results have been obtained for S doped Si in which an insulator–metal transition has been reached [18]. Moreover, $2 \times 10^{21}$ cm$^{-3}$ is roughly the Ti concentration present in the 80 nm layer according to ToF-SIMS measurements in Fig. 5, which is over the IB theoretical formation limit. This enormous hole concentration cannot come from an increase in the carrier concentration in the valence band, since Ti is not a shallow dopant, and thus the hypothesis of a metallic semi-filled IB formation is consistent. Conversely, the sample implanted with the lowest dose presents a Ti concentration below the Mott limit except for a very thin superficial layer that slightly surpass this limit. In light of the presented results, we suggest that in the sample implanted with the highest dose an IB has been formed, showing a metallic behavior and a positive Hall effect. The sample implanted with the lowest dose shows a progressive behavior toward the insulator-to-metal transition.

Finally, and in order to unambiguously support the hypothesis of an insulator–metal transition in highly Ti impurified Si samples, the conductivity data for the same samples analyzed in Figs. 3 and 4 is presented in Fig. 5. The conductivity of the unimplanted sample dramatically decreases at low temperatures, due to the freeze out effect of the shallow dopants. However, the sample implanted with a dose of $10^{18}$ cm$^{-2}$, presents a conductivity that does not have an abrupt drop at low temperatures, indicating a transition between the unimplanted reference substrate and the sample with IB. At temperatures over 50 K, the conductivity of this sample is almost equal to the substrate conductivity, as expected.

The sample with the highest implanted dose presents an almost constant conductivity in the whole range, even at the lowest temperature measured, corresponding to a metal behavior. Again, to represent the conductivity, the substrate thickness (300 μm) has been used. If the IB layer thickness is introduced in the calculation a rather high conductivity of about 170 $\Omega^{-1}$ cm$^{-1}$ is obtained at low temperatures. In Ref. [18], the authors claim that an insulator–metal transition has been surpassed in Si samples highly impurified with S using similar fabrication techniques. In fact, the implantation doses used in Ref. [18] and in the present work are in the same order, and once the transition has been overcome, samples S impurified present conductivities in the same range as samples impurified with Ti (close to 200 $\Omega^{-1}$ cm$^{-1}$). This could indicate that the origin of the insulator–metal transition would be similar in both systems, claimed to be the formation of an IB.

![Fig. 4](image-url) Arrenius plot of Hall carrier concentration as a function of the sample inverse temperature of a Si unimplanted reference sample and of two Ti implanted samples with $10^{14}$ and $10^{16}$ cm$^{-2}$ doses. The inset shows the carrier concentration at low temperature of the sample implanted with the $10^{14}$ cm$^{-2}$ dose.

![Fig. 5](image-url) Conductivity as a function of the sample temperature of a Si unimplanted reference sample and of two Ti implanted samples with $10^{14}$ and $10^{16}$ cm$^{-2}$ doses. The inset shows the Ti depth concentration measured by ToF-SIMS.
4. Conclusions

Si samples implanted with high Ti doses have been electrically measured and analyzed using a recently developed two-layer model. The differences found between the sample implanted with a dose of $10^{14}$ cm$^{-2}$ and the sample implanted with a dose of $10^{16}$ cm$^{-2}$ suggest that the Mott limit is in between, and that in the sample implanted with the highest dose an IB has been formed. The formed IB would be semi-filled and populated by holes as we have deduced from Hall effect measurements.

An enormous increase in the Hall carrier concentration has been measured in the sample with IB behavior with respect to the sample implanted with the lowest dose, showing a carrier concentration roughly equal to the Ti concentration in the implanted layer. Conductivity measurements support the hypothesis of an insulator–metal transition on the onset of the IB formation. All these results are of extreme importance for the IB theory, and represent an advancement in the understanding of IB materials based on Si.

Acknowledgments

Authors would like to acknowledge the C.A.I. de Técnicas Físicas of the Universidad Complutense de Madrid for ion implantation experiments and the Nanotechnology and Surface Analysis Services of the Universidad de Vigo C.A.C.T.I. for ToF-SIMS measurements. This work was partially supported by the Projects GENESIS-FV (CSD2006-0004) funded by the Spanish Consolider National Programme, NUMANCIA II (S-2009/ENE-1477) funded by the Regional Government of Comunidad de Madrid and grant GR58/08 funded by the Universidad Complutense de Madrid.

References