**Supporting information**

In Fig. S1 we plot, for the SI-GaP:Ti sample implanted with 8×1014 cm-2, the different fits to four classical formulae related to absorption transitions relating bands (*R. H. Bube, Photoconductivity of solids, pp. 212 – 215, 1960*; and *G. Lucovsky, Optical absorption associated with deep impurity centers in semiconductors, Bull. Am. Phys. Soc., 11, 206, 1966*):

* for indirect bandgap transitions.
* for direct bandgap transitions.
* for transitions from the VB to a gap state.
* for transitions from a gap state to the CB.

Note that the magnitude shown is different for every formulae, and that the ordinates axis is shown in logarithmic scale in order to better see all the fits in the same graph. All the experimental curves are the transformation to a linear fit of the previous formulae. For example, the magnitude shown for the formula is , being the measured sheet photoconductance. With this particular transformation we would obtain the energy of the transition, , by a linear fit.

As it can be seen, the best fit to all the energy range is the one related to indirect band-to-band transitions. In order to obtain a good linear fit for the other formulae, we would have to reduce the energy range used.



**Figure S1.** Transformation of the measured sheet photoconductance of the SI-GaP:Ti sample implanted with the 8×1014 cm-3 as a function of the photon energy to the four classical formulae referenced above. Symbols are the measured data, while lines are the linear fit (note that the ordinates axis is in a logarithmic scale).

In the following table we show the coefficient of determination, R2, of all the linear fits to the formulae presented above, for all the samples analyzed. As it can be seen, the best fit is the one for indirect bandgap transitions, although the fit to the formula of transitions from a gap state to the conduction band is also quite good. Therefore we suggest that the transitions related to the Ti levels are indirect transitions from the valence band to the Ti impurity band or from the Ti impurity band to the conduction band, or both at the same time, since the energy of the transition is just at the middle of the GaP bandgap and both transitions would be overlapping.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Indirect** | **Direct** | **VB to state** | **State to CB** |
| **Un-GaP:Ti 8×1014 cm-2** | 0.9487 | 0.9143 | 0.8283 | 0.9755 |
| **Un-GaP:Ti 2×1015 cm-2** | 0.9881 | 0.8210 | 0.7008 | 0.9608 |
| **SI-GaP:Ti 8×1014 cm-2** | 0.9843 | 0.5462 | 0.4409 | 0.8934 |
| **SI-GaP:Ti 2×1015 cm-2** | 0.9759 | 0.7268 | 0.5932 | 0.9578 |

Figure S2 shows the fits of the sheet photoconductance spectra presented in Fig. 2 to the equation describing transitions of an indirect bandgap.





**Figure S2.** Linear fits of the sheet photoconductance spectra of the four GaP:Ti samples analyzed in the paper. The fits yield the energy of the transition corresponding to the GaP:Ti material, as depicted in Fig. 2 Left.

Figure S3 shows XTEM images of an unimplanted SI-GaP substrated PLM processed. As it can be seen the crystalline “bubble” has the same grown direction of the substrate, and the surface of the sample can be perceived (Left image). In Fig. S3 Right a detail of the passivating amorphous layer is shown, and no extended defect are present.

 

**Figure S3.** XTEM images of an unimplanted SI-GaP sample PLM processed.

In Fig. S4 we show XTEM images of SI-GaP:Ti samples PLM processed. In both images the stacking faults with twins, a “bubble” and the passivating layer can be observed. The sample with the highest dose (Right) is more defective. Also the “bubble” presents a “volcano” structure that could be an indication of cellular breakdown, but a deeper analysis is mandatory to confirm this hypothesis.

 

 

**Figure S4.** XTEM images of two SI-GaP:Ti samples PLM processed. The doses are 8×1014 cm-2 (top-left) and 2×1015 cm-2 (top-right). The bottom images are a magnification of the features in the top-right image.

Fig. S5 shows some ToF-SIMS measurements that support the XEDS results about the composition of the surface passivation layer. As it can be seen, the Ga+/P+ ratio decreases at the surface for the Un-GaP:Ti sample, while for the Un-GaP reference sample the ratio is almost constant. Consistently, the O+ signal emerges at the surface for the Un-GaP:Ti sample, confirming the presence of a measurable quantity of oxygen. Since the XEDS data was obtained from unimplanted SI-GaP samples and the ToF-SIMS data was measured on Un-GaP:Ti samples, these results are independent of the type of substrate and the Ti implantation, and are originated by the PLM process. However, due to the very thin nature of the surface layer and the surface artifacts of the ToF-SIMS technique, more dedicated experiments are needed to definitively quantify the composition of the oxide surface layer.



**Figure S5.** ToF-SIMS signals obtained for Ga+ and P+ (combined in the Ga+/P+ ratio), and O+ measurements. The experimental details can be obtained in Ref. **¡Error! Marcador no definido.** of the manuscript. Blue plots are for an Un-GaP unimplanted reference sample (not PLM processed), while red plots are for an Un-GaP:Ti sample PLM processed inside the process window.

Finally, Fig. S6 show the phase of the GaP:Ti samples analyzed in the paper. As it can be seen, for the samples showing the collapse in the photoconductivity (Un-GaP:Ti) there is an abrupt phase change of about 40˚, at the same wavelength of the collapse. Intuitively, if positive and negative photoconductivity are shown in the same spectrum, a 180˚ change in the lock-in phase should have been measured in between. However, as pointed in [32], the phase of the measurement depends not only on this effect, but more generally on the response time of the sample. This response time would be dependent on the properties of the sample, and it does not have to be the same at all wavelengths. Measured phase corresponding to the spectra shown in Fig. 2 are included in the Supporting Information section. Only a 40˚ phase change was measured at the wavelength of the collapse, but its abrupt nature would point also to a change from negative to positive photoconductivity.



**Figure S6.** Measured phase obtained with the lock-in amplifier of the same samples analyzed in the paper (see Fig. 2 Left).