Hyperdoped germanium photodetectors by ion implantation and pulsed laser recrystallization

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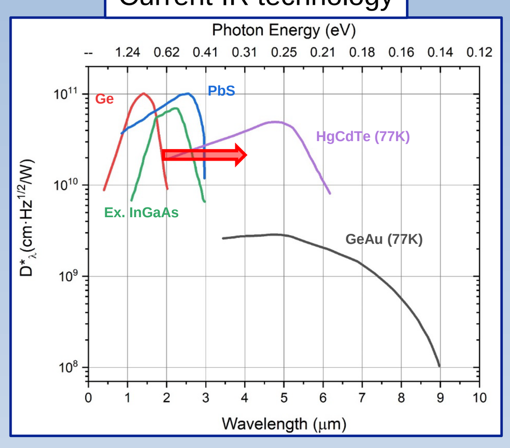
MOTIVATION

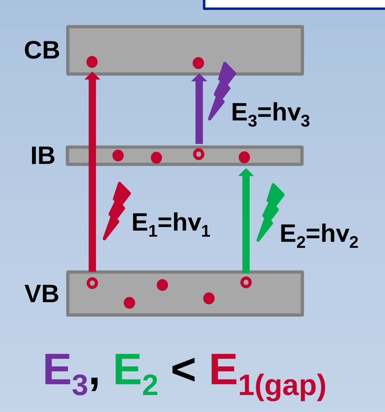
To extend the IR photoresponse of Ge to longer wavelengths **at room temperature**

Current IR technology



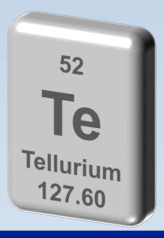
Ge advantages:
- Bandgap photoresponse up to 2 μm
- CMOS compatible
- Neither contaminant nor toxic
- Abundant in the earth's crust
- Mature technology

Intermediate Band concept



E_3, E_2 < $E_{1(gap)}$

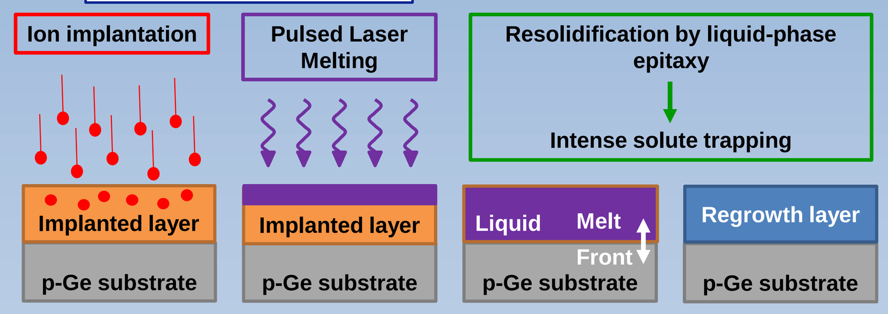
The **intermediate band** (IB) concept was introduced by Luque and Marti in 1997 [1]. If a concentration of impurities is introduced in a semiconductor **overcoming the Mott Limit**, the wave functions of the electrons overlap, giving rise to a band which could allow transitions not only from the valence band (VB) to the conduction band (CB), but also **from the VB to the IB and from the IB to the CB.**



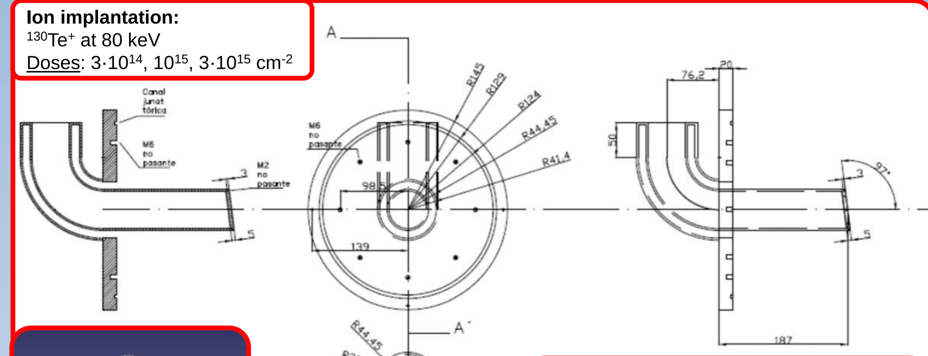
Te properties as an impurity:
- Donor levels: E_C – 0.11 and E_C - 0.3 eV
- Low diffusion coefficient: $2\cdot10^{-11}$ cm^2·s^{-1} at 800 ºC
- High Solid Solubility Limit: $2\cdot10^{15}$ cm^{-3} at 800 ºC

EXPERIMENTAL

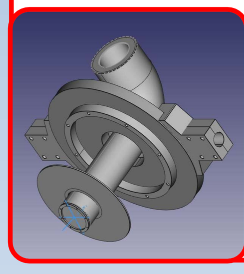
Fabrication processes



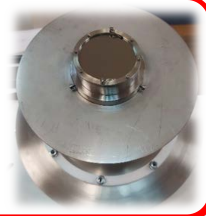
Substrate: p-Ge <100>, 300 μm thickness, ρ = 1 Ω·cm



Ion implantation:
^{130}Te$^+$ at 80 keV
Doses: $3\cdot10^{14}$, 10^{15}, $3\cdot10^{15}$ cm^{-2}



A modification of the Ion Implanter located at CAI de Técnicas Físicas has been **designed and assembled** for implanting at LN2 temperatures **(77K)**

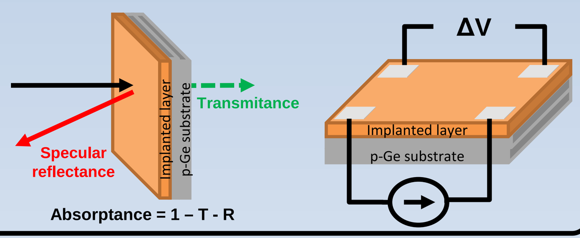


Characterization

Structural measurements
- **Scanning electron microscopy (SEM)** JSM-7600F at 15 kV operation voltage and 8 mm working distance.
- **Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)** ToF-SIMS IV model with a 25 keV pulsed Bi3$^+$ beam at 45° incidence.
- **Raman** NT-MDT NTegra Spectra at 532 nm Raman Shift from 165 to 398 cm^{-1} and 0,21 cm^{-1} step.

Optical measurements
Transmittance + Reflectance
Spectrometer **Perkin Elmer 950**
Wavelength: **400 nm to 3000 nm**

Electrical measurements
van der Pauw configuration
Sheet resistance and **Hall Effect** between 15 and 300 K.

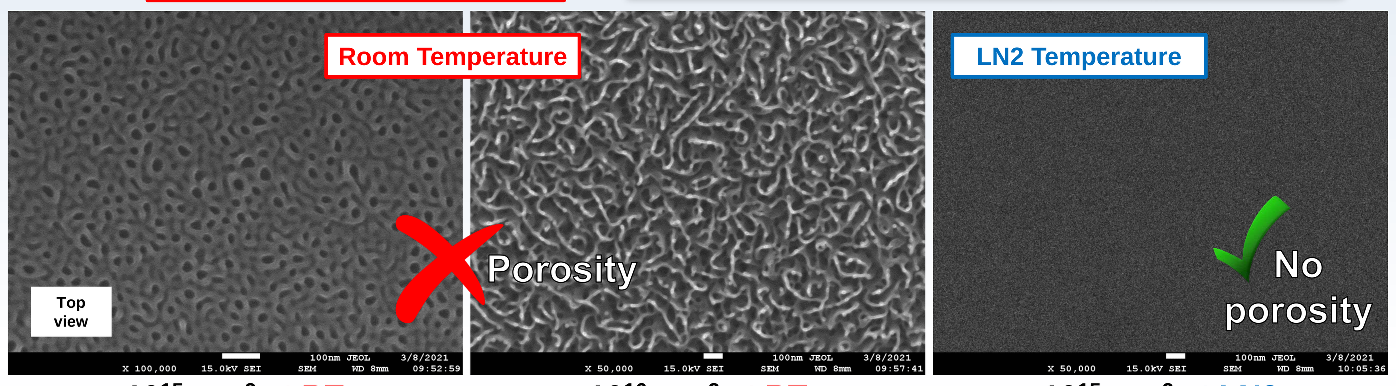


Pulsed Laser Melting: two different lasers
- **NdYAG** laser (UCM)
  - Wavelength: **355 nm**
  - Pulse duration: **4 ns**
  - Maximum Energy: 800 mJ
- Excimer laser (HZDR collaboration)
  - Wavelength **XeCl: 308 nm**
  - Pulse duration: **28 ns**
  - Energy Density: 0.5 J·cm^{-2}

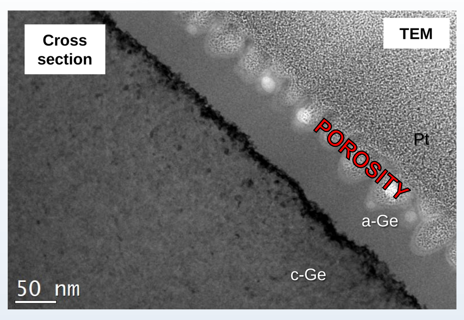
RESULTS

Structural results

Scanning Electron Microscopy — Porosity avoided by implanting at LN2 temperature



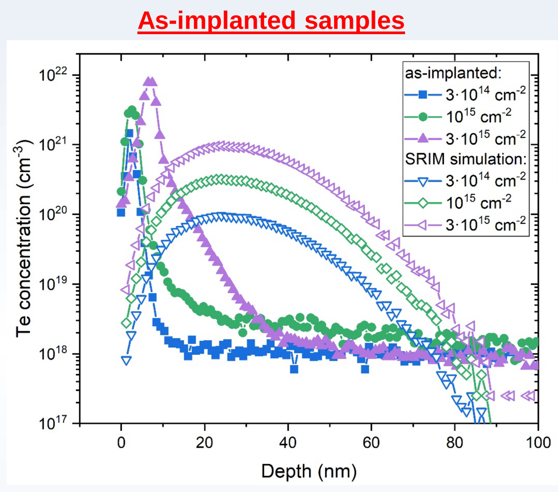
10^{15} cm^{-2} at RT — 10^{16} cm^{-2} at RT — 10^{15} cm^{-2} at LN2



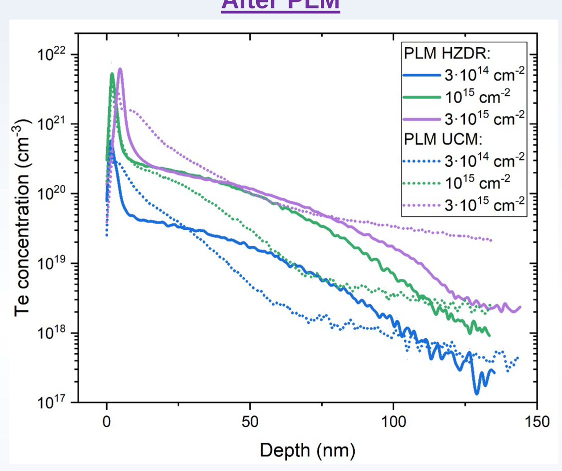
- **Ion implantation in germanium at room temperature** with heavy ions, at high doses or at high energies **produces porosity** in the substrate surface.
- This undesirable effect makes it **impossible to recover the crystallinity** of the material after any conventional annealing process.
- The porosity is increased as we increase the ion implantation dose.
- **Ion implantation at LN2 temperatures** (77K) **avoids** this **porosity** effect, leading to an a-Ge implanted layer, ready for laser annealing treatment.

ToF-SIMS — Implantations do not follow the simulations

As-implanted samples

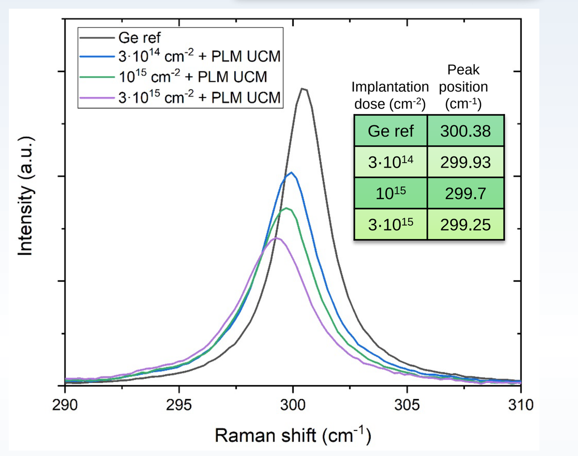


After PLM



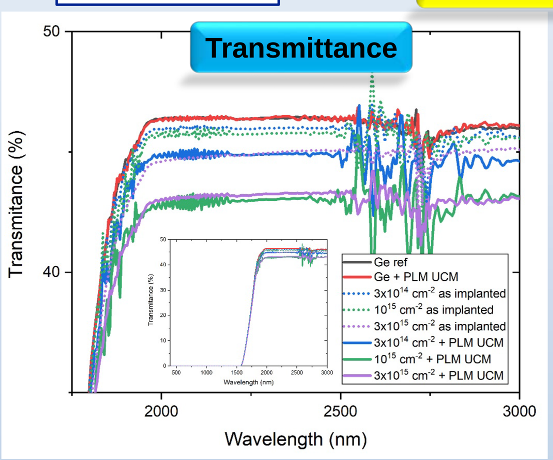
- We have overcome the **Solid Solubility Limit of Te in Ge** by several orders of magnitude.
- The as-implanted samples do not fit the SRIM simulations at room temperature. More experiments are underway.
- **After PLM**, the **Te$^+$ concentration profiles redistributes deep into substrate** for all samples and laser treatments.
- With the **UCM laser**, the **impurities** are redistributed **closer to the surface**, trapping more impurities than with the HZDR laser, probably because of its **shorter pulse duration**.

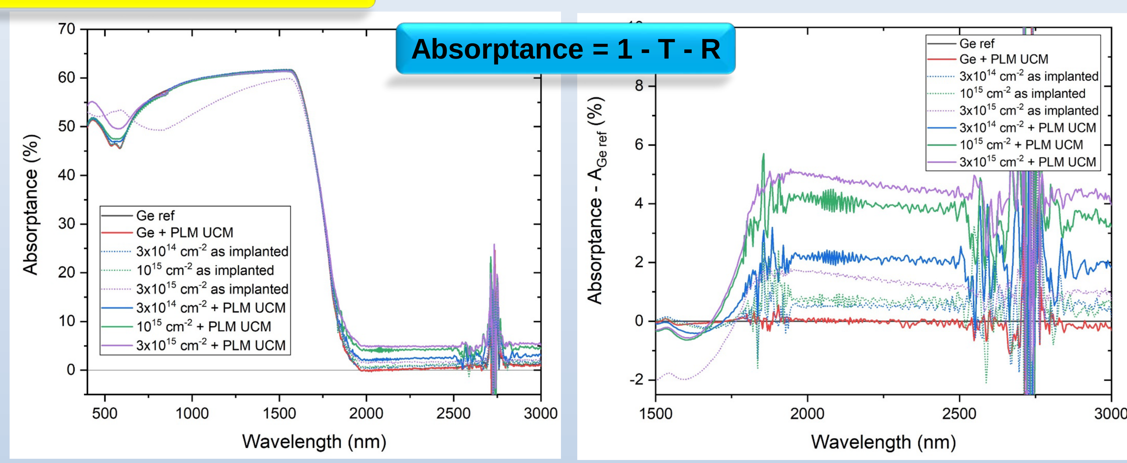
Raman — Strain produced by Te incorporation

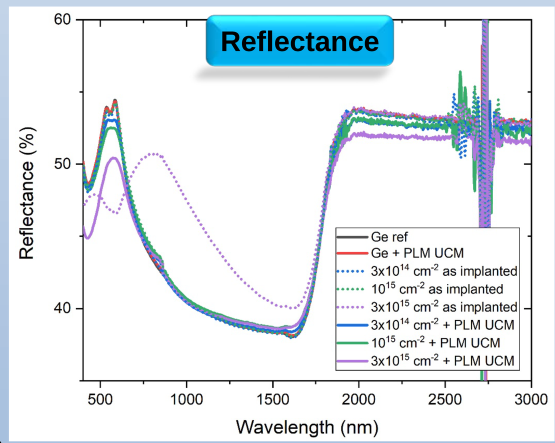


- The 300 cm^{-1} Ge-Ge Raman peak indicates that every annealed sample is perfectly crystalline the first 50 nm (the supersaturated region).
- The down-shift of the Ge-Ge peak is increased as we increase the dose, and it is likely originated from **strain induced by the Te incorporation**.
- The samples processed with the HZDR laser follows the same tendency (not shown).

Optical results — 5% sub-bandgap optical absorption

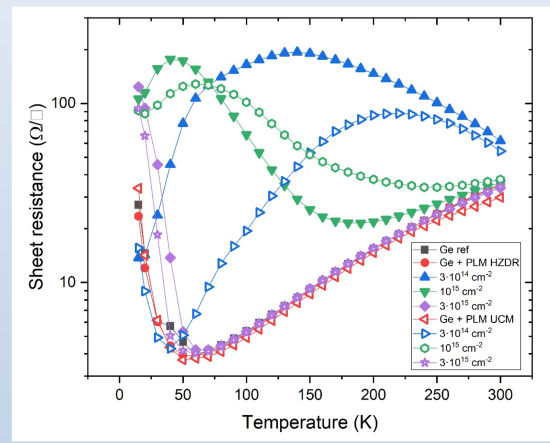


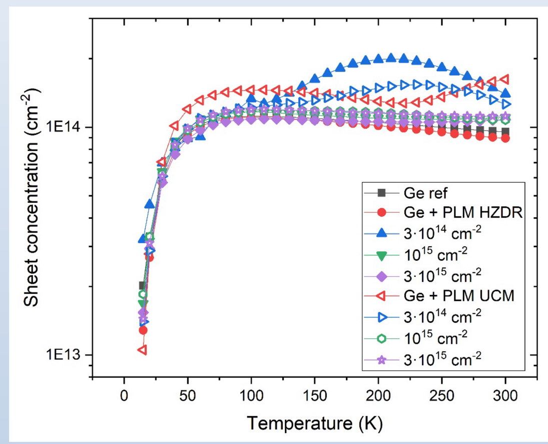




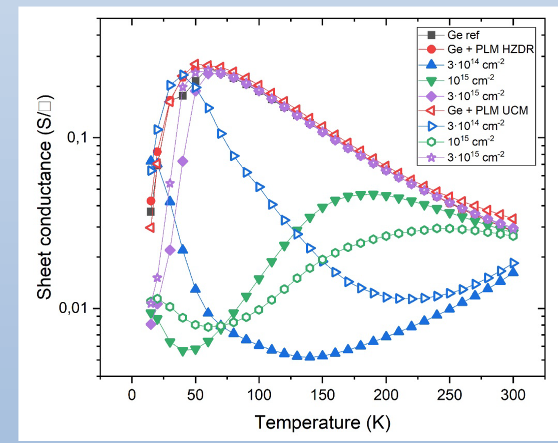
- The **transmittance of the implanted samples is lower than the reference** sample of Ge for every wavelength. After PLM, the transmittance is even lower.
- The **specular reflectance** of the implanted samples is similar to the reference Ge for **wavelengths longer than the *gap***. For the implanted samples and laser annealed this reflectance is **slightly lower**.
- The lower reflectance measuring in specular mode could be for not collecting the diffuse reflectance but measuring with an integration sphere the results are the same.
- Considering the transmittance and the reflectance of those samples we obtain absorptance of light at wavelengths longer than the *gap*. **This absorptance at wavelengths longer than the gap** is luckily **related to the deep centers** introduced in the semiconductor, which is the first step for electrooptical response.
- **This absorption** is not due to defects or an amorphous layer because the absorptance is much **higher in the annealed samples** than in the as implanted ones, reaching a **5%**.

Electrical results — Electrical decoupling



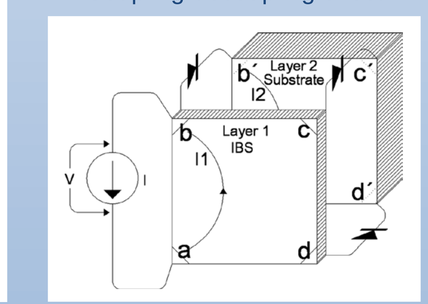


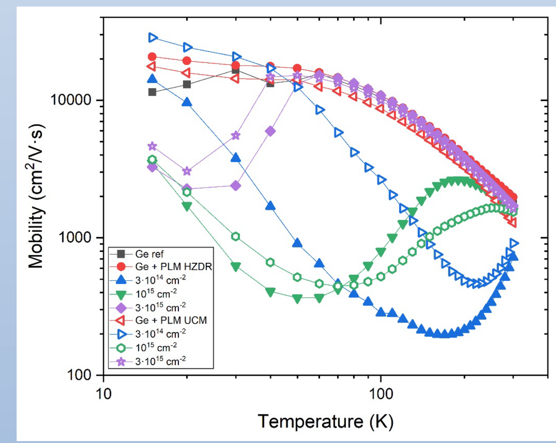
- There is a **coupling-decoupling effect** between the implanted layer and the substrate, and it is not straightforward to extract the properties of the implanted layer because it is never fully isolated.
- At **high temperatures**, the two layers are coupled, and we measure the **resulting layers** connected **in parallel.**
- As we **increase the dose**, the **temperature for decoupling is lower** (for the highest dose they are coupled down to 50 K).
- The behavior is the same regardless of the laser used.



Two-layer Hall effect model [2]

Coupling-decoupling effect





CONCLUSIONS

- We have fabricated **Te supersaturated Ge layers** with concentrations well above the **Solid Solubility Limit**.
- We **suppress the porosity** effect by **implanting at** liquid nitrogen temperature (**77K**). We successfully designed and assembled a modification to the ion implanter.
- The as-implanted samples **do not follow the SRIM simulations**. Experiments are being carried out to find out the reason for this accumulation at the surface.
- **Raman** measurements also **confirms the Te incorporation** and there is an induced strain dependent with the dose.
- We observe an **optical absorption** of light in the range we are interested in (**from 2000 nm onwards**).
- There is a **decoupling effect** observed in the bilayer. The behavior can be explained and model in terms of IB formation.

References

[1] Luque, A., & Martí, A. (1997). Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels. Physical Review Letters, 78(26), 5014.
[2] Olea, J., González-Díaz, G., Pastor, D., Mártil, I., Martí, A., Antolín, E., & Luque, A. (2011). Two-layer Hall effect model for intermediate band Ti-implanted silicon. Journal of Applied Physics, 109(6), 063718.
[3] Caudevilla, D., Berencén, Y., Algaidy, S., Zenteno, F., Olea, J., San Andrés, E., ... & García-Hemme, E. (2021, June). Overcoming the solid solubility limit of Te in Ge by ion implantation and pulsed laser melting recrystallization. In 2021 13th Spanish Conference on Electron Devices (CDE) (pp. 1-3). IEEE.

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