PICOSECOND LASER ANNEALING OF IMPLANTED Si AND GaAs: A COMPARATIVE STUDY WITH A RAMAN MICROPROBE

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Abstract - The transformation of implanted amorphous Si and GaAs induced by a single pulse of a picosecond laser is studied. In both materials a clear multiannular pattern was produced by the irradiation. The different patterns have been investigated by scanning the surface with a 1 μm spatial resolution Raman microprobe. Sharp transitions between amorphous and crystalline rings are observed for Si. In GaAs the transitions are smoother between nearly amorphous and nearly crystalline rings. A multiple melting-resolidification process within the laser pulse duration could explain the formation of these patterns.

INTRODUCTION

When a pulsed beam is used to anneal implanted semiconductors, it is likely that melting of a surface layer under irradiation followed by a liquid phase epitaxial regrowth occurs. However there is a threshold in the speed of the resolidification process above which the crystalline structure does not recover, resulting in amorphous material formation. Resolidification rates above this threshold can be obtained in semiconductors with extremely short pulses (picosecond /1/) or with laser pulses of extremely high absorption (U.V. light /2/).

The annealing of implanted amorphized silicon and GaAs with a picosecond Nd:YAG laser is reported here. Raman scattering measurements were performed to investigate the structure of an annealed spot obtained by a single pulse irradiation. Spatial resolution up to one micron was obtained with a microprobe. The resulting structure of the annealed spots is composed of concentric rings made by an alternation of "crystalline like" and "amorphous like" material. These patterns do not correspond to a continuous change of structure but to a periodic structure. Since the laser pulses have a gaussian spatial and temporal profile, a more complex melting-solidification process than the one presented for single crystal silicon irradiation /3/ is proposed here.

SAMPLE PREPARATION, ANNEALING AND RAMAN SCATTERING SET UP

Single crystal silicon and gallium arsenide (100) oriented were implanted with heavy ions in order to create a 1000 Å thick amorphous layer. For the silicon

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substrates As⁺ ions were utilized at a dose of 1x10¹⁵/cm² and at an energy of 100keV. Te ions at a dose of 1x10¹⁵/cm² and at an energy of 250keV were implanted in the GaAs substrates. The annealing was carried out with a mode locked Nd:YAG laser described in ref/4/. Single pulses of average duration 27 psec at 1.06 μm can be extracted from this system. The sample was placed at the focal point of a one meter focal length lens. Each pulse focused through the lens had a gaussian profile (spatial and temporal) with a diameter of 450 μm at the 1/e intensity points. The laser was operated at a low repetition rate in combination with a shutter, so that the sample could be translated between each pulse.

Raman scattering is a versatile and non destructive tool for thin film characterization. The whole surface of a sample can be analyzed with a spatial resolution of the focused analyzing beam. From light absorption considerations, depth profiles can be also investigated by this technique. Single crystals can be easily distinguished from polycrystalline or amorphous semiconductors as they all give rise to quite different Raman spectra. Furthermore the presence of strain and damages in crystalline material can be identified by a change in the shape and position of the Raman peaks. Raman measurements were performed in the backscattering arrangement. A conventional Raman set up was first used to study the annealed semiconductors and to perform polarized light scattering investigations. The spatial resolution was subsequently improved by the use of a Raman microprobe described in ref[5] with a resolution of 1 μm.

ANNEALING OF SILICON

The results presented in this section are described in ref/4/ and /5/, but the relevant properties are summarized here as a background for comparison with the results obtained on GaAs and for the modeling. A very sharp recrystallization pattern was obtained at 1.06 μm just below the threshold of laser induced damage (E=2/7/cm²). The pattern obtained under these conditions is shown in the Nomarski optical micrograph of Fig.1. This pattern was scanned along the arrows with a Raman microprobe. Crystalline silicon exhibits one Raman active peak related to the interaction of a photon induced electron-hole pair with the zone-center optical phonon whose frequency is 521 cm⁻¹. This peak is taken as an intensity reference for all the annealed regions investigated. The reduced Raman intensity (r = Iannealed/Icrystal) of the 521 cm⁻¹ line is then plotted as a function of position in Figure 1. The thickness of residual non crystalline layers can be deduced from this ratio for a given exiting wavelength with absorption depth consideration /4/. These results combined with polarized light measurement have allowed to obtain a detailed description (lateral as well as in depth) of the multiannual pattern. This is presented in the table below:

<table>
<thead>
<tr>
<th>E = 2 J/cm²</th>
<th>λ = 1.06 μm</th>
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<tbody>
<tr>
<td>Central region</td>
<td>stress free (100) single crystal diameter = 180 μm</td>
</tr>
<tr>
<td>First ring</td>
<td>amorphous width = 30 μm thickness = 100 Å</td>
</tr>
<tr>
<td>Second ring</td>
<td>stress free (100) single crystal width = 25 μm</td>
</tr>
<tr>
<td>Third ring</td>
<td>amorphous width = 20 μm thickness = 330 Å</td>
</tr>
<tr>
<td>Fourth ring</td>
<td>not identified</td>
</tr>
</tbody>
</table>

Finally it is important to mention that within the resolution of the microprobe, no transition region between the rings could be observed.
Picosecond laser annealed spot of ion implanted amorphized silicon for $E=2J/cm^2$ and $\lambda=1.06\mu m$:
Nomarski optical micrograph of the annealed area and spatial evolution of the intensity of the 521 cm$^{-1}$ line of silicon obtained with the microprobe.

Fig.2: Raman spectra of the different regions of a picosecond laser annealed ion implanted amorphized GaAs spot for $E=1.5J/cm^2$ and $\lambda=1.06 \mu m$.

Fig.3: Raman spectra of the different regions of a picosecond laser annealed ion implanted amorphized GaAs spot for $E=0.85J/cm^2$ and $\lambda=1.06 \mu m$. 
ANNEALING OF GaAs

Similar experiments were carried out with an implanted GaAs substrate. Single pulse annealing from the same laser at 1.06 μm resulted in a multiannular pattern. The resulting optical micrographs are a less contrasted, indicating a different crystal reconstruction within the rings of the annealed area. The best optical contrast was obtained above the damage threshold of the substrate. The Raman microprobe was utilized to investigate a spot annealed at 1.5 J/cm² which was degraded at the center. Crystalline GaAs exhibits two Raman active peaks related to the interaction of a photon induced electron-hole pair with the zone-center optical phonons whose frequency are 292 cm⁻¹ for the LO mode and 267 cm⁻¹ for the TO mode. The Raman scattering were performed in the experimental arrangement Z(XY)Z on samples oriented perpendicular to Z. In this backscattering configuration only the LO mode is allowed. This is illustrated in the spectrum (A) of Fig.2 obtained from a single crystal reference. All the spectra presented in this figure are taken in the same experimental conditions. The probing light is the green line (λ=5145 Å) of an argon ion laser. The first ring surrounding the damaged center is essentially recrystallized. As can be seen from the spectrum (B) of Fig.2, the LO peak intensity is about 30 % lower than for a perfect crystal and is downshifted by 2cm⁻¹. Furthermore a very small peak appears at 267 cm⁻¹ which is assigned to the TO mode and could be a consequence of a slight disorder in this recrystallized area. When the Raman microprobe is translated outside the pattern the spectrum (E) of the starting amorphous material is obtained. It reflects the one-phonon density of state of the crystal broadened by a convolution with a Gaussian factor /6/. The spectra (C) and (D) of Fig.2 obtained from the other rings of the pattern are clearly intermediate states between crystalline (B) and amorphous (E) states. This could be the signature of a polycrystalline material. The low frequency peak of (C) and (D) are TO-like and their high frequency peak, LO-like. The first one is a signature of disorder and the second one is a consequence of order. The intensity ratio between this two peaks is then significant of the degree of disorder. With these considerations, the region (D) is more ordered than the region (C). To summarize the study of this annealed pattern one can notice that it is formed of an alternation of rather ordered and rather disordered rings.

When the incident energy is reduced to 0.85 J/cm² at 1.06 μm wavelength, a similar annular recrystallization pattern is obtained with no visible damage at the center. The spectra resulting from the Raman microprobe scan are shown in Fig.3. The calculation of the ratio between the LO like and TO like intensity peak permits to conclude that the central region (A) is amorphous-like, the first ring (B) is ordered and the second one (C) disordered. The order in region (B) is accentuated by the upshift of the LO-like peak towards its single crystal position. For this incident energy (E=0.85 J/cm²), the central region is amorphous like rather than crystalline as was determined at higher energy (E=1.5 J/cm²). This indicates that the diameter of the rings can be controlled with the energy of the annealing beam like in silicon /3/.

DISCUSSION AND CONCLUSION

The annealing of Si and GaAs with a picosecond laser reveals strong differences in the resulting material state. The differences between these two semiconductors in the threshold resolidification speed for the lattice to reconstruct as well as the difficulty for the compound semiconductor to recrystallize epitaxially are responsible for these structural differences. However the annealed patterns display similar tendency to form multiannular structures with more than one amorphous or amorphous-like ring. Since the semiconductor substrates are good heat sink, no lateral variation of heat can account for the formation of these patterns. Therefore these annular structures cannot be explained within the resolidification process.

To investigate further the physics of the phenomenon, multiple shots from the picosecond laser with energy of 2 J/cm² each were sent on a stationary implanted
sample. The resulting structure is shown in the optical micrograph of Fig.4. The areas that were recrystallized after the first pulse (center and second ring) are now degraded and the amorphous rings are damage free. It is worth mentioning that the first pulse will result in selective absorption with higher absorption in the amorphous regions. This experiment shows that more energy has been deposited in the recrystallized center and second ring although the laser beam is perfectly gaussian.

A possible explanation of the multiannular structure could be a multiple melting-resolidification process during the pulse duration leading to the superposition of basic structures (crystalline center surrounded by an amorphous ring) of different sizes. The higher reflectivity of the molten layer could provide enough shielding from the laser light to prevent any further energy deposition before resolidification. Recently very high resolidification speeds were measured after melting with a picosecond laser /7/. These measurements support this model.

REFERENCES