Fabrication of GePb-Alloys by Means of Pulsed Laser Induced Epitaxy

M. C. J. Weiser*, D. Schwarz*, H. S. Funk*, D. Weißhaupt*, C. Serra***, J. Schulze* and S. Chiusi**

* Institut für Halbleitertechnik (IHT), Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany
** C.A.C.T.I., Univ. de Vigo, Rua Maxwell s/n, Campus Universitario Lagoas Marcosende, Vigo, Spain
*** Dpto. Física Aplicada, Univ. de Vigo, Rua Maxwell s/n, Campus Universitario Lagoas Marcosende, Vigo, Spain

st101565@stud.uni-stuttgart.de

Abstract – Theoretical simulations predict that direct band transitions are favored in Germanium-Lead (GePb) alloys with Pb concentrations of \( c_{Pb} \approx 3.4\% \). This could enable the creation of semiconductor lasers that are directly structured on Ge substrates. However, the formation of alloys with these properties is hindered by the low equilibrium solubility of Pb in Ge. Therefore, the usage of out-of-equilibrium growth methods, such as pulsed laser induced epitaxy (PLIE), is necessary. The contribution focusses on the formation of GePb alloys with varying Pb concentrations.

To cover a wide range of Pb concentrations, pulsed laser deposition (PLD) was utilized to deposit thin and smooth Pb films of varying thicknesses on Ge samples. After deposition, PLIE was used for alloying. For both processes, an Argon-fluoride (ArF) excimer laser emitting radiation at a wavelength of \( \lambda = 193 \) nm was used. The quality of the resulting alloys is evaluated by using Raman spectroscopy and the impact of different process parameters of PLIE is discussed.

Keywords – pulsed laser deposition; pulsed laser induced epitaxy; GePb; PLD; PLIE

I. INTRODUCTION

Because unconditional recombination of excited charge carriers is a requirement for stimulated emission, direct band gap semiconductors are necessary for the fabrication of semiconductor lasers. As both Si and Ge are indirect band gap semiconductors, recombination in these materials is unlikely. However, numerous applications could emerge from a laser source directly integrated on Si, e.g. optical interconnects for highly integrated logic circuits [1] or optoelectronic circuits with integrated logics and error correction [2].

Group III-V compound semiconductors typically feature direct band transitions and are commonly used for the fabrication of semiconductor lasers. However, their integration into the Si platform is hindered by numerous problems, like lattice mismatch, diverging expansion coefficients, highly stressed films, and more [3]. Alternatively, simulations indicate that by introducing substitutional Pb into the Ge crystal, a direct band gap semiconductor can be obtained. In case of relaxed GePb, the transition is predicted to occur at a Pb concentration of \( c_{Pb} \approx 3.4\% \) [4].

In this work, GePb alloys have been created in two processing steps: First, a thin layer of Pb was deposited on a Ge wafer by means of pulsed laser deposition (PLD). PLD utilizes pulsed laser radiation to excite the surface of a target to a plasma state. The expanding plasma plume reaches the opposing sample surface and covers the sample with a thin layer of the target material. In contrast to thermal evaporation used in a previous work [5], PLD is a sputtering process, which facilitates the growth of very thin and uniform layers. Therefore, very smooth surfaces can be obtained [6]. Furthermore, in contrast to the continuous growth of thermal evaporation, growth in the PLD process occurs pulse by pulse, which enhances the controllability of the resulting Pb layer thickness.

After the Pb layer deposition, pulsed laser induced epitaxy (PLIE) was utilized for alloying. The main issue for GePb formation is the low equilibrium solubility of Pb in Ge [7]. Therefore, out of equilibrium growth methods, such as PLIE, are necessary and particularly PLIE has recently been applied for the creation of GePb alloys [5]. During the PLIE process, the sample surface gets molten through laser radiation. Because of the higher diffusivity in the molten state, the Pb layer intermixes with the Ge substrate underneath and almost immediately after the laser exposure, the liquid resolidifies from bottom to top, using the substrate as a heat sink and recrystallization seed (see Fig. 1). As both the deposition and the epitaxy process rely on an ArF excimer laser beam as primary energy source, this work flow opens up the possibility of an all 193 nm laser-assisted process with PLD and PLIE within one single HV-UHV chamber, thus avoiding Pb oxidation.

Figure 1. Schematic of the working principle of PLIE.
II. SETUP

To optimize the PLD process, 200 mm Si (100) wafers have been used. The cleaning procedure involved immersing the samples in piranha solution (30% H₂SO₄:H₂O₂ in proportion 3:1) for 10 minutes, rinsing with deionized water and immersion in two stages of an ultrasonic bath of deionized water for 5 minutes each. The samples were then dried with a N₂ dispenser.

The Ge wafers were prepared with a 6” molecular beam epitaxy (MBE) system in which C, Si, Ge and Sn are used as matrix materials and B and Sb as p- and n-type dopants, respectively. Growth was performed on 4” p-doped Si (100) wafers with a sheet resistance of 10 Ωcm to 20 Ωcm. First, the native oxide was removed through thermal desorption at 900 °C [8]. To reduce the resulting surface roughness, a 50 nm thick Si buffer was grown at a substrate temperature of T_sub = 600 °C. A 100 nm thick i-Ge buffer layer was grown at T_sub = 330 °C and annealed for 5 minutes at T_sub = 850 °C to reduce the dislocation density [9]. A 900 nm-thick Ge layer was then grown at T_sub = 330 °C. The Ge-layer is much thicker than in the previous work, aiming to provide a larger Ge-matrix to solve the Pb in, thus reducing the total Pb concentration. Additionally, through the thicker Ge layer, the laser heated volume is confined to the Ge layer solely, as in the previous work, the heat gradient was deep enough to partially melt the Si substrate and create SiGe [5]. After the Ge deposition, the sample was cleaned by immersion in acetone for 8 minutes and isopropanol for 3 minutes. For half of the samples processed, a 150 nm-thick SiO₂ hard mask was deposited using an Oxford plasma-enhanced chemical vapor deposition (PECVD) system. Deposition rate and temperature were chosen as 50 nm/min and 250 °C, respectively. An Azmir 701 positive photoresist was spun on the hard mask and structured using contact photolithography. The hard mask was then structured using a SENTech SI591 reactive ion etching (RIE) system with 100 sccm CHF₃ flow and a BHF dip was used to open the windows. The completed hard mask featured rectangular and square windows with edge lengths ranging from 0.1 µm to 100 µm. The cleaning of the completed samples included a dip in isopropanol to remove residuals, a dip in deionized water to remove the native oxide and drying with N₂ flow.

For both laser processes, a Lambda Physik LP220i excimer laser was used. The gas filling consisted of ArF with a Ne buffer, resulting in a wavelength of λ = 193 nm. Lasers of this kind see widespread use in CMOS processes like UV photolithography. For the PLD process, a beam splitter and a cylindrical converging lens were placed in between the laser exit and the process chamber. The beam splitter was used to measure the laser fluence indirectly but “in situ”, while the lens was placed 12 mm in front of its focal position to modify the energy density on the target, as both an attenuator and a fly-eye homogenizer caused high losses. The resulting energy density on the target can be approximated to H = 700 mJcm⁻². The optical setup for PLIE featured the beam splitter, the attenuator to control the energy density on the sample, the fly-eye homogenizer and the process chamber, an acrylic box with a detachable lid and a 1,000 sccm Ar intake. The acrylic box featured a chuck with a vacuum suction which was mounted on a triaxial translation table to move the sample to the focal point of the homogenizer and achieve a top-hat-shaped fluency profile. This was necessary because reliable characterization of PLIE products depends on a highly homogeneous laser spot. The laser repetition rate was set to 1 pulse/s for all experiments to ensure complete cooling of the irradiated zone between two successive laser pulses.

III. METAL DEPOSITION

The creation of high-quality GePb alloys by means of PLIE requires the deposition of thin and homogeneous layers. Unfortunately, this is a challenging task for PLD, as through the high energy density, several undesired processes can happen alongside the desired laser ablation, including melting, splashing and target exfoliation [10], which will lead to particulate generation. Furthermore, the plume shape and direction may change during processing due to target surface modification [11][12].

The PLD experiments were conducted inside a laser induced chemical vapor deposition (LCVD) chamber. The target holder could be shifted horizontally and tilted towards the incident laser. The sample holder was attached to the chamber lid. When tilting the target holder by 45°, target and sample were directly facing each other. The distance between target and sample was set to d_Ts = 8.7 cm, as while testing d_Ts from 5.6 cm to 8.7 cm, this distance showed the largest uniform area of PLD deposited Pb. One- to two hundred laser pulses impinged on the same spot of the target surface before it was shifted to the next position. For vertical target realignment, the chamber needed to be purged with Ar (99.995%) and opened, as no automated elements for target rotation and translation were present. This way, a target was used for several 1,000 laser pulses.

Processing of the first samples started after evacuating the chamber to a pressure of p = 5×10⁻⁶ kPa, first. The ablation targets used were Pb slices which were cut off from a sample of c = 99.99% pure Pb, pressed to a thin slab and then polished with fine-grain polishing tools and isopropanol-soaked clean room cloths. To determine the resulting Pb layer thickness after PLD processing, dots of silver solution were placed on the wafers prior to the dep-

![Figure 2. Phase-shifting interferometry measurement of a sample processed at HV (left) and at 1.33 kPa (right).](image-url)
position step. After their removal, the resulting step height was measured using tactile profilometry. The surface texture was investigated using phase-shifting interferometry. As observable in Fig. 2, both the roughness and the particulate density of the grown layer turned out to be very high. As a first improvement measure, an Ar atmosphere was introduced to the chamber after chamber evacuation. Through the higher pressure, the mean free path of the larger, undesired particulates is expected to decrease faster than the one of the small plasma species. As the collected data in Fig. 2 and Tab. 1 shows, the particulate density is reduced when choosing higher Ar pressures, suggesting that this measure is working as intended.

Furthermore, as target surface features are known to increase particulate ejection [12][13], a target with a surface as smooth as possible is preferable. For this reason, a Si wafer was cleaned with piranha solution as described above, and a dip in a solution of 40% HF:H2O in proportion 1:5 was used to remove the native oxide. After rinsing with deionized water, a 2.4 µm-thick Pb layer was deposited via thermal evaporation and the wafer was used as deposition target. During PLD processing, the chamber atmosphere was set to 0.053 kPa of Ar. The phase-shifting interferometry measurements of the layers grown by PLD and the corresponding data is shown in Fig. 3 and Tab. 2, respectively. With the Pb-coated Si wafer as target, the particulate count and surface roughness on the sample could be reduced further, yielding the highest quality layer so far while even retaining a favorable layer growth rate.

To investigate the reasons for this great improvement, two spot of laser exposure, one on the Pb bulk target and one on the Si wafer-based target, were compared by means of tactile profilometry. The measured data is shown in Fig. 4. The surface on the Si wafer-based target is much smoother, which probably contributes to a smaller particulate ejection. Both in the tactile profilometry measurement of the Pb bulk target in Fig. 4 and in the optical profilometry measurement of the same target in Fig. 5, pillar-like elevations can be observed, which extend above the zero level. These may form as a result of the melting and resolidification process described as hydrodynamical growth, which has been reported for pulsed laser processing of Si [14]. They cannot be observed on the Si wafer-based target, which could indicate a suppression of the molten phase, possibly through the higher thermal conductance of Si, \( \kappa_{Si} = 124 \ \text{Wm}^{-1}\text{K}^{-1} \) compared to the one of Pb, \( \kappa_{Pb} = 34.9 \ \text{Wm}^{-1}\text{K}^{-1} \) [15]. As particulate generation through splashing of a molten phase is a known issue [10], this could explain the lower particulate count. It has to be noted that the depth of the spot on the coated target roughness equals the initial Pb layer thickness before PLD processing, suggesting an ablation stop at the Pb-Si interface.

However, using wafers as the base for targets yields the possibility of wafers being ablated. To check for undesired ablation, two wafers were prepared for the usage as deposition targets: one Si wafer and one Ge wafer. Both were coated with 1.0 µm of Pb via thermal evaporation and then used as target to deposit Pb on both a Si sample and a Ge sample simultaneously. This way, the feasibility of a Ge based target could be checked, the applicability of the process on Ge samples could be examined and undesired ablation could be reviewed: In case of Si or Ge ablation, the ablated Ge would be visible in Raman spectroscopy measurements of the Si sample and vice versa. The lower Pb layer thickness on the targets yielded even lower particulate generation rates, some as low as 0.46x10^3/mm² per pulse, underlining the effectiveness of the particulate suppression through the coated target and suggesting the usage of thinner Pb layers. The properties of the grown layers were similar for both sample materials, indicating that the process can successfully be transferred to the deposition of Pb layers on Ge wafers.

As the Raman spectroscopy measurements in Fig. 6 show, neither Ge nor Si is getting ablated, underlining the assumption of self-termination at the interface and suggesting that both materials can be used for the preparation of deposition targets. The development of the plasma plume during PLD processing, shown in Fig. 7, also suggests the theory of self-termination at the Pb-Si interface.

![Figure 4](image4.png) **Figure 4.** Comparison of the surface texture of a spot on the bulk target and on the Pb-coated Si wafer-based target.

![Figure 5](image5.png) **Figure 5.** Optical profilometry measurement of the target surface.

![Figure 3](image3.png) **Figure 3.** Phase-shifting interferometry measurements of the samples processed at 0.053 kPa with the Pb bulk target (left) and the Pb-coated Si wafer (right).

<table>
<thead>
<tr>
<th>TABLE II.</th>
<th>TARGET VARIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target type</td>
<td>Pb bulk</td>
</tr>
<tr>
<td>Thickness/ mm</td>
<td>30.54</td>
</tr>
<tr>
<td>RMS roughness/ nm</td>
<td>4.8</td>
</tr>
<tr>
<td>Growth rate/ (pm/pulse)</td>
<td>8.04</td>
</tr>
<tr>
<td>Particle generation rate/ (pulse^-1mm^-2)</td>
<td>99.22x10^-3</td>
</tr>
</tbody>
</table>
The plume is very bright in the early stages of ablation and decreases to a slight afterglow of the laser spot after roughly 100 pulses, indicating a decrease in the amount of ablated material, and thus, the stop of the ablation process.

As the usage of the Si wafer-based target with a Pb layer thickness of 1.0 µm in an atmosphere of 0.053 kPa of Ar yielded optimized results, this process was chosen for the preparation of Ge samples for PLIE.

IV. GE/Pb ALLOYING

PLIE was now used to form the desired GePb-alloys. The thicknesses of the deposited Pb layers were chosen as \( t_{\text{Pb}} = 5 \) nm, 10 nm, 20 nm and 30 nm to gather information about the scalability of the PLIE process. To evaluate the alloys grown, Raman spectroscopy was used. The Raman wavelength was chosen as \( \lambda = 633 \) nm. Two characteristic Raman spectroscopy measurements are shown in Fig. 8.

A. Evaluation of the Grown Alloys

When utilizing Raman spectroscopy, a few properties are generally shared between the samples processed. First, the main Ge peak is shifted to smaller wave numbers. This effect has already been reported in recent work [16] and is a sign of tensile strain through the incorporation of Pb atoms into the Ge lattice. This behavior could be similar to the effect of the Sn percentage in GeSn alloys on the Raman spectrum, which has been investigated in more detail [17]. Additionally, the peak is broadened, which indicates a decline in crystal quality. The left side is broadened further, hinting at an inhomogeneous distribution of Pb.

The Raman spectroscopy results were evaluated as follows: The shift of the Ge-Ge mode was used as an indication of the concentration of Pb inside the Ge crystal, as a larger shift means more tensile strain, and thus, a larger Pb concentration. The asymmetry of the peaks was evaluated using a Lorentzian fit in the bounds of the top 80% of the measured peak and calculating the correlation coefficient of the measured and fitted data. A high correlation coefficient therefore means that the measured signal resembles the one of a perfectly homogeneous composition, and thus, indicates a preferable Pb distribution.

In Fig. 9, the obtained data from this work and a previous work [5], is shown. By using PLD, the Pb concentrations can be decreased significantly while the Raman peaks are much thinner, indicating preferable crystal quality and more homogeneous Pb distribution compared to [5]. It also shows that a broad range of Pb concentrations can be achieved with this method.

B. Influence of the Pb Layer Thickness

To examine the properties of samples with different initial Pb layer thicknesses, unmasked samples were coated with Pb layers of the thicknesses \( t_{\text{Pb}} = 5 \) nm, 10 nm, 20 nm and 30 nm. After deposition, the GePb alloy was created using two different laser fluences, 275 mJcm\(^{-2}\) and 550 mJcm\(^{-2}\), with 50 laser pulses per sample.

The Raman peak shift- and peak half width at half maximum (HWHM) are shown in Fig. 10. The shift of the Ge-Ge mode increases with the thickness of the Pb layer prior to PLIE processing. This is an expectable result, as more Pb inside the crystal will lead to a greater degree of strain, and thus, a larger Raman peak shift. Furthermore, the broadness of the peak increases, which indicates that the crystal quality in the observed volume decreases. It has to be noted that a large difference in peak position and broadness can be observed when comparing the two energy densities: Not only is the peak shift smaller, but the peak broadness also yields much smaller values when choosing the higher fluence. This indicates that the layer
homogeneity increases massively when choosing higher pulse energies and suggests that higher laser fluences are preferable for more homogeneous Pb distributions. These results are further backed by the peak correlation coefficients shown in Fig. 11. When increasing the Pb dose, the correlation coefficient decreases, indicating a less homogeneous layer composition. For higher fluences however, a high peak correlation coefficient is retained much better.

C. Influence of the Laser Pulse Energy
To investigate the dependency of the laser fluence, a set of unmasked samples was coated with 10 nm of Pb before PLIE processing with 50 laser pulses. For each sample, a different laser fluence was chosen. Fig. 12 shows the peak shift vs. peak HWHM data. Unfortunately, the peak shifts are scattered, making interpretation difficult. This might be due to Pb layer thickness deviations, which have not been investigated. Still, the peak correlation data in Fig. 13 shows that the higher the laser fluency, the smaller the peak HWHM values for a given peak shift, which again underlines the importance of the fluence. Furthermore, the correlation coefficients in Fig. 15 show that the samples processed at elevated fluences scatter at the top for each Pb layer thickness, indicating a higher layer homogeneity. For a Pb layer thickness of $t_{Pb} = 5$ nm, however, the lowest energy density seems to return favorable results. This may coincide with Pb layer thickness deviations, as these two layers also yield much smaller peak shifts, suggesting that the total Pb dose in these samples is smaller than expected.

D. First-Order Approximation of the Pb Concentration
In the previous work, at laser fluences of $H = 580$ mJ/cm$^2$, the generation of SiGe could be confirmed with Raman spectroscopy [5]. The Ge-Si interface was located 250 nm below the Ge surface and PLIE led to partial melting of the Si surface, and thus, to SiGe for-
mation. When considering the lower melting temperature of Ge, \( T_{\text{Mel}} = 938 \, ^\circ\text{C} \) compared to \( T_{\text{Mel}} = 1414 \, ^\circ\text{C} \) \cite{15}, it is reasonable to assume that in this work, the molten pool will extend to a depth of at least 300 nm below the Ge wafer surface at similar fluences. When considering a perfectly homogeneous Pb concentration in a cuboid volume while neglecting Pb ablation during the first pulses of PLIE processing as a crude first-order approximation, the Pb concentrations in Tab. 3 are obtained. The real Pb concentrations and the amount of strain inside the crystal are not known, yet especially strain is reported to have a significant impact on the Pb concentration needed for the transition towards direct band gap GePb alloys. As a broad range of Pb concentrations is suggested to yield GePb alloys with direct band transitions \cite{4}, it is likely that at least the samples with higher initial Pb layer thicknesses match the requirements.

V. HARD MASK INTEGRITY

In the previous work, the damage threshold of the hard mask has been identified as \( H \approx 300 \, \text{mJcm}^{-2} \) \cite{5}. As higher laser fluences turned out to be favorable, the mask integrity has to be evaluated. In the optical microscope, severe damage can be observed for elevated fluences, such as \( 550 \, \text{mJcm}^{-2} \), even after only 5 pulses, as shown in Fig. 16. This suggests that more durable hard mask materials should be chosen to reliably confine the GePb creation to the unmasked areas.

VI. CONCLUSION

PLD was introduced as a suitable approach for the deposition of Pb. The greatest challenge turned out to be the reduction of the particulate emission. This problem was solved using an Ar environment inside the process chamber and a Pb-coated Si wafer as deposition target. The later one proved to yield the largest improvement.

After the PLD optimization, the GePb alloying using PLIE was investigated. It turned out that the laser fluence is highly important, mainly because the layer homogeneity is increased, and the broadness of the Raman peaks decreased at higher fluences. Therefore, to obtain high-quality alloys, a high energy density is a necessity. Unfortunately, the SiO\(_2\) hard masks suffered severe damage at higher fluences, which suggests the usage of more durable materials for future investigation. Furthermore, a more detailed analysis of the layer composition and strain should be undertaken in future investigation, aiming at an “All 193 nm laser assisted” process for GePb formation.

ACKNOWLEDGMENT

M. C. J. Weiser thanks the ERASMUS+ Placement program for financial support.

REFERENCES

\[1\] D. A. B. Miller, „Optical Interconnects to Silicon“, \textit{IEEE journal on selected topics in quantum electronics}, Vol. 6, pp. 1312-1317, 2000
\[17\] A. S. Vasin, F. Oliveira, M. F. Cerqueira, J. Schulze, M. I. Vasilevskiy, “Structural and vibrational properties of Sn,Ge\(_x\), modeling and experiments”, \textit{Journal of Applied Physics}, Vol. 124, 2018

Figure 16. SiO\(_2\) hard masks after exposure. Left: 5 pulses at \( H = 550 \, \text{mJcm}^{-2} \). Right: 30 pulses at \( H = 550 \, \text{mJcm}^{-2} \).

<table>
<thead>
<tr>
<th>( t_0 )</th>
<th>Depth of the molten pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 nm</td>
<td>300 nm</td>
</tr>
<tr>
<td>5 nm</td>
<td>1.488%</td>
</tr>
<tr>
<td>10 nm</td>
<td>2.976%</td>
</tr>
<tr>
<td>20 nm</td>
<td>5.953%</td>
</tr>
<tr>
<td>30 nm</td>
<td>8.929%</td>
</tr>
</tbody>
</table>