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# Parameter tunable GaInNAs saturable absorbers for mode locking of solid-state lasers

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## Abstract

Passively mode-locked solid-state lasers require semiconductor saturable absorber mirrors (SESAMs) with a recovery time up to 10–30 times longer than the final pulse duration. GaInNAs SESAMs normally have a high defect concentration that supports a fast picosecond recovery time and have been used to passively mode-lock lasers at 1.3  $\mu\text{m}$ . Post-growth annealing is a very useful technique to adapt the absorption edge of the GaInNAs absorber to the laser. However, larger absorption edge tuning reduces the defect concentration and increases the recovery time too much for picosecond pulse generation. We have developed a novel growth technique that allows wavelength tuning with post-growth annealing, but without any increase of the recovery time and without degrading the absorber performance. This was achieved by exposing the GaAs barrier to nitrogen from a plasma source for about 20 s before the GaInNAs quantum well was grown.

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## 1. Introduction

Semiconductor saturable absorber mirrors (SESAMs) [1–3] for passive mode locking of solid-state lasers in the wavelength range of 1.3–1.5  $\mu\text{m}$  are still a challenge. Optimized defect engineering is needed to obtain a desirable modulation depth, negligible nonsaturable losses and a picosecond recovery time. At 1.3  $\mu\text{m}$ , InGaAs absorbers provide a band gap in the proper wavelength region but are strongly lattice mismatched to GaAs-based distributed Bragg reflectors (DBRs). A large lattice mismatch degrades the SESAM to such a level that the nonsaturable losses become comparable to the modulation depth and the output coupler transmission, which strongly degrades the performance of a modelocked laser. It is known that the quaternary dilute nitride GaInNAs provides both a low lattice mismatch to GaAs and an

absorption in the desired wavelength range [4]. The incorporation of nitrogen induces a drastic redshift of the band gap already at low concentrations of a few percent. In addition, the lattice constant is decreased with increasing nitrogen in the compound. Therefore, using GaInNAs, it is possible to keep the indium concentration sufficiently low for successful growth on GaAs substrates. Dilute nitrides are known for large numbers of defect-induced nonradiative recombination channels that are strongly dependent on the applied growth conditions. So far we have demonstrated that these defects do not generate excessive nonsaturable losses with a picosecond recovery time [2,3]. Several solid state lasers were successfully modelocked at frequencies up to 10 GHz using GaInNAs-based SESAMs [5]. Recently, we also demonstrated a GaInNAs-based VECSEL at 1.3  $\mu\text{m}$  modelocked using a GaInNAs SESAM [6]. However, post-growth annealing for wavelength tuning of the absorption edge was limited. In this paper, we provide a simple solution.

The nonlinear optical parameters of the SESAM strongly depend on the position of the absorption edge

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with respect to the laser wavelength [7]. Therefore, post-growth wavelength tuning is very useful. However, rapid thermal annealing (RTA) applied for wavelength fine-tuning removes defects from the material and increases the recovery time. Nitrogen pretreatment of the growth surface is a way toward more flexible SESAMs even better matched to the specific application. Previously, it was demonstrated for InGaAs quantum wells that the carrier recombination time could be drastically reduced by incorporating a thin GaNAs layer into the adjacent GaAs barriers [8]. Here, we have explored the option of growing a GaInNAs quantum well directly on such a nitrogen-enriched layer.

## 2. Experimental details

### 2.1. SESAM fabrication details

Test structures and SESAMs with GaInNAs single-quantum wells (SQWs) were grown on semi-insulating GaAs (100) substrates by molecular beam epitaxy (MBE) using group III solid sources, an arsenic valved cracker and a VEECO UNI-Bulb nitrogen plasma source. The test structure consisted of an 11 nm GaInNAs SQW grown on a GaAs buffer layer at a temperature of 450 °C monitored by diffuse reflectance spectroscopy (DRS) and capped with a 60 nm GaAs layer. The SESAMs incorporated the same SQW absorber. The quantum well growth rate was 1.7  $\mu\text{m}/\text{h}$  at an  $\text{As}_2/\text{III}$  beam equivalent pressure (BEP) ratio of 25. For the nitrogen-enriched layer at the barrier/quantum well interface, the normal growth was interrupted and the surface was exposed to a nitrogen and  $\text{As}_2$  flux for different time intervals before the growth was continued with the GaInNAs SQW using the same nitrogen flux. This resulted in a thin GaNAs layer between the barrier and the quantum well. The N exposure time was varied between 5 and 145 s. A sample without such a nitrogen-enriched interface was grown as a reference. The growth interface was monitored in situ by reflection high-energy electron diffraction (RHEED) to determine the degree of deterioration of the interface by the nitrogen species from the plasma source. Both the test structures and SESAMs were partially treated with RTA at 600 °C for 1 min. With the test structures, we determined the as-grown and annealed photoluminescence (PL) wavelength of the GaInNAs SQWs because the underlying DBR of a SESAM can alter the PL emission spectrum of the SQW and give a false position of the absorption edge.

The antiresonant GaInNAs SESAMs were based on a 30-pair AIAs/GaAs DBR with 93 nm GaAs spacer layer, an 11 nm GaInNAs SQW absorber and 93 nm GaAs cap layer. Such SESAMs have been described in more details in Ref. [2], but without the additional nitrogen treatment before the GaInNAs SQW. The composition of the GaInNAs SQWs was obtained by X-ray rocking curve (XRC) measurements after a 35.2% In concentration was determined using an additional InGaAs SQW test structure

grown under the same conditions. This resulted in a nitrogen concentration in the GaInNAs SQWs between 1.05% and 1.10% depending on the nitrogen exposure time before the overgrowth by a GaInNAs SQW. This slight increase in nitrogen content explains the PL wavelength redshift with increasing pre-growth nitrogen exposure (Fig. 1).

### 2.2. Time-resolved optical characterization

Pump-probe measurements were carried out to characterize the recovery time of nitrogen-treated GaInNAs SESAMs. The SESAMs were characterized using a degenerate pump-probe measurement setup [9]. The pump and probe wavelengths were chosen 10 nm above the PL emission peak using 200 fs pulses from a commercial optical parametric oscillator (OPO). The energy for the pump pulses was two times the saturation fluence. A double exponential fit of the pump-probe measurements

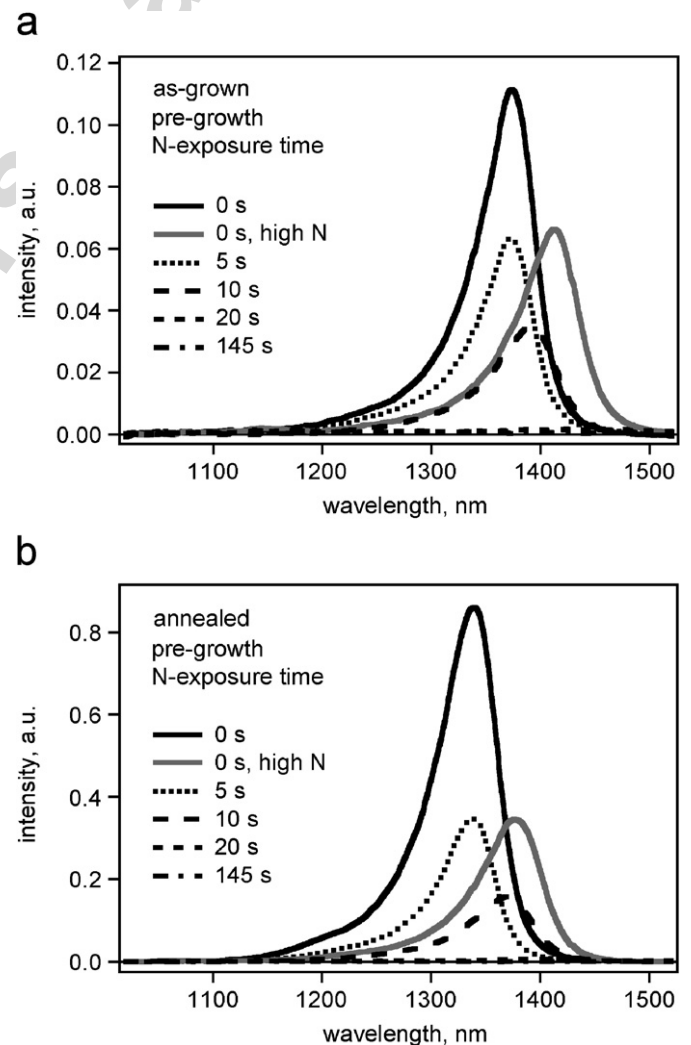


Fig. 1. Photoluminescence (PL) spectra of GaInNAs SQW test structures for different N exposure time, as-grown (a) and annealed at 600 °C for 1 min (b). Annealing significantly increases the PL intensity while the intensity ratios between the different samples remain mostly unchanged.

was used. The slow decay time is the relevant component to quantify the defect-related recovery dynamics in such SESAM devices [1].

### 3. Results and discussion

#### 3.1. Formation of nonradiative defects

Nitrogen treatment affects a growth interface by surface damage and nitrogen accumulation.

Surface damage is generated by unintentional N ion bombardment from the plasma cell. The damage increases with increasing exposure time until the growth interface becomes noticeably rough. This can be observed by a change of the RHEED image that turns from a streaky pattern for the 2D growth to blurred lines with weaker intensities to a spotty pattern finally representing 3D growth. The surface morphology of the subsequent GaInNAs SQW, depends strongly on the underlying growth interface and turns to 3D growth for longer exposure times. For a low exposure dose of 5 and 10 s, there was a slight 3D growth immediately from the beginning of the GaInNAs SQW, which recovered already during the SQW growth and completely restored to 2D growth during the subsequent capping layer. For an exposure time of 20 s, the 3D growth was already stronger from the beginning and only recovered quickly during the GaAs capping layer growth. For even longer exposure times of 65 and 145 s, the stronger 3D growth needed almost the complete cap layer growth time to recover to 2D. High-resolution XRC showed later that no recognizable quantum well was obtained for the longest exposure times. Fig. 2 clearly shows the transition from acceptable SQW growth at 20 s exposure to complete deterioration of the growth process at 65 s exposure time.

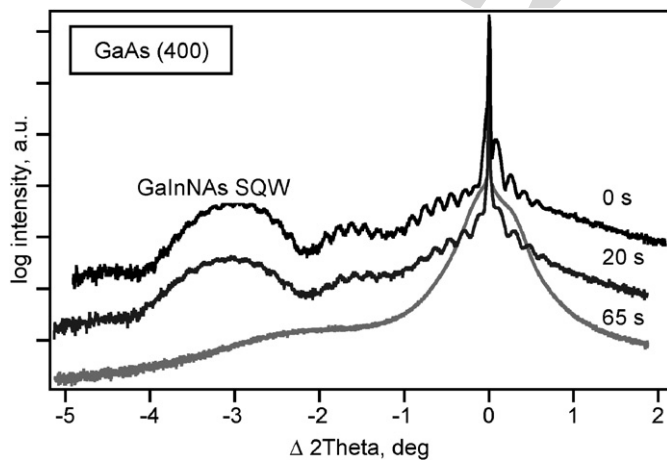


Fig. 2. X-ray rocking curve (XRC) measurements of test structures with different N exposure times (each shifted up in intensity for clarity). Good single-quantum well (SQW) growth is observed up to a 20 s N exposure time. For longer treatments, we observe a deterioration of the growth from a shallow SQW signal and a broadened GaAs signal from the cap layer.

Nitrogen accumulation occurs at the growth interface and contributes to a higher nitrogen concentration in the SQW with increasing N exposure time. The red shift in the PL measurements and reduced PL intensity (Fig. 1—black curves) indicate a higher average nitrogen concentration for longer N exposure times. Fig. 1 also shows the PL of a different GaInNAs SQW sample without any interface treatment but with a higher N concentration (gray curve). This PL peak intensity is higher than the analogous curve with the same redshift from the N-treated sample (i.e. an N exposure time of 10 s). Thus, the decay of the PL intensity, with increased N exposure time, is much stronger than by just alloying more nitrogen.

RTA of the samples was performed for 1 min at 600 °C under reduced nitrogen pressure of about 10 mbar using a GaAs proximity capping to prevent As evaporation. All samples improved in PL intensity by roughly the same factor as shown in Figs. 1a and b. Only samples that start without any PL emission do not recover during the annealing. The blue shift induced by annealing is 23 meV for the samples with 0 and 5 s nitrogen treatment. The sample with 10 s N exposure time blueshifted only by 14 meV, which indicates a change in the material properties compared to quantum wells grown under usual conditions. For the other samples, no PL emission was observed.

#### 3.2. Fast carrier recombination

Nitrogen exposure of the growth surface strongly decreased the carrier recombination time (Fig. 3). RTA has been performed on the test structures as well as on the SESAMs used for nonlinear characterization. Note that Fig. 1 showed that, for a N exposure time of 20 s and longer, no PL signal was measured. The absorber, however, is still working but with lower performance (as will be discussed in the next section). In this regime, we see no change in the recovery time after annealing. Therefore, these defects do not heal out during annealing in contrast

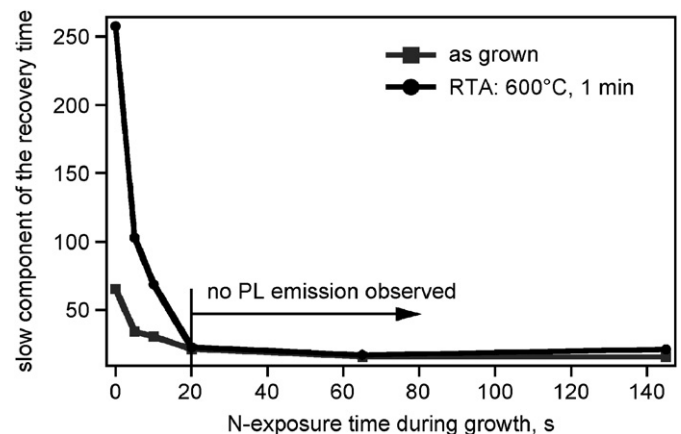


Fig. 3. The slow component of the recovery time from a double exponential fit of pump-probe measurements clearly indicates the strong effect of the nitrogen exposure. At exposure times longer than 20 s, no PL was measurable, even after annealing.

to the native defects generated by nitrogen incorporation in GaInNAs.

Below the 20 s N exposure time, the as-grown absorbers show relatively low PL intensity and fast carrier recombination below 66 ps (Fig. 3). The recovery time of the untreated absorber is 65.4 ps and increases after RTA to more than 250 ps. For the nitrogen treated absorber structures, this effect is strongly reduced and the absorbers remain much faster even after the annealing procedure. The sample with an exposure time of 20 s changed only from 21.6 ps as grown to 22.3 ps after annealing.

### 3.3. Saturation fluence and nonsaturable losses

We fully characterized the SESAM parameters according to the method described in Ref. [9] (Table 1). The saturation fluence and nonsaturable losses of SESAMs are important parameters that have to be tightly controlled. The product  $F_{\text{sat}} \times \Delta R$  must be low to suppress Q-switched mode locking [7].  $\Delta R$  denotes the modulation depth of the SESAM, which is the difference in reflectivity between the fully saturated and the recovered states of the SESAM. Nonsaturable losses  $\Delta R_{\text{ns}}$  denote the difference between 100% reflectivity and the reflectivity of the fully saturated SESAM. They absorb intracavity power, reduce the efficiency of the laser and can lead to thermal damage of the SESAM. Samples with exposure times up to 10 s do not show remarkable differences in the saturation fluence for both as-grown and annealed samples. However, for longer nitrogen exposure times ( $>10$  s), we notice a strong increase in  $F_{\text{sat}} \times \Delta R$ . The reason for this increase is the strongly growing saturation fluence with exposure time, which is caused by the deteriorated SQW structure, and is further recognized by RHEED and XRC measurements. A more bulk-like material typically has a higher saturation fluence because of a higher density of states. All these

Table 1  
Measured SESAM parameters

Exposure time (s)	$F_{\text{sat}}$ ( $\mu\text{J}/\text{cm}^2$ )	$\Delta R$ (%)	$\Delta R_{\text{ns}}$ (%)	$F_{\text{sat}} \times \Delta R$
<i>As-grown</i>				
0	12.6	0.7	0.21	8.8
5	21.3	0.6	0.15	12.8
10	25.5	0.6	0.15	15.3
20	81	0.6	0.1	48.6
65	193.3	0.8	0.12	154.6
145	261.7	1.2	0.1	314.0
<i>Annealed</i>				
0	13.4	0.8	0.06	10.7
5	17.7	0.7	0.13	12.4
10	14.1	0.6	0.5	8.5
20	67	0.6	0.18	40.2
65	48.4	0.4	0.62	19.4
145	185.9	1.1	0.21	204.5

Saturation fluence  $F_{\text{sat}}$ , modulation depth  $\Delta R$  and nonsaturable losses  $\Delta R_{\text{ns}}$  for different nitrogen exposure times together with the product  $F_{\text{sat}} \times \Delta R$ . These values are measured at 1360 nm using 200 fs pulses.

observations indicate a strong change of the electronic band properties of the absorber.

The nonsaturable losses for the as-grown samples are significantly lower than the modulation depth. RTA reduces these nonsaturable losses in samples exposed to N for up to 10 s without degrading the modulation depth. Better performance is generally obtained up to about 20 s N exposure time. The much higher nonsaturable losses at 10 s are most likely an artifact and due to increased surface scattering of the sample induced by the RTA process and not something inherent to the structure. However, the increased losses after RTA in the samples exposed to N for 65 and 145 s suggest that such long exposure times are not recommended for high-performance SESAMs.

## 4. Conclusion

Nitrogen exposure of the growth surface is a suitable method to grow fast absorbers based on GaInNAs using RTA as a fine-tuning tool for the absorber wavelength. At the same time, it is possible to keep the recovery time low despite the defect-removal effect of thermal annealing. These results allow for more flexible SESAM designs with the possibility of post-growth wavelength tuning by RTA without changing the recovery time, saturation fluence, modulation depth and nonsaturable absorption of the absorber in an unacceptable way. Nitrogen exposure times from 0 to 20 s result in SESAMs with suitable parameters for mode locking of solid-state lasers. For the annealed SESAMs, an exposure time of 20 s resulted in a fast absorber with a recovery time of 22 ps and a saturation fluence of  $81 \mu\text{J}/\text{cm}^2$ , and an exposure time of 10 s resulted in 79 ps and  $25.5 \mu\text{J}/\text{cm}^2$ . The main difference between 10 and 20 s exposure times is seen in Fig. 3. An exposure time of 20 s completely suppresses the increase of the recovery time during annealing of the SESAM, while a 10 s exposure still results in a significant increase. Depending on the requirements of the laser, a suitable nitrogen exposure time of the barrier/quantum well growth interface can be chosen for optimum nonlinear optical parameters.

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## References

- [1] U. Keller, K.J. Weingarten, F.X. Kärtner, D. Kopf, B. Braun, I.D. Jung, R. Fluck, C. Hönninger, N. Matuschek, J. Aus der Au, IEEE J. Sel. Top. Quantum Electron. 2 (1996) 435–453.
- [2] V. Liverini, S. Schön, R. Grange, M. Haiml, S.C. Zeller, U. Keller, Appl. Phys. Lett. 84 (2004) 4002–4004.
- [3] A. Rutz, R. Grange, V. Liverini, M. Haiml, S. Schön, U. Keller, Electron. Lett. 41 (2005) 321–323.
- [4] M. Kondow, T. Kitatani, Semiconduct. Sci. Technol. 17 (2002) 746–754.

- [5] G.J. Spühler, L. Krainer, V. Liverini, S. Schön, R. Grange, M. Haiml, A. Schlatter, S. Pawlik, B. Schmidt, U. Keller, *Phot. Technol. Lett.* 17 (2005) 00.
- [6] A. Rutz, V. Liverini, D.J.H.C. Maas, B. Rudin, A.-R. Bellancourt, S. Schön, U. Keller, *Electron. Lett.* 42 (2006) 926.
- [7] R. Grange, A. Rutz, V. Liverini, M. Haiml, S. Schön, U. Keller, *Appl. Phys. Lett.* 87 (2005) 132103.
- [8] M. Le Du, J.C. Harmand, K. Meunier, G. Patriarche, J.L. Oudar, *Optoelectron. IEEE Proc.* 151 (2004) 254.
- [9] M. Haiml, R. Grange, U. Keller, *Appl. Phys. B* 79 (2004) 331–339.

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