



Application of reflectance anisotropy spectroscopy to laser diode growth in MOVPE

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Abstract

The growth of layer structures for visible and near-infrared laser diodes is investigated in metal-organic vapour phase epitaxy (MOVPE) under production-like conditions using reflectance anisotropy spectroscopy (RAS). For this purpose the dependence of the reflectance anisotropy (RA) signal on doping type and level is studied for AlGaAs and AlGaInP. The growth of complete layer structures can then be fingerprinted by the significant features of the RA spectra. The reproducibility of the growth process is controlled using the RA transients taken with a high time resolution at a fixed photon energy. Additionally, the emission wavelength of a GaAsP quantum well (QW) can be correlated to the RA level during QW growth. Information about buried interfaces can also be gained from the RA transients as demonstrated for AlGaInP laser structures.

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1. Introduction

Semiconductor edge-emitting laser diodes are on the way to replace solid-state lasers in many applications (e.g. material processing). Further-

more, these lasers are the only potential light source in telecommunication, data storage, and medical applications. Growth of layer structures for such devices in production scale is mainly done in metal-organic vapour phase epitaxy (MOVPE) due to its high efficiency. The stringent requirements on the final laser parameters require a highly reproducible growth process. In situ investigations enable an early and efficient

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detection of deviations in the growth process from the desired parameters [1]. Under gas-phase conditions, unfortunately only *optical* in situ investigations can be used in contrast to e.g. molecular beam epitaxy (MBE) where electron-based techniques like reflection high-energy electron diffraction (RHEED) can be applied.

In this paper, we report on the in situ application of reflectance anisotropy spectroscopy (RAS [2]; also known as reflectance difference spectroscopy, RDS [3]) to the growth of layer structures for edge-emitting laser diodes. These structures consist either of AlGaAs cladding and waveguide layers with a GaAsP quantum well for the near-infrared (NIR) region or Al(Ga)InP cladding and waveguide layers with an InGaP quantum well for visible (VIS) emission. Undoped AlGaAs layers have intensively been studied using RAS [4], while doped AlGaAs layers are studied only marginally [5]. More results are available for the dependence of the RA on doping of GaAs [6–9].

Here, we report on the doping dependence of the RA signal for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with a composition of $x = 0.7$. N-doping was carried out using silicon (Si), while for p-doping zinc (Zn) and carbon (C) was used. Furthermore, the resolution limit of the RA signal dependence for p:AlGaInP growth using Zn-doping is studied at growth conditions. With this information the complete growth process of different laser structures is fingerprinted. By comparing spectral and time-resolved measurements of different growth runs, the reproducibility of the growth process can be controlled. The emission wavelength of the laser quantum well (QW) is correlated to the RA signal during QW growth. Furthermore, information about buried interfaces can also be gained from the RA transients as will be shown for AlGaInP laser structures.

2. Experimental procedure

All epitaxial layer structures discussed in this work were grown in an AIX 200/4 low-pressure MOVPE system. The sources used are trimethylgallium (TMGa), trimethylaluminum (TMAI), arsine (AsH_3) and phosphine (PH_3). Dopants used

were Si from Si_2H_6 for n-doping, and Zn from diethylzinc (DEZn), extrinsic carbon doping using tetrachlorobromide (CBr_4) or intrinsically incorporated carbon by growth at low V/III ratios for p-doping, respectively. The growth pressure was 150 mbar and a typical growth temperature was 770 °C. Exactly oriented (100) n^+GaAs substrates and 6° misoriented towards $\langle 111 \rangle_A$ were used.

The MOVPE system is equipped with a strain-free, UV-transparent viewport for normal incidence optical access and with a small corresponding hole in the liner-tube. A LayTec EpiRAS-200 spectrometer is attached to the MOVPE system, giving the possibility of performing reflectance anisotropy measurements also on rotating samples [10].

RAS measurements are highly sensitive to the optical anisotropy induced by the semiconductor surface. RAS measures the complex difference in reflectance for linear polarized light along the two principal axis on the surface. For a (001) surface the RAS signal is given by

$$\frac{\Delta r}{r} = \text{Re}\left(\frac{\Delta r}{r}\right) + i\text{Im}\left(\frac{\Delta r}{r}\right),$$

$$\frac{\Delta r}{r} = 2 \frac{r_{[110]} - r_{[\bar{1}10]}}{r_{[110]} + r_{[\bar{1}10]}}. \quad (1)$$

In Eq. (1) $r_{[110]}$ and $r_{[\bar{1}10]}$ are the complex reflectances of light polarized linearly along the indicated directions in the surface (see Ref. [1] and references therein). Please note that all spectra are taken on rotating samples (except Fig. 5a). Therefore, all viewgraphs show the absolute values of the RA signal (except Fig. 5a). Doping profiles were obtained using an Accent C/V-Profiler.

3. Results and discussion

3.1. AlGaAs doping

Fig. 1a shows RA spectra of $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ at a temperature of 770 °C. The spectra are all taken during growth at layer thickness of approximately 350 nm. Starting from the undoped layer (straight

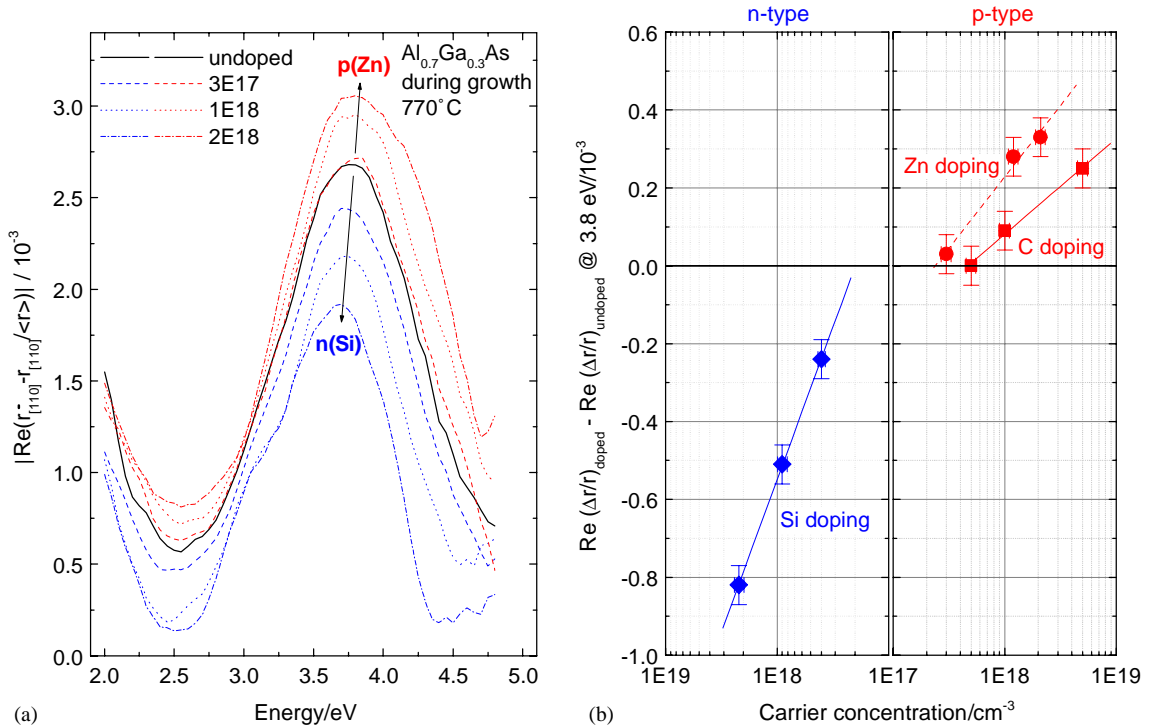


Fig. 1. (a) RA spectra of undoped, Si-doped and Zn-doped $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ taken during growth at 770°C . The respective doping concentration is given in the figure. (b) Resulting calibration curves correlating the RA signal at 3.8eV to the Si, Zn and C carrier concentration.

line) the layers were n- and p-doped using the indicated values. As can be seen from the figure n-doping leads to a decrease in the RA signal over the whole spectral range while p-doping leads to an increase in the RA values. Since the penetration depth decreases with increasing photon energy, the RA values taken at the higher photon energies are sensitive only to the uppermost layers. Therefore, for calibration the dependence of the RA value at 3.8eV is plotted against the doping concentration in Fig. 1b. This is done for p-doping using Zn and C and n-doping using Si. The dependence of the RA signal on doping concentration is the strongest for Si. It is slightly smaller for Zn and much smaller for C doping. The Zn doping is done by adding DMZn to the gas phase at standard V/III ratios while the intrinsic carbon doping is obtained by growing the layers at a low V/III ratio [11]. Therefore, it can be assumed that the growth mechanism is different as was found for GaAs [12],

resulting in a different dependence of the RAS signal on doping concentration.

The lower limit of the detection of a certain doping concentration using RAS at MOVPE growth conditions is in the range of a carrier concentration below $5 \times 10^{17}\text{cm}^{-3}$. The RA spectrum of the p-doped layer with a carrier concentration of $3 \times 10^{17}\text{cm}^{-3}$ is very similar to the one of the undoped layer. For the n-doping the effect on the RA spectra is slightly stronger. Therefore, the lower detection limit can be assumed to be near $1 \times 10^{17}\text{cm}^{-3}$. Anyway, a clear dependence of the RA signal on doping concentration is given for carrier concentrations of $5 \times 10^{17}\text{cm}^{-2}$ and higher as normally used in laser diodes.

3.2. AlGaInP doping

As already published, the general behaviour of the Al(Ga)InP RA spectra with changing doping

concentration is similar to the AlGaAs system. P-doping leads to an increase in the RA signal while n-doping results in a decrease [13]. This effect, however, is restricted to higher photon energies and the effect is stronger for p-doping using Zn than for n-doping using Si [13].

To identify the lower detection limit in the AlGaInP system, the doping dependence of the RA signal was followed by a transient measurement which has a higher resolution. Fig. 2b shows the RA transient at a photon energy of 3.8 eV (326 nm) taken during growth of Zn-doped $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.52}\text{In}_{0.48}\text{P}$ grown on GaAs at 690 °C together with the switching sequence (Fig. 2a) and the ex situ doping profile determined by a C/V measurement (Fig. 2c). It can be seen that the different doping levels (undoped, 2×10^{17} and $5 \times 10^{17} \text{ cm}^{-3}$) can clearly be resolved. It can also be seen that only a short response time is needed. This is caused by the fact that a small number of layers is sufficient to establish the surface field which is needed to give the different response in the RA signal. Here, the response time is about 80 s which corresponds to a layer thickness of about 20 nm when switching on the DMZn source. This value is in the order of the penetration depth

of the light used. When ramping the DMZn flux the response time is longer which may be caused by a delayed increase of the DMZn concentration in the reactor caused by a retarded dilution decrease in the DMZn line. Furthermore, when comparing the in situ RAS measurement with the ex-situ C/V measurement it can be seen that the depth resolution of the non-destructive in situ signal is much better than the destructive C/V profiling. The reason for this is the unfavourable etching behaviour of the AlGaInP material during the C/V measurement.

3.3. NIR laser structure

The complete NIR laser structure grown on exactly oriented substrates consists of a GaAsP-QW embedded in $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ waveguide and $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ cladding layers. The growth of the whole laser structure is fingerprinted by taking RA spectra continuously and color-coding the RA signal [7]. The resulting fingerprint (sometimes also called ‘color-plot’ [1]) is shown in Fig. 3. The different layers of the laser structure can clearly be visualized. With increasing time the following growth states are resolved: oxidized substrate,

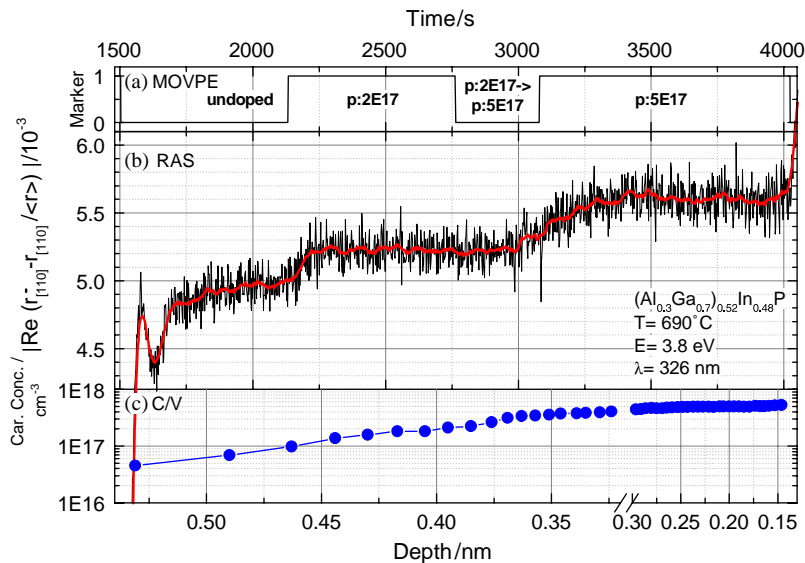


Fig. 2. RAS transient taken at 3.8 eV (b), ex situ C/V measurement (c), and MOVPE switching sequence (a) of $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.52}\text{In}_{0.48}\text{P}$ grown on GaAs at 690 °C.

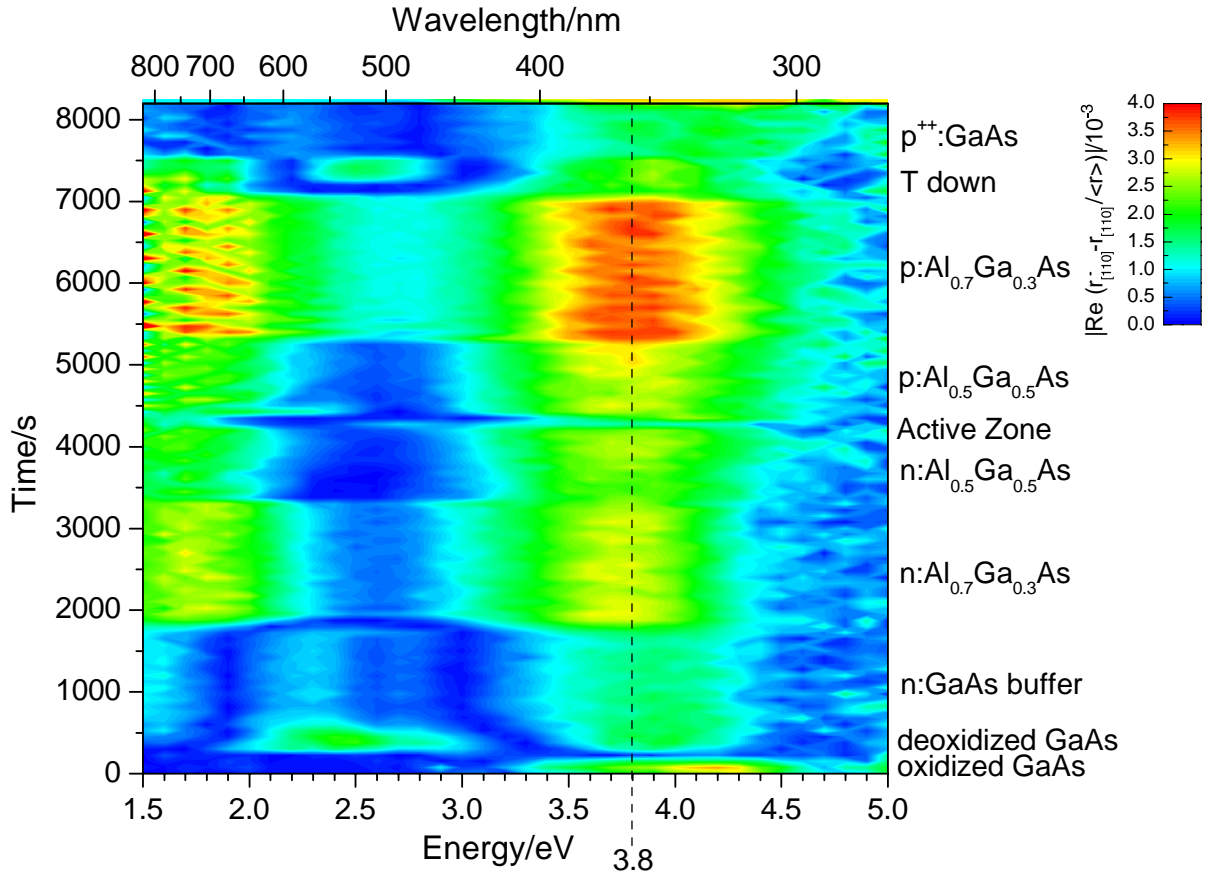


Fig. 3. Fingerprint (color-plot) of the complete growth process for a NIR laser diode at 770 °C. The respective layers and steps of the growth process are indicated in the figure. The photon energy of the transients shown in Fig. 4 is marked by a dashed line.

surface deoxidation, buffer growth, n-cladding layer, n-waveguide layer, quantum well, p-waveguide layer, p-cladding layer, and contact layer. Focusing on the AlGaAs layers it can clearly be seen that the RA spectra are different for the different compositions, doping types and levels. As reported the line shape of RA spectra for undoped AlGaAs with different compositions is rather similar despite a small energetic shift of the first minimum around 2 eV [4]. However, a strong increase in the RA values over the whole spectral range is reported with increasing Al content [4]. This can also be seen in Fig. 3 when comparing the waveguide and cladding layers. The cladding layers with high aluminium content have higher RA signals than the cladding layers with the low

aluminium content. This is superposed by the doping effect introduced in Fig. 1. The higher RA values of the p-doped layers as compared to the n-doped layers can be seen by the higher proportion of the yellow and red regions and reduced portion of blue regions. Due to the addition of different effects (composition and doping) each layer has its own significant RA fingerprint. The different GaAs layers (n-buffer and p⁺⁺-contact layer) can also clearly be distinguished, since the RA signal dependence on doping behaves similar as for AlGaAs [7].

To obtain a higher time resolution transient measurements have been carried out. For this purpose, a photon energy of 3.8 eV (326 nm) was chosen (dashed line in Fig. 3) where the

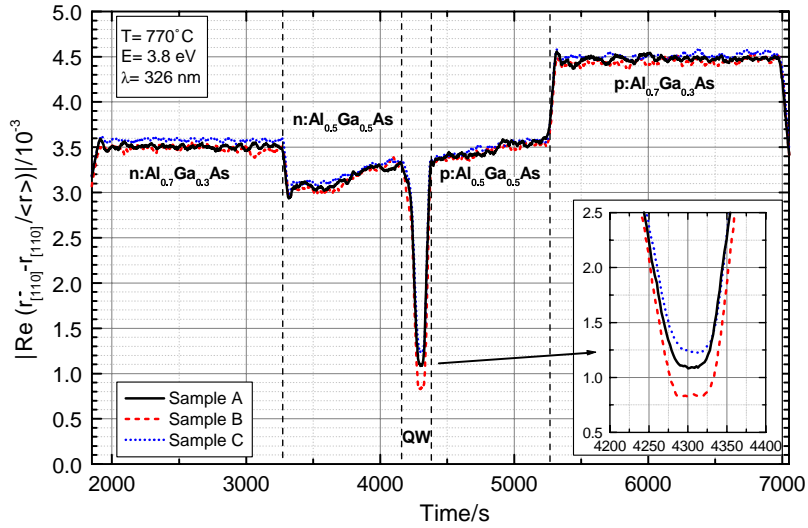


Fig. 4. RA transients showing cladding, waveguide, and QW layers of three different laser growth runs taken at 3.8 eV and 770 °C. The three structures have the same cladding and waveguide layers and differ only in the QW region. The inset shows a magnification of the RA transients during QW growth.

penetration depth of the light into the AlGaAs layers is in the range of 10 nm. Measurements are taken continuously with a time resolution of about 1 Hz. The lower limit for the time resolution is given by the wafer rotation frequency because at least one full wafer rotation is needed per measured point [10]. Fig. 4 shows RA transients of the inner part of the laser structure (cladding, waveguide and QW layer) shown in Fig. 3. By comparing the three transients which correspond to three different growth runs for the same laser structure with different QWs, a very high reproducibility of the growth process as well as the RAS measurement can be stated. Small deviations in the growth process (especially in composition or doping concentration) would be detected easily in such transients. Taking a closer look at the QW growth, the RA signal shows a different level for each structure since the GaAsP QWs are different. This is magnified in the inset in Fig. 4. To investigate this effect in detail, the influence of the emission wavelength on RA signal is studied in a test sample. This test sample contains three $\text{GaAs}_y\text{P}_{1-y}$ QWs with different compositions, y resulting in different emission

wavelengths. A strong dependence of the RA signal on GaAsP composition grown on GaAs is reported in the literature [14,15] for photon energies around 2.5 and 3.8 eV at growth temperature, respectively. Taking into account the reduced penetration depth with increasing photon energy the growth of the QWs was monitored here at 3.8 eV (326 nm). Fig. 5a shows the RA transient taken during growth of the three QWs. The first QW has the highest P content, while the P content is decreased in the next two QWs. As expected, the QW with the highest P content (QW1) shows the strongest change in the RA signal. The RA value reached during growth of the next two QWs (QW2 and QW3) is less different from the AlGaAs signal. Fig. 5b shows the corresponding low-temperature photoluminescence (PL) measurement of the sample taken at 10 K. Three different peaks with a small FWHM can be distinguished. These peaks can easily be correlated to the RA signal taken during growth of the QW (arrows between Fig. 5a and b). A linear dependence between the RA signal during QW growth (dashed lines in Fig. 5a) and the QW emission wavelength can be obtained giving the

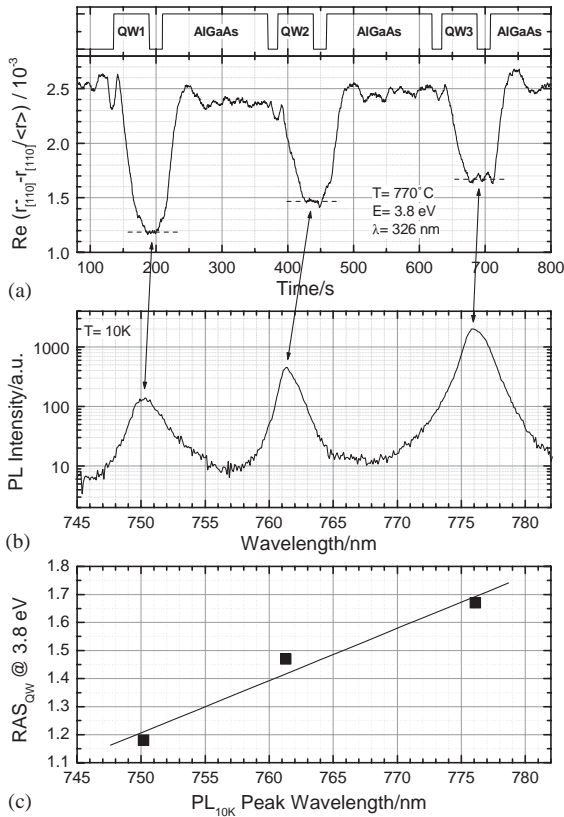


Fig. 5. (a) RA transient taken during growth of a three QW structure at 3.8 eV and 770°. (b) Low-temperature photoluminescence measurement (10 K) of the QW structure. (c) Resulting calibration curve correlating the RA signal during QW growth (dashed lines) to the PL peak wavelength at 10 K.

possibility to establish a calibration curve as shown in Fig. 5c.

3.4. VIS laser structure

Fig. 6b shows two RA transients taken during growth of laser structures for visible (red) emission together with the temperature profile used during the growth process (Fig. 6a). A corresponding fingerprint can be found in Ref. [16]. The structures are grown on substrates off-oriented 6° towards $\langle 111 \rangle$ A. In contrast to the structures reported before, these laser structures consist of InGaP QWs embedded in AlGaInP waveguide and

cladding layers. The RA transients again resolve the different layers with their different compositions and doping levels which enables an early information about the reproducibility of the growth process. Special attention should be given to the n:InGaP/n:AlGaInP interface (circle in Fig. 6b). The two transients have different heating procedures of the n:InGaP layer before the n:AlGaInP growth starts. This is also the reason for the time shift between the two transients of about 250 s after the n:InGaP/n:AlGaInP interface is grown. One of the transients shows a very high RA level of about 36×10^{-3} at the n:InGaP/n:AlGaInP interface, while the other one grown using an improved sequence shows a RA level of only about 5×10^{-3} . Ex situ investigation of the layer structure by microscopy showed that the surface corresponding to the transient with the high RA value at the n:InGaP/n:AlGaInP interface showed a rough surface, while the other sample has a smooth one. The very high RA signal at the n:InGaP/n:AlGaInP interface can therefore be correlated directly to a rough interface. With the help of the RA measurement it is therefore possible to locate problems in the growth process (e.g. interface properties) which were very elaborate to locate by ex situ means.

4. Summary

The MOVPE growth of NIR and VIS laser diodes is studied using RAS. AlGaAs and AlGaInP grown on GaAs show a clear dependence in the RA signal to the doping type and level for carrier concentrations down to values of $1\text{--}5 \times 10^{17} \text{ cm}^{-3}$. Using this effect, the different stages of the whole growth process can clearly be detected by its significant RA signal. Spectral and time-resolved measurements give the possibility to fingerprint and control the reproducibility of the growth process. The RA signal during GaAsP QW growth can be correlated directly to the emission wavelength of the laser structure. Buried interfaces can also be investigated using RAS as demonstrated for an AlGaInP laser structure.

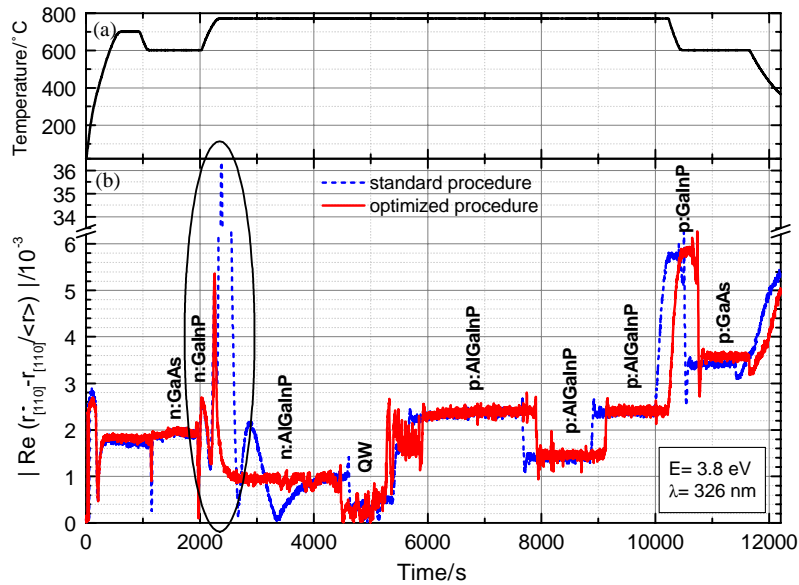


Fig. 6. Laser transients taken during growth of two different VIS laser structures (b). The growth temperature profile is given in (a). The n:InGaP/ n:AlGaInP interface is marked by a circle. Please note the axis break (b, left axis).

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