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In situ reflectance-difference spectroscopy of GaAs grown at low temperatures

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We present the results of *in situ* reflectance-difference spectroscopy (RDS) investigations of GaAs grown by molecular beam epitaxy at low substrate temperatures (LT-GaAs). The linear electro-optic (LEO) features in the vicinity of the E_1 and $E_1+\Delta_1$ optical transitions are found to depend on growth temperature T_g and V:III flux ratio. The observed LEO amplitude was found to decrease linearly with the measured neutral As antisite point defect concentration $[\mathrm{As}_{\mathrm{Ga}}^0]$ for growth temperatures $200\,°\mathrm{C}<T_g<300\,°\mathrm{C}$. This behavior relies on the influence of As antisite defects on the optical response of GaAs. The nonstoichiometry of LT-GaAs can be estimated in real time through the LEO amplitude vs $[\mathrm{As}_{\mathrm{Ga}}^0]$ relation. This makes RDS very attractive not only for *in situ* growth control but also for real-time tuning of the electronic properties of LT-GaAs.
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The growth of III-V semiconductors by molecular beam epitaxy (MBE) at low substrate temperatures has become very attractive due to the exceptional material properties obtained, which lead to a wide range of electronic and optoelectronic applications.[1,2] The most important of this class of materials is low temperature grown GaAs (LT-GaAs), i.e., grown at a substrate temperature between 200 °C and 350 °C. The normally used growth temperatures in MBE of GaAs lie around 600 °C. LT-GaAs is highly nonstoichiometric, containing up to 1 at. % of excess As, which is incorporated during growth mainly in the form of As antisite point defects ($\mathrm{As}_{\mathrm{Ga}}$).[3] The high concentration of excess As results in the formation of a broad band of deep donor trap states close to the midgap[4] which is associated with the donor states of $\mathrm{As}_{\mathrm{Ga}}$. Among other interesting properties related to the high concentration of deep donor traps, LT-GaAs displays ultrashort carrier trapping times and high absorption coefficients in the near infrared. Optical investigations of LT-GaAs focus mainly on short pulse nonlinear dynamics, in view of applications in fast optoelectronics. Therefore, the influence of excess As on the static optical properties has not been investigated in detail.

In situ reflectance-difference spectroscopy (RDS) has been successfully employed in MBE of III-V semiconductors for monitoring surface reconstruction and coverage,[5] as well as determining carrier concentrations.[6] The second case applies to doped III-V samples with (001) surfaces, where the optical anisotropy is induced by the near surface electric field (NSEF) via the linear electro-optic (LEO) effect. As a result, a broad resonance is observed in the RD spectra in the vicinity of the E_1 and $E_1+\Delta_1$ optical transitions.[7] Recently, LEO features were found also in *ex situ* RD spectra of LT-GaAs with a (001) surface.[8,9] By comparing the LEO resonance lineshape with that corresponding to doped samples, the NSEF of LT-GaAs was concluded to be of *n*-type (upward band bending). The NSEF in LT-GaAs originates from depleted deep donors due to the band bending close to the surface.

In order to investigate the correlation between the NSEF appearing in LT-GaAs and the presence of As antisites, we have studied by means of *in situ* RDS the behavior of the LEO resonance with respect to growth temperature T_g and V:III flux ratio. Our results show that the strength of the LEO resonance in the RD spectra does not depend only on the magnitude of the NSEF, as previously assumed,[8–10] but has a more complex behavior as a function of $\mathrm{As}_{\mathrm{Ga}}$ concentration. Moreover, the present study reveals the important potential of RDS as a real *in situ* method, not only to control the growth of LT-GaAs, but also to tailor its electronic properties during growth.

The samples used in this study were grown by MBE on semi-insulating (001) GaAs substrates at T_g ranging from 200 °C to 450 °C, As_4:Ga beam equivalent pressure (BEP) ratios between 9 and 50, and a growth rate of 0.5 μm/h. Prior to LT-GaAs, a 100 nm undoped buffer layer was grown at 580 °C. The growth temperature was measured with a thermocouple at the back side of the substrate. In order to calibrate the thermocouple reading in the temperature range used here, the melting points of In and Sn were used. Furthermore, the same holder and a constant substrate size were used throughout the study to ensure reproducibility of the results.

In situ RD spectra were recorded using a commercial spectrometer based on the standard design introduced by Aspnes *et al.*[11] RDS measures the relative difference

$$\Delta R/R=(R_{[110]}-R_{[\bar{1}10]})/(R_{[110]}+R_{[\bar{1}10]}) \qquad (1)$$

between the normal incidence reflectivities $R_{[110]}$, $R_{[\bar{1}10]}$ of light polarized along the [110] and $[\bar{1}10]$ principal axes of a zinc-blende-type semiconductor with a (001) surface, respectively. Optical access to the sample in the MBE chamber was provided through a strain free window, in order to reduce background signals.

Typical *in situ* RD spectra of LT-GaAs are shown in Fig. 1. The spectra presented here were recorded at T_g of 300 °C and a BEP ratio of 15. The positions of the E_1 and $E_1+\Delta_1$ transitions at this temperature[12] are denoted by arrows. Spectrum (a) was recorded during growth, while spectrum (b) was recorded at a growth interruption. The peak and dip in both curves (a) and (b), appearing close to the E_1 and $E_1+\Delta_1$ energies, respectively, are due to the LEO effect.[7] Except

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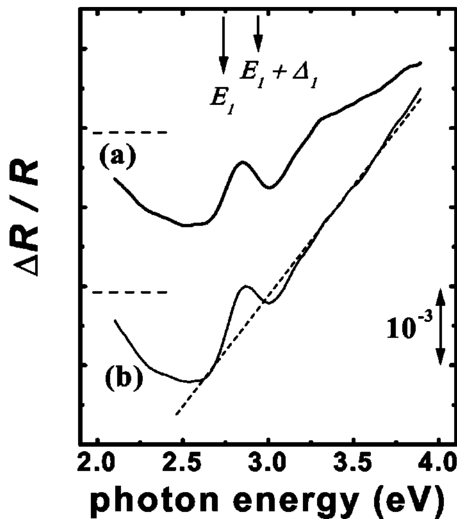

FIG. 1. Typical *in situ* reflectance-difference spectra of GaAs in the vicinity of the E_1 and $E_1+\Delta_1$ transitions, at a growth temperature of 300 °C (a) during growth, (b) at a growth interruption.

from the LEO component, the RD signal contains also a part owing to structural anisotropy of the surface, which varies between curves (a) and (b) due to the different As surface coverage conditions prevailing in the two cases. The LEO contribution, though, has almost the same magnitude in (a) and (b).

We define the peak-to-valley amplitude A_{pv} of the LEO resonance as the difference between the RD signal at the peak and dip, respectively, after subtraction of the surface contribution background, denoted for curve (b) by the dashed line in Fig. 1. Measurements of the RD spectrum as a function of layer thickness show that the LEO resonance appears as soon as the first GaAs monolayers have been grown at low substrate temperature. A_{pv} subsequently increases, acquires its final value when the LT-GaAs layer thickness has reached 20 nm and remains constant thereafter. This thickness is comparable to the light penetration depth in GaAs at a photon energy of 3.0 eV. RDS measurements on samples removed from the ultra-high vacuum chamber, to examine possible differences between *ex situ* and *in situ* RD spectra, reveal that the strength of the LEO features remains constant. Differences observed in the background signal are probably due to the influence of surface oxidation.

It is important to note here that a similar observation of the LEO resonance during growth or at an interruption is not possible when working at ''normal'' GaAs growth temperatures (500–600 °C), because the LEO effect is strongly reduced at high temperatures.[6] From this point of view, RDS appears very attractive for low substrate temperature MBE growth, where it can be used for *in situ* characterization not only via surface structure, but more directly by probing nonstoichiometry through the induced NSEF. We will return to this point later.

Figure 2 shows the dependence of A_{pv} on the growth temperature of LT-GaAs layers. The corresponding RD spectra were measured immediately after growth, at a substrate temperature of 250 °C, in order to rule out the weak dependence of A_{pv} on temperature as well as the temperature shift of the E_1 and $E_1+\Delta_1$ transitions. As can be seen in Fig. 2, A_{pv} exhibits a broad maximum around the growth temperature of 310 °C. The variation of the peak-to-valley amplitude of the LEO resonance with T_g is related to the incorporation of excess As during growth, which depends also strongly on growth temperature.

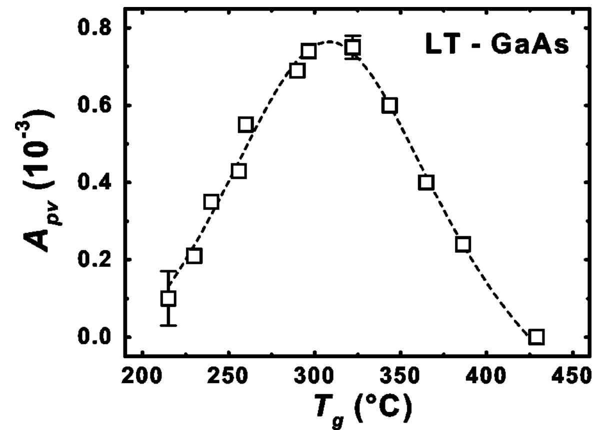

FIG. 2. Linear electro-optic amplitude A_{pv} of LT-GaAs samples as a function of growth temperature. Measurements were carried out at 250 °C during growth interruptions. The dashed curve is only a guide to the eye.

To further exploit the *in situ* monitoring capability of the method, we investigate the dependence of A_{pv} on the V:III flux ratio for various growth temperatures, since it is known that this also affects the incorporation of excess As. For the results shown in Fig. 3, A_{pv} was again measured at a substrate temperature of 250 °C. At $T_g=240$ °C, A_{pv} decreases with increasing V:III flux ratio, saturating at a constant value of 1.8×10^{-4}. Similarly, at 270 °C, A_{pv} also decreases but with a weaker tendency, while at 300 °C it remains constant.

In order to correlate the observed dependence of A_{pv} with nonstoichiometry, an independent measurement of the As antisite concentration is needed. The As_{Ga} point defect in LT-GaAs is associated with its infrared absorption properties, where an EL2-like absorption spectrum is observed,[13] as well as with its lattice expansion, due to the longer As-As

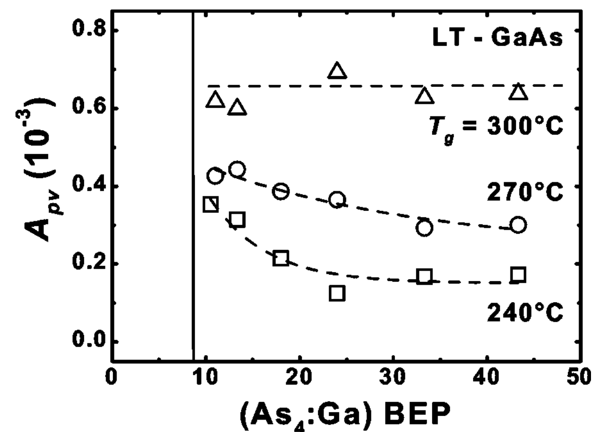

FIG. 3. Dependence of peak-to-valley linear electro-optic amplitude A_{pv} on As_4:Ga beam equivalent pressure (BEP) ratio for GaAs layers grown at different temperatures. Measurements were carried out at 250 °C during growth interruptions. The vertical line divides the As-rich from the As-limited growth regimes and the dashed curves are only guides to the eye.

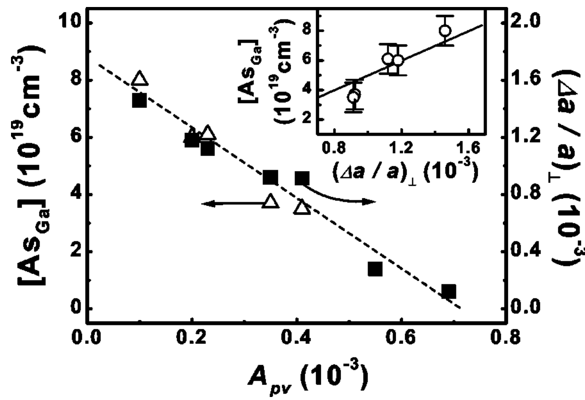

FIG. 4. Correlation between neutral antisite concentration $[\mathrm{As}^0_{\mathrm{Ga}}]$, lattice expansion $(\Delta a/a)_\perp$, and linear electro-optic amplitude A_{pv}, in GaAs layers grown at temperatures between 200 °C and 300 °C. The inset shows $[\mathrm{As}^0_{\mathrm{Ga}}]$ as a function of $(\Delta a/a)_\perp$.

bond.[14] We have performed near infrared absorption (NIRA) and double crystal X-ray diffractometry (DCXRD) measurements on our samples, to determine the neutral As antisite concentration $[\mathrm{As}^0_{\mathrm{Ga}}]$ and the lattice expansion, respectively. All samples grown at temperatures below 300 °C showed lattice expansion, as confirmed by the two peaks observed in DXRD rocking curves at the (004) reflection. The mismatch in growth direction $(\Delta a/a)_\perp$ was derived from the peak separation. NIRA measurements were performed at 77 K on samples grown at $T_g<260\,°\mathrm{C}$, and $[\mathrm{As}^0_{\mathrm{Ga}}]$ concentrations were determined using the known photoionization cross sections[15] of $\mathrm{As}_{\mathrm{Ga}}$. $[\mathrm{As}^0_{\mathrm{Ga}}]$ was found to vary linearly with $(\Delta a/a)_\perp$, according to $[\mathrm{As}^0_{\mathrm{Ga}}]=(5.0\pm0.3)\times(\Delta a/a)_\perp \times 10^{22}\ \mathrm{cm}^{-3}$, in agreement with previous results.[14] Figure 4 shows the correlation between $[\mathrm{As}^0_{\mathrm{Ga}}]$, $(\Delta a/a)_\perp$, and A_{pv} in the growth temperature range between 200 °C and 300 °C. The dependence of $[\mathrm{As}^0_{\mathrm{Ga}}]$ on $(\Delta a/a)_\perp$ is depicted in the inset. As seen in the figure, the LEO amplitude decreases almost linearly with $[\mathrm{As}^0_{\mathrm{Ga}}]$ and, consequently, $(\Delta a/a)_\perp$. At growth temperatures higher than 300 °C the concentration of As antisites is too low ($\leqslant 10^{17}\ \mathrm{cm}^{-3}$) to be detected by NIRA or to cause a measurable lattice mismatch.

For a discussion of the behavior of A_{pv} as a function of $[\mathrm{As}^0_{\mathrm{Ga}}]$ and T_g we have to consider the influence of the NSEF of LT-GaAs on the RD spectra. For III-V semiconductors with (001) surface in the presence of an electric field F in [001] direction, RDS measures the dielectric function change due to the linear electro-optic effect.[16] The peak-to-valley LEO amplitude A_{pv} will also depend linearly on F and can be written as

$$A_{pv}=Q\times F, \tag{2}$$

where Q is a material dependent coefficient. Equation (2) applies also to the NSEF. In this case, however, due to the spatial variation of the field, F has to be substituted with a properly averaged value, taking also into account the finite penetration depth of light. The magnitude of the NSEF is determined by the density of dopant atoms and the surface potential V_s. For a concentration N_{sd} of shallow donors[16] $F\propto\sqrt{N_{sd}V_s}$. In LT-GaAs, where a high concentration N_{dd} of deep donors is present, the NSEF originates from depleted deep donors in the region close to the surface. For $N_{dd}=N_{sd}$, a smaller field is expected due to a lower value of the surface potential. The dependence of F on concentration, nevertheless, will remain roughly the same as in the case of shallow dopants.

The concentration of $\mathrm{As}_{\mathrm{Ga}}$ in LT-GaAs, and consequently the magnitude of the NSEF, increases monotonously with decreasing growth temperature.[14] This would explain the observed increase of A_{pv} for $310\,°\mathrm{C}<T_g<400\,°\mathrm{C}$ (Fig. 2), in agreement with relation (2). As T_g continues to decrease one would expect a further increase of A_{pv}, due to a higher $\mathrm{As}_{\mathrm{Ga}}$ concentration and thus a higher value of F. However, A_{pv} is seen to decrease for $T_g<300\,°\mathrm{C}$. Furthermore, Fig. 4 represents the direct correlation between A_{pv} and $[\mathrm{As}^0_{\mathrm{Ga}}]$, where an almost linear decrease of A_{pv} with increasing $[\mathrm{As}^0_{\mathrm{Ga}}]$ is seen. According to relation (2), this would mean that either the magnitude of the NSEF or the LEO coefficient Q are decreasing in this concentration region. As for the NSEF, a decrease in its magnitude could be expected if (a) the intrinsic Fermi level of LT-GaAs moves towards midgap or (b) the condition of midgap surface Fermi level pinning is no longer valid. Both of these effects would lead to a lower surface potential. However, recent experiments[10,17] and calculations[18] have shown that for not annealed LT-GaAs the intrinsic Fermi level lies above midgap and that midgap surface Fermi level pinning is an adequate assumption. On the other hand, it is well known that heavy doping has a considerable effect on the optical properties of semiconductors. It was observed experimentally[19] that the broadening parameter Γ of the optical transitions at E_1 and $E_1+\Delta_1$ is larger in heavily *n*- and *p*-doped GaAs, leading to ''washed out'' features in the optical spectra. The high concentration of $\mathrm{As}_{\mathrm{Ga}}$ point defects present in LT-GaAs are expected to have a similar effect on the optical transitions, causing the decrease of the LEO coefficient Q, and hence the observed weakening of the LEO feature when T_g decreases below 300 °C. Thus, the LEO features observed in the RD spectra of LT-GaAs do not only depend on the strength of the NSEF, but also on the modification of the optical properties of GaAs by the $\mathrm{As}_{\mathrm{Ga}}$ point defects. More experimental and theoretical work is needed in order to describe quantitatively the behavior of the LEO effect in LT-GaAs for the whole growth temperature range.

As far as the behavior of the LEO amplitude as a function of BEP ratio is concerned (Fig. 3), the decrease of A_{pv} for T_g of 240 °C and 270 °C means that the density of incorporated $\mathrm{As}_{\mathrm{Ga}}$ increases with the BEP ratio. The observed dependence is in agreement with previously reported results.[20,21] At $T_g=300\,°\mathrm{C}$ we do not observe any dependence of A_{pv} on BEP ratio. The high value of A_{pv} indicates that the density of incorporated excess As is low in this case (Fig. 4), therefore a vanishing BEP ratio dependence can be expected.

As already pointed out, the present results are also very important from the viewpoint of applying RDS as a tool to characterize LT-GaAs layers and tuning their electronic properties *in situ*. Such a method to examine the specific properties of this material was lacking up to now. For this purpose, the linear relation between $[\mathrm{As}^0_{\mathrm{Ga}}]$ and A_{pv} shown in Fig. 4 can be utilized, in order to determine *in situ* the anti-

site defect concentration. The estimated accuracy of this method is $\pm 20\%$. As the LEO features can be observed during growth as well as at growth interruptions (see Fig. 1), measurements of RD spectra yield information about the level of nonstoichiometry in LT-GaAs in real time. This is important for the reproducible growth of the material with well defined properties as well as for its utilization in single or multilayer semiconductor structures. It should be noted, however, that the linear correlation between $[\mathrm{As}_{\mathrm{Ga}}^0]$ and A_{pv} is restricted to T_g in the range between 200 °C and 300 °C.

In summary, we presented the results of an *in situ* RDS investigation of GaAs grown by MBE at low substrate temperatures between 200 °C and 400 °C. The peak-to-valley amplitude A_{pv} of the LEO resonance as a function of growth temperature T_g exhibits a broad maximum at 310 °C. For $T_g > 310$ °C the reduction of A_{pv} is attributed to the decreased As antisite concentration, while the decrease of A_{pv} when $T_g < 310$ °C is ascribed to the influence of $\mathrm{As}_{\mathrm{Ga}}$ on the LEO coefficient of GaAs. NIRA was used to independently determine the concentration $[\mathrm{As}_{\mathrm{Ga}}^0]$ of neutral As antisites and a linear correlation was observed between $[\mathrm{As}_{\mathrm{Ga}}^0]$ and A_{pv} for growth temperatures between 200 °C and 300 °C. The present results also show that RDS can be utilized for the *in situ* determination of the concentration of As antisites in LT-GaAs, allowing the first real-time estimate of nonstoichiometry. It hence provides a means to control the growth conditions during MBE at low substrate temperatures, which has not been possible before.

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