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Full Length Article

Influence of UDMHy on GaAs (0 0 1) surface reconstruction before and during growth of Ga(NAs) by MOVPE

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ABSTRACT

III–V semiconductors containing small amounts of Nitrogen ("dilute nitrides") are very promising material systems for optoelectronic applications. There are many studies about growth characterization of Ga(NAs) in metalorganic vapor phase epitaxy (MOVPE), but very little is known about the nitridation process on the GaAs (0 0 1) surface and the influence of the surface reconstruction on the Nitrogen (N) incorporation. Therefore, we investigated GaAs (0 0 1) surfaces under different tertiarybutylarsine (TBAs) and 1,1-dimethylhydrazine (UDMHy) ambient conditions in MOVPE. For in situ surface characterization reflectance anisotropy spectroscopy (RAS) was used. Under sufficient TBAs stabilization the surface forms an As rich c(4 × 4)β surface reconstruction. This changes towards a more Ga rich (2 × 6)/(6 × 6)-like reconstruction if additional N is supplied. Therefore, UDMHy seems to enhance the As desorption from the surface or the surface reconstruction changes due to incorporated N. This conversion occurs rapidly within 5 s when UDMHy is supplied and was observed in a temperature range from 450 °C to 600 °C. The measured RAS spectra are then compared to the RAS spectra obtained during Ga(NAs) growth. These also exhibit a (2 × 6)/(6 × 6)-like surface reconstruction which seems to be necessary to incorporate a sufficient amount of N into the GaAs crystal.

1. Introduction

In investigations with reflectance anisotropy spectroscopy (RAS) - also known as reflectance difference spectroscopy (RDS) - many reconstructions of gallium arsenide (GaAs) (0 0 1) surfaces have been characterized and modeled. Especially in molecular beam epitaxy (MBE) this is possible by using electron based techniques like reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) or other ultra high vacuum (UHV) techniques like scanning tunneling microscopy (STM) to identify the surface reconstructions [1,2]. With the help of UHV transfer systems and by comparison to the MBE results these reconstructions were also observed in metalorganic vapor phase epitaxy (MOVPE), where the use of electrons is hindered by the rough vacuum in the reactor [3,4]. Furthermore there are also theoretical attempts in modeling the RAS spectra for known reconstructions [5–7]. With regard to nitrogen (N) containing GaAs, which is discussed for optoelectronic devices, the incorporation of N into the GaAs crystal is not fully understood. The incorporation efficiency depends on different factors like the choice of the precursor, gas phase ratios and temperature [8]. The incorporation might also be connected to surface interactions therefore it is of high interest to understand more about the nitridation processes on the GaAs (0 0 1) surface. For the use of tertiarybutylhydrazine (TBHy) as N precursor the GaAs surface seems to form a (3 × 3)-like reconstruction which was correlated to MBE results [9,10]. For growth of dilute nitrides however, 1,1-dimethylhydrazine (UDMHy) is mostly used as a nitrogen precursor in MOVPE [8]. Therefore we used the photon based RAS to investigate the influence of UDMHy on the GaAs (0 0 1) surface reconstruction under various partial pressures of UDMHy and different temperatures closely to typical growth conditions. In addition, the Ga (NAs) surface was analyzed during growth.

2. Experimental procedure

The investigated samples where grown in an Aixtron Aix 200 horizontal GFR reactor which is operated under a constant reactor pressure of 50 mbar (37.5 Torr) and a total flux of 6800 sccm palladium purified Hydrogen. The reactor is heated by 6 halogen lamps. To ensure identical GaAs (0 0 1) surface quality a 250 nm thick GaAs Buffer layer was grown at 625 °C under optimized growth conditions on each sample. For homogeneous growth the samples were additionally rotated with 50–70 rpm. In between the experiments and while changing the temperature in the reactor (450 °C to 600 °C) tertiarybutylarsine (TBAs) stabilization has been provided to prevent As desorption. For the

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growth experiments triethylgallium (TEGa) has been used as group III precursor and TBAs as well as UDMHy as group V precursors. For the nitridation process TBAs ($2.04{\cdot}10^{-2}$ mbar) has been kept constant and the partial pressure of UDMHy has been varied between $4{\cdot}10^{-2}$ mbar and $9.3{\cdot}10^{-1}$ mbar. During Ga(NAs) growth $8.151{\cdot}10^{-3}$ mbar TEGa was supplied additionally.

The surface anisotropy has been monitored by a Laytec EpiRAS 200 setup which is attached above the reactor of the MOVPE system. RAS basically measures the difference in normal-incidence reflectance between two orthogonal polarizations of light. In [1,2] the experimental setup of RAS is described and the measured value $\Delta r/r$ is introduced. Due to our growth oriented setup we execute our measurements under wafer rotation. Therefore it cannot be distinguished between positive and negative RAS values, gaining the absolute RAS signal $|\Delta r/r|$. To regain information about the sign we carried out reference measurements without rotation and compared them to spectra from the literature. RAS allows investigations in two different modes. By measuring the whole energy range of the light source (Xe-lamp, 1.52–5 eV) a spectrum is detected. The RAS spectrum is a "fingerprint" for each surface reconstruction and therefore known surface reconstructions can be identified. At a fixed photon energy, a time transient can be measured to achieve a good time resolution ($\Delta t = 1$ s).

For composition analysis high resolution X-ray diffraction (HRXRD) using a Panalytical X́Pert Pro system with the Cu Kα1 wavelength (1.5405 Å) has been applied. The diffraction pattern around the GaAs (0 0 4) reflex was obtained and simulated with the X́Pert Epitaxy software.

3. Results and discussion

In this paper the influence of UDMHy on GaAs (0 0 1) surface reconstruction in MOVPE has been investigated by RAS. By using transients the time dependence of the nitridation process was observed. Additionally the reconstruction of Ga(NAs) (0 0 1) surface has been monitored during the growth process.

In Fig. 1a a GaAs (0 0 1) surface was investigated at 550 °C under various N/As ratios while keeping the TBAs partial pressure constant at $2.04{\cdot}10^{-2}$ mbar. Under pure TBAs ambient a c(4 × 4)β reconstruction is observed (black solid line) which is a common surface reconstruction of a GaAs [2]. By adding UDMHy into the reactor the spectra start to change. The peaks at 1.7 eV and 2.6 eV swap their signs and slightly shift their positions to higher energies (black to grey spectrum). Additionally the peak at around 4 eV decreases in intensity. For the highest V/V value (N/As = 46, grey solid line) a (2 × 6)/(6 × 6)-like reconstruction can be identified [2,3]. The (2 × 6)/(6 × 6) model consists of some As-As dimers (33% of a monolayer of As) on top of nearly one monolayer of Ga. In comparison the c(4 × 4)β model consists of 3 As-As dimers per unit cell on top of a monolayer of As. Therefore the (2 × 6)/(6 × 6) surface reconstruction is significantly more Ga-rich compared to the c(4 × 4)β model. Due to the fact that nitrogen was added to the surface one can assume enhanced As desorption from the surface (more Ga on top of the surface) or nitrogen building in the surface reconstruction (sitting on top of Ga places or indiffusion of N [9,11]) leading to a (2 × 6)/(6 × 6)-like spectrum.

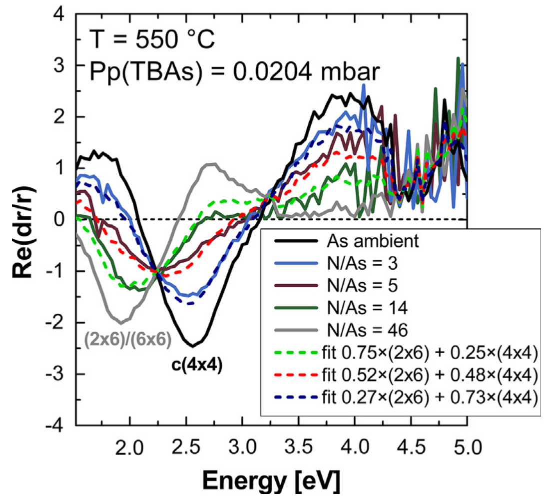

Fig. 2. RAS spectra of the GaAs (0 0 1) surface at 550 °C under a partial pressure of $2.04{\cdot}10^{-2}$ mbar of TBAs and at different partial pressures of UDMHy out of Fig. 1. The dashed lines indicate a linear combination between the c(4 × 4)β and the (2 × 6)/(6 × 6) surface reconstruction to fit N/As ratios of 3, 5 and 14 respectively.

The reconstruction of the changing surface is shown in Fig. 1b in form of a transient at 2.1 eV. Starting with a ratio of N/As = 14 the reconstruction changes from the more (2 × 6)/(6 × 6)-like surface reconstruction to the As rich c(4 × 4)β surface reconstruction in TBAs ambient (corresponding to the green solid line and black solid line respectively from Fig. 1a). At around 100 s the conversion to the more Ga rich surface under a ratio of N/As = 5 is depicted. The change of the reconstruction from N/As = 14 to pure As ambient occurs within roughly 5 s which is seen in the inlet of Fig. 1b. This rapid change could be a sign for rapid N-desorption from the surface and was observed for all individual N/As ratios out of Fig. 1a.

Another remarkable feature in Fig. 1a is the fix point at around 2.3 eV. This hints to some linear combination of the two reconstructions on the surface. Noting the grey spectrum as (2 × 6)/(6 × 6)

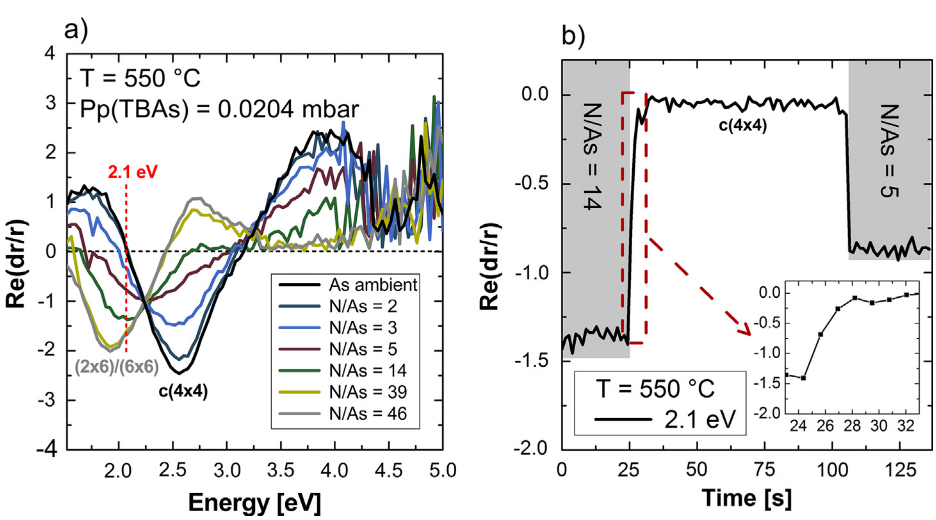

Fig. 1. (a) RAS spectra of the GaAs (0 0 1) surface at 550 °C at a partial pressure of $2.04{\cdot}10^{-2}$ mbar of TBAs and under different partial pressures of UDMHy. The surface reconstruction changes from a c(4 × 4)β (black spectrum) towards a (2 × 6)/(6 × 6) reconstruction (grey spectrum). RAS transient at 550 °C at an photon energy of 2.1 eV following the change between different N/As ratios out of a). The change of the surface reconstruction occurs within 5 s as indicated in the inlet.