Characterization of GaSb thin films from tailor-made single source precursors

Andreas Seemayer*, Alexander Hommes, Sascha Hümann† and Klaus Wandelt

Institute for Physical Chemistry – University of Bonn

Wegelerstr. 12, 53115 Bonn, Germany

Stephan Schulz

Institute for Inorganic Chemistry – University of Essen

Universitätsstr. 6, 45117 Essen, Germany

Abstract:

We investigated the growth and the surface properties of GaSb on Si(001) substrate by using a tailor-made fully-alkyl-substituted heterocyclic single-source precursor. The precursor properties during the evaporation process were monitored by RGA. The initial film growth was monitored by AES. Using a HV cold wall reactor, dense GaSb films could be produced and were characterized by AES, AFM and S-XPS. The results are discussed in terms of a correlation of the electronic and geometrical properties with the composition and structure of the films.

Note: This is a short version of the submitted abstract. The journal (Journal of Crystal Growth) does not accept formatted text in the abstract. The total length of the proceedings paper is limited to 4 pages.

* Electronic Address: seemayer@pc.uni-bonn.de

† New address: Max-Planck-Institute für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

1. Introduction

III-V semiconductor films used for opto- and microelectronic devices have traditionally been grown by (MO)MBE and LPE processes. An alternative metal-organic CVD-Process, which has been established in the last two decades for high-throughput and low-cost fabrication works for nitrides, phosphides and arsenides, but is problematic for antimonides. In particular, for the production of GaSb thin films, an alternative synthesis route is a CVD-process using fully-alkyl-substituted heterocyclic single-source precursors of the general form $[R_2 GaSb R'_2]_n$.

Tetraalkyldistibines $Sb_2R'_4$ tend to react with trialkylgallanes GaR_3 under Sb-Sb bond cleavage. The reaction proceeds stepwise with the initial formation of a distibine Lewis acid-base adduct, which subsequently reacts under Sb-Sb and Ga-C bond cleavage and formation of heterocyclic stibinogallanes. All presented experiments were performed by using the precursor $[^iBu_2 GaSb Et_2]_2$ (1).

2. Experimental

The used precursor (1) were synthesized by a literature method [1] using standard Schlenk-techniques and a glovebox with N_2 atmosphere as a storage. The compound was transferred into the UHV chamber by using a closed glass vessel.

In a first step, the precursor properties were monitored during the evaporation process under UHV conditions (base pressure $< 10^{-9}$ mbar). Due to the very high cleanliness any influence of other species to the growth process could be excluded. The gas phase during the growth process was monitored via Residual Gas Analysis by using a quadrupole mass spectrometer (Balzers QMG 112) and the produced films were characterized using Auger Electron Spectroscopy (Perkin Elmer PHI 3017 Auger Subsystem). For sample cleaning

the UHV chamber is equipped with a sputter gun, which produces an ion current of about 10 μ A on the sample, which is equivalent to a sputter rate of about 0,8 ML/min.

Additional growth experiments were performed in a cold wall CVD reactor under HV conditions. The HV grown films were stored in glass vessels under ambient conditions and transferred to the just described UHV chamber.

Using a commercial PicoSPM I AFM in contact mode and in tapping mode, the morphology of the produced surfaces was investigated. All AFM measurements were made under ambient conditions.

The S-XPS measurements were performed at the SoLiAs UHV chamber at BESSY II. The sample were cleaned by sputtering with argon ions by using a beam energy of 500 eV and a ionisation current of 20 mA. All spectra were taken under normal emission. Under this condition the photoelectron escape depth is equal to the inelastic mean free path.

3. Results and Discussion

Due to former DSC results [2] the precursor molecule shows thermal decomposition at 464 K and 486 K. Therefore it should be possible to sublime the species without decomposition at lower temperatures. Monitoring the base pressure during evaporation shows an increasing pressure at temperatures above 370 K (figure 1). By identifying the compounds fragments by residual gas analysis with the constraint of a reasonable growth rate but low background pressure of residual fragments which may lead to carbon contamination of the produced films, evaporation temperatures around 400 K were found to be a good process value.

In UHV, gallium and antimony could be deposited on Si(001) substrate, but due to the high contamination of the residual gas, an excess of antimony species was detected. During deposition the sample was heated to temperatures in the range of 670 K to 770 K. In

general lower deposition temperatures could be used, but then the quality of the produced films would be rather low in terms of full coverage [2]. After sputtering, the carbon contamination was eliminated (figure 2a), but the Sb:Ga ratio was still greater than unity. Therefore the carbon intoxication is a post deposition process, whilst the antimony excess leads to the assumption, that the precursor molecule undergoes some reactions in the gas phase. Comparing the adsorbent and substrate Auger intensities during sputtering a Frank-van-der-Merwe growth mode could be excluded (figure 2b).

Using a home-made cold wall MOCVD reactor, dense GaSb films of the thickness of about 1 μm could be produced [2]. Comparison of the Auger spectra of the UHV- and HV-grown films shows that there is a chemical shift within the Sb MNN Auger electrons, which is due to the antimony excess during the UHV growth process (figure 3). The Auger intensities of the HV-grown films were constant within the grown area of about 1 cm^2 . Due to the transport the surface region was contaminated with carbon and oxygen species. Cleaning by argon ion sputtering leads to a carbon free surface after 40 minutes, whereas a sputter time of about 90 minutes was needed for cleaning the samples from any oxygen contamination.

The chemical composition of the HV-grown films was characterized by S-XPS. Due to the transport oxygen and carbon impurities were found to be present on top of the GaSb film. No other species could be identified on the surface. By using different primary energies, namely 150 eV, 650 eV and 1070 eV the composition of the surface and the bulk region could be investigated due to the different escape depth of the produced photoelectrons. In particular by high resolution spectra the Sb4d, Sb3d and Ga3d photoelectrons were investigated. The impurities were characterized by O1s and C1s region scans. The presence of GaSb was proven due to the binding energy of the considered Ga and Sb peaks. They agree with reference spectra of pure GaSb (Sigma Aldrich 99,99%) as well as literature data [3], [4]. The results are shown in table 1 and

figure 4. The presence of pure Ga or Sb moieties could be excluded. The samples could be cleaned by argon ion sputtering within 20-40 minutes. Due to the sputtering process the surface region was found to be gallium-rich in agreement with [5]. In the case of thin film production on pure Si(001) the bulk compound was found to be stöchiometric under consideration of experimental errors. When preoxidized silicon wafers are used, the films were found to be gallium-rich.

Due to geometry optimization in respect to former experiments [2], the surface roughness could be reduced by about 2 magnitudes. The topography is strongly dependent on the substrates temperature during the deposition process. The higher the temperature, the bigger the single crystallites are. At higher deposition temperatures the typical cubic shape of GaSb single crystals could be identified. At a deposition temperature of 723 K the average height is 58 nm and the RMS is 14.3 nm. At a deposition temperature of 773 K the average height could be measured as 125 nm and the RMS value is 26 nm. The roughness histograms of films which are grown at the presented substrate temperatures are shown in figure 5. If the growth process is initiated on preoxidized silicon wafers, an additional ordering effect takes place since all crystallites have the same spatial alignment. Measurements in non-contact mode did not show any contrast in the phase image. This means that there are besides GaSb no other gallium or antimony moieties present on the surface, which is in agreement with the AES and S-XPS results.

4. Conclusion

It has been shown that tailor-made single source precursors of the general type $[R_2GaSbR'_2]_n$ can be used for GaSb thin film production whereas the precursor (1) is the most promising candidate for a MOCVD process under HV conditions. The film density and roughness can easily controlled by changing the substrates temperature during the

deposition process at a given geometry. The achieved GaSb films were pure when clean Si(001) wafers were used as a substrate. Carbon and oxygen contaminations could be found at the surface only, which was due to the ambient conditions while storing the films.

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Peak	binding energy [eV]	splitting [eV]	ratio
Ga3d	18,77(20)	0,446(38)	0,665(93)
Sb4d	31,72(20)	1,269(33)	0,733(83)
Ga3p	104,02(20)	3,36(15)	0,425(86)
Sb3d	527,80(20)	9,368(32)	0,676(5)

table 1: peak position and spin orbit splitting of Ga and Sb photoelectrons

figure 1: base pressure during evaporation of (1)

figure 2a: auger spectrum of a sputtered uhv grown film
figure 2b: relative intensity of silicon and antimony auger signals as a function of sputter time

figure 3: SB MNN photoelectrons of the hv-grown and the uhv-grown film

figure 4: s-xps survey spectra at different primary energies

figure 5: histogram of afm topography images of films deposited at different temperatures

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