Molecular beam epitaxy of GST controlled by quadrupole mass spectrometry

Wolfgang Braun*, Ferhat Katmis, Karthick Perumal, Roman Shayduk
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany
* email: braun@pdi-berlin.de, phone: +49-(0)30-20377-366, fax: +49-(0)30-20377-201.

Introduction

Growth of epitaxial GST in ultrahigh vacuum is a challenge, as it has a very narrow growth regime, and the presence of one flux affects the sticking coefficient of the other at higher substrate temperatures. In addition, RHEED growth oscillations are not observed that could otherwise be used for growth rate calibration.

Experiment and Results

When growing GST from the elements in ultrahigh vacuum by molecular beam epitaxy (MBE), we have noticed that the material desorbs from the substrate at temperatures below the transition to the hexagonal phase in the bulk. A rapid decrease of the sticking coefficient around 200°C indicates an unequal distribution of the bond strength in GST: molecules with strong internal bonds are less strongly bound amongst themselves, with an intermolecular bond strength low enough to let the crystal disintegrate at desorption temperatures similar to the desorption temperatures of Te, the element with the highest vapor pressure amongst Te, Sb and Ge.

To further investigate this finding, we have used reflection mass spectroscopy (REMS) in our growth chamber to investigate atomic and molecular fluxes emanating from the surface (Fig. 1) similar to studies on III-V and II-VI compounds. The Hi-den HAL IV quadrupole mass spectrometer (QMS) installed in a source port of our deposition chamber analyzes the fluxes reemitted from the substrate and its holder up to masses of 510 amu. This allows the analysis of molecules up to Sb4. The shutter in front of the QMS port is opened and closed with a period of 20+20 s to alternatingly measure the signal and its background, producing a square wave as shown in the plots. We deduce a typical temperature difference between substrate and substrate holder of more than +150 K at temperatures around 250°C. The desorption signal from the substrate therefore intrinsically separates from the holder signal in the range 150 K above complete sticking, producing good signal to noise ratios.

At high temperatures above 260°C, all deposited material reflects or redesorbs, the growth rate is zero. The data of selected mass/charge ratios shown in Fig. 1 demonstrate that GST desorbs incongruently, with GeTe constituting the only reemitted species.

Figure 1: Different species reemitted from the sample surface irradiated with Ge, Sb and Te fluxes at a ratio 2:2:5 as a function of substrate temperature.

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containing more than one element we have detected so far. Since the cubic structure that forms on the substrate during deposition contains only heteroelemental bonds, the fact that GeTe is the only heteromolecule observed in the reemitted flux indicates that the Ge-Te bond is the strongest bond in the metastable cubic phase. While Ge follows GeTe in Fig. 1, Te and Te$_2$ continue to desorb at lower temperatures. The desorption behavior does not significantly depend on the substrate material (Fig. 2) nor on its orientation. The main difference is a constant temperature offset between different substrate / substrate holder combinations. This finding is extremely useful, since it allows us to define the growth conditions without direct reference to the substrate temperature, a quantity notoriously difficult to measure in MBE. Instead of defining the growth conditions in terms of the substrate temperature, we have therefore begun to control the growth by using the QMS signal as in situ feedback. Good epitaxy is only obtained in a narrow range of substrate temperatures where a significant amount of material already desorbs. Our current growth procedure, shown in Fig. 3, therefore starts at high substrate temperature, in the complete desorption regime. The GeTe signal measured at high temperature serves as a reference for growth. The QMS is set at an electron energy of 20 eV to not doubly ionize the Sb$_2$ molecules, and the emission current is 800 $\mu$A. The substrate temperature is then lowered at a rate of 0.1 K/s until all material sticks for nucleation, and subsequently raised again to a value of 20% GeTe desorption. In Fig. 3, the substrate thermocouple temperature was not changed after having reached the 20% level, resulting in a subsequent increase of the GeTe desorption. This indirectly indicates a temperature increase of the substrate surface due to increasing absorption of heater power with increasing film thickness, an effect well known in MBE of small band gap materials on larger band gap substrates. The thermoelement behind the back of the substrate is not sensitive enough to detect these changes and therefore does not adequately correct the heater power. In addition to stable growth conditions, we have found that a high quality of the surface prior to GST deposition is crucial for obtaining films with a high degree of epitaxial order. Further studies will focus on investigating the development of the interface between GST and various substrates.

Conclusion

Using QMS as an in situ feedback, we can accurately control the growth conditions of a material such as GST that needs to be grown in a regime with non-negligible desorption. Since the desorption signal is a direct measure of the growth conditions at the surface, REMS allows us to accurately transfer growth conditions for GST epitaxy from substrate to substrate and run to run.