Structure and composition of Ge-Sb-Te thin films grown by molecular beam epitaxy on Si(111) substrates

A. Giussani, P. Karthick, P. Rodenbach, M. Hanke, W. Braun, R. Calarco, and H. Riechert

1Paul Drude Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin
2CreaTec Fischer Co. GmbH, Industriestr. 9,74391 Erligheim, Germany
*email address: giussani@pdi-berlin.de

ABSTRACT

Ge-Sb-Te thin films were grown by molecular beam epitaxy on Si(111) substrates. The growth was monitored in situ by means of reflection high-energy diffraction and quadrupole mass spectrometry, in order to control structural and compositional properties of the epilayers, respectively. Stoichiometry was assessed by x-ray fluorescence. Films with a Ge:Sb:Te content close to 2:2:5 were characterized by synchrotron radiation x-ray diffraction, showing that films grow (111) oriented with a strongly preferred in-plane orientation GST<-110>\|\langle1-10\rangle.

Key words: GST, MBE, XRD, RHEED.

1. INTRODUCTION

Phase change memories based on Ge₂Sb₂Te₅ thin films are considered the most promising class of non-volatile memories for the future, featuring fast write and read speeds, bit alterability, high endurance and scalability. The standard technique employed for the growth of Ge₂Sb₂Te₅ is physical vapor deposition, which provides polycrystalline layers. However, it was recently reported that structural ordering of chalcogenides’ cubic metamaterials reduces the switching threshold energies, anticipating that layers with a preferred orientation exhibit superior properties to the polycrystalline ones. In this perspective, the preparation of truly single crystalline Ge₂Sb₂Te₅ thin films is of extremely high interest, and molecular beam epitaxy (MBE) represents the growth technique of choice. Hereafter it is shown that epitaxial Ge₂Sb₂Te₅ thin films can be achieved on the (111) surface of silicon, although a mismatch of approximately 10% exists between the cubic metastable phase of the epilayer and the substrate.

2. EXPERIMENTS

Si(111) substrates with 0.03° miscut were wet cleaned, transferred into a MBE system from CreaTec Fischer Co. GmbH and here annealed at 715°C for 15 min, until a (7x7)-reconstructed (111) surface was observed by reflection high-energy electron diffraction (RHEED). Thin films of chalcogenides were grown by evaporating Ge, Sb, and Te from three separate effusion cells. Growth was followed by means of a line of sight quadrupole mass spectrometer (QMS). Epilayers grown at different substrate temperatures and constant Ge, Sb, and Te fluxes were investigated by x-ray fluorescence (XRF) for compositional analysis. Finally, a Ge-Sb-Te (GST) specimen with a stoichiometry close to Ge₂Sb₂Te₅ was studied by synchrotron radiation x-ray diffraction (SR-XRD) at BESSY II in Berlin, using a beam energy of 13keV.

3. RESULTS & DISCUSSION

Fig. 1a) shows that the growth rate decreases with substrate temperature, due to thermal decomposition of GST at temperatures as low as ~ 125°C. Species desorbing from the surface are monitored with the QMS. Desorption rates are kept constant by adjusting the substrate temperature in course of deposition. This approach aims at reducing the presence of compositional gradients in the film, especially close to the interface with the substrate, where changes of the sample surface temperature are more pronounced. Vertical markers in Fig. 1a) highlight the existence of four growth regimes with increasing substrate temperature: (1) amorphous, (2) polycrystalline, (3) epitaxial, and (4) no growth, respectively. Structural properties of the growing layers were assessed by RHEED. Fig. 1b) displays, for instance, the RHEED image of the GST(111) surface at the end of the growth at ~ 245°C (region (3) of Fig. 1a)). The RHEED pattern presents no polycrystalline rings and is streaky, indicating epitaxy of a smooth film. Instead, attempts
to grow epitaxial GST on Si(001) resulted in polycrystalline layers. It is noted that a similar behavior was reported for GST growth on GaSb and InAs: for both substrates, films exhibit higher structural quality on (111) than on (001). A possible explanation resides in the fact that GST has a rhombohedral distortion along a <111> direction, which makes the (111) surface more suitable for epitaxial growth than the (001). XRF compositional analysis showed that stoichiometry varies with growth temperature, owing to relative changes in the desorption rate of Ge, Sb, Te and their molecular aggregates from the sample surface. It was found that the film stoichiometries lie close to the GeTe-Sb2Te3 tie-line. Epitaxial films with composition close to 2:2:5 could be achieved at ~245°C. On such a specimen, a synchrotron radiation SR-XRD in-plane reciprocal space map (RSM) around the GST(-220) reflection was acquired, as illustrated in Fig. 2. The detected Bragg peaks agree with the pattern of a (111)-oriented epilayer with in-plane epitaxial relationship GST<-110>||Si<1-10>. It is noted that the observed polycrystalline rings have an intensity which is almost 3 orders of magnitude lower than the Bragg spots, and are visible only because of the high brilliance of the synchrotron.

4. CONCLUSION

Successful heteroepitaxial growth of GST thin films on Si(111) substrates was demonstrated. In situ RHEED and QMS indicated that epitaxial growth is achievable only within a narrow window of substrate temperature, ranging from ~215°C to ~245°C. Ex situ XRF showed that, for constant Ge, Sb, and Te fluxes, film composition varies with substrate temperature close to the GeTe-Sb2Te3 tie-line. Ex situ SR-XRD demonstrated that GeSb2Te5 epilayers grow with GST[111]||Si[111] and GST<-110>||Si<1-10> out-of-plane and in-plane epitaxial relationships, respectively. Further experiments are on-going to improve growth control in terms of film composition and crystalline perfection. In especial, investigation of the defect structure via XRD and TEM is in progress to understand the mechanism of film relaxation on the highly lattice-mismatched Si substrate.

REFERENCES


![Fig. 1: a) growth rate of GST versus substrate temperature; b) RHEED image at the end of the growth performed at ~245°C.](image1)

![Fig. 2: In-plane RSM around the GST(-220) peak. GST(111) surface coordinates are used for the axes, Bragg peaks are labeled in cubic bulk coordinates.](image2)

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