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Growth control of epitaxial GeTe–Sb_2Te_3 films using a line-of-sight quadrupole mass spectrometer

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ABSTRACT

A narrow growth window combined with highly temperature dependent compositional variations poses a serious problem for the growth of epitaxial GeTe–Sb_2Te_3 (GST) thin films. The problems are further aggravated by the weak coupling of the radiatively heated non-contact thermocouples to the substrate. An increase in surface temperature during growth as inferred from the increase in desorption of GeTe heteromolecules and the resulting change in alloy composition are studied. Using the desorption signal as a feedback to control the surface temperature, the thermocouple temperature was varied over the duration of the growth to maintain a constant desorption and hence constant surface temperature. Interestingly, the composition of the grown films varies along the GeTe–Sb_2Te_3 pseudobinary line just by varying the desorption without changing the supplied flux. The out-of-plane lattice constant of the epitaxially grown GST thin film increases with an increase in Ge concentration.

1. Introduction

Ever since the phenomena of resistive switching by Te based chalcogenide alloys were reported by Ovshinsky [1], there has been a considerable interest in understanding and exploiting the switching properties of this class of materials. Distinctive features are large optical and electrical contrast between the amorphous and crystalline states, rapid and reversible switching between the two phases, high thermal stability, good scalability and low cost. On these grounds the commercialization of optical discs such as CDs, DVDs and Blu ray discs for data storage [2–6] was enabled. In addition, recently the electrical contrast is utilized to fabricate non-volatile phase change RAM: considered as a promising candidate for the replacement of conventional charge based storage technologies [7–12].

A novel concept for a low power consumption phase change memory is based on alloys with a controlled stacking sequence that exhibits lower switching energies, enhanced cyclability, lower atomic migration, better stability and thinner cells than their monolithic polycrystalline counterparts [13–15]. Single crystalline GeTe–Sb_2Te_3 (GST) epitaxial films prepared by molecular beam epitaxy (MBE) are expected to display highly ordered atomic layers, which could also show improved switching performances. In previous publications, the successful growth of epitaxial single crystalline GST films on lattice matched [16–19] and highly mismatched substrates [20,21] such as GaSb, InAs and Si was shown. Switching studies on $Ge_2Sb_2Te_5$ epitaxial films grown on Si(111) showed that the layer retains its crystalline orientation upon recrystallization [22]. The switching speed was experimentally found to strongly depend on the GST composition, increasing with the Sb content [23,24]. The uniform switching speed is mandatory for device applications and hence homogeneous composition. Thus, it is necessary to accurately control the GST film composition. In the present manuscript, the use of line-of-sight quadrupole mass spectrometer (QMS) for *in situ* growth control of GST epitaxial film on Si(111) is presented, together with the study of GeTe desorption which correlates to compositional changes. It is observed that the composition of the epitaxial GST film is strongly depended on the growth temperature. However in our system, we observe that the substrate temperature as measured by the thermocouple is constant, while the surface temperature increases during the growth as deduced from an increase in desorption of the various atomic species. This indicates a change in sticking coefficients of the supplied atomic species. A feedback from the GeTe desorption is necessary to keep the desorption constant, which in turn helps to maintain a constant surface temperature. An effective feedback control using a line-of-sight QMS was implemented to achieve constant desorption, which is expected to help in attaining homogeneous composition along the film thickness.

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2. Experimental procedure

The epitaxial growth of GST is performed in a custom built compact Createc MBE system located at the Pharao beamline of the HZB-BESSY II synchrotron [25]. Dual filament hot lip effusion cells for evaporation of elemental Ge, Sb and Te are used. Typical base/hotlip temperatures of 1097.8/1117.8 °C (Ge), 470.3/620.3 °C (Sb) and 340.8/483.7 °C (Te) are set and correspond to a flux ratio Ge:Sb:Te of 2:2:5. It is to be noted that at a selected flux ratio of 2:2:5, the GST film composition attained after the growth can have varying ratios of different atomic species, depending on the growth temperature. Thin film growth studies are performed under ultrahigh vacuum conditions with a typical chamber base pressure of 6×10^{-10} mbar. A Hiden line-of-sight QMS capable of scanning atomic and molecular species up to 500 amu is installed at one of the effusion cell ports of the MBE chamber. A shutter in front of the QMS is closed every 20 s to monitor the real time change in the background signal. Within the scanning limit of the QMS, the following atomic/molecular species are observed: Ge, Sb, Te, GeTe, Sb_2, Te_2, Sb_3 and Sb_4. Compositional analysis of the grown samples is carried out at Siemens, Munich by a x-ray fluorescence spectroscope. The grown films are characterized *ex-situ* by x-ray diffraction using a PANalytical XPERT™ triple axis diffractometer utilizing Cu Kα_1 radiation and a Ge(220) hybrid monochromator.

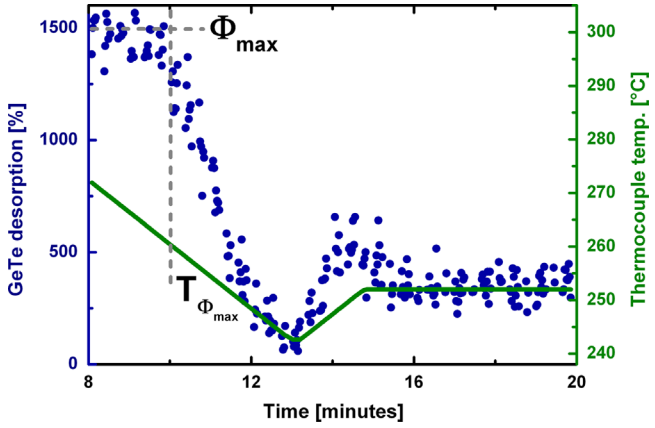

Fig. 1. GeTe desorption (blue/dots) and thermocouple temperature (green/line) as a function of time during the initial stages of the growth procedure. Φ_{max} is the maximum desorption and $T_{\Phi_{max}}$ is the temperature at which desorption starts to decrease.

Si(111) substrates are wet cleaned using standard chemical cleaning [26] followed by 5% HF dip for 10 mins and then rinsed with de-ionised water to form a stable hydrogen terminated surface [27]. The substrates are subsequently loaded into the MBE system. For water desorption a substrate temperature (T_s) of 150 °C is used followed by degassing at T_s=350 °C before introducing into the growth chamber. T_s is ramped up to 720 °C at 0.1 °C/sec to attain 7×7 reconstruction. The substrates are heated radiatively by the emission from resistively heated coils and the temperature is measured by a non-contact thermocouple behind the substrate, resulting in temperature accuracies of $\pm$50 °C [17,28]. Care was taken to avoid temperature anomalies by ensuring that one end of the thermocouple is kept at room temperature while the other end measures the substrate temperature. The temperature control of the substrates and cells is performed by means of proportional-integral-derivative (PID) controllers.

3. Results and discussion

Three GST epitaxial films grown under equal nominal substrate temperature conditions (220 °C as given by the thermocouple reading) showed significantly different compositions, namely $Ge_{25}Sb_{19}Te_{56}$, $Ge_{27}Sb_{17}Te_{56}$ and $Ge_{33}Sb_{12}Te_{55}$. Analysis of the desorption signal acquired by QMS during the growth runs displayed a different GeTe desorption: 27%, 30% and 39% of the maximum desorption (for details see below). Interestingly compositional analysis shows that the Ge/Sb composition increases/decreases with the increase in GeTe desorption. Thus we propose to investigate the use of the desorption percentage as a relative measure of the surface temperature for the growth of GST epitaxial films.

Fig. 1 shows the typical line-of-sight QMS signal observed for GeTe during GST growth on a Si(111) substrate and the recorded thermocouple temperature. The origin of the time axis corresponds to the simultaneous opening of all the shutters at T_s=300 °C, which is high enough to ensure no sticking of the impinging species, and thus maximum desorption (Φ_{max}, see Fig. 1). The blue curve shows the desorption of the GeTe molecule and the green line represents the thermocouple temperature versus time. After about 3 min of opening the shutter, T_s is ramped down at 0.1 °C/sec to enable the sticking of the atoms/molecules on to the substrate, which can be observed by the corresponding decrease in GeTe desorption. The temperature at which the desorption starts to decrease is labelled by $T_{\Phi_{max}}$. T_s is further

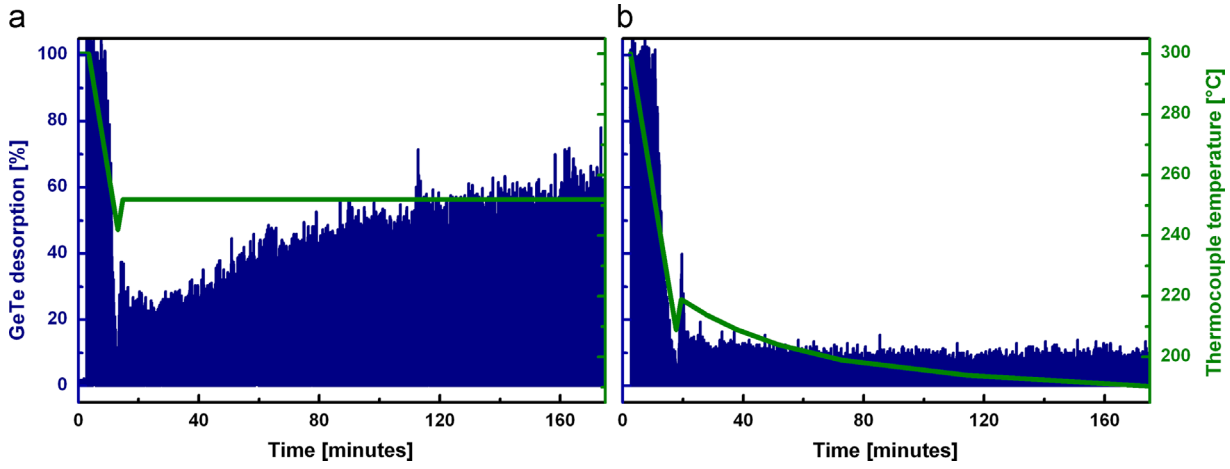

Fig. 2. GeTe desorption (blue/shaded) and thermocouple temperature (green/line) as a function of time. (a) Growth at constant thermocouple temperature. (b) Growth at constant desorption.

decreased till almost zero desorption is measured and subsequently increased to obtain a 20% desorption signal. The growth is sustained at constant thermocouple temperature.

However, the desorption increases over time as shown in Fig. 2(a). The thermocouple temperature is highly stable, whereas the desorption increases from 20% to almost 60% within 150 min. A 40% change in desorption reflects a considerable composition gradient.

The change in desorption can be attributed to the change in surface temperature. In our experiment, a rough estimate of 20–30 °C temperature increase can be deduced from the desorption versus temperature curve of the first 14 min deposition shown in Fig. 1. The failure of the thermocouple to monitor the increase in surface temperature is ascribed to the bad coupling (non-contact mode) with the substrate [29–31]. Pyrometry offers a more accurate measurement of the true temperature of the film surface. However at typical growth temperatures of GST (T_s= 200–250 °C) common pyrometry cannot be used.

The change in surface temperature during the growth can be ascribed to either of the following two reasons: (1) Upon deposition, the emissivity of the surface changes due to various reasons such as different material systems than the substrate, change in surface morphology upon growth and increase in film thickness. (2) Crystalline GST has a smaller band gap (0.5–0.61 eV) [32] compared to Si (1.1 eV). That means GST epitaxial films exhibit large absorption bands in the infra-red wavelength region where Si is transparent (> 1.1 μm). The additional infra-red radiation with energy lying between the band gaps of the film and substrate will be absorbed by the film resulting in an increase in surface temperature. Shanabrook et al., based on MBE growth studies of lower band gap materials (GaSb, InAs) on higher band gap material (GaAs), found that the band gap mismatch plays a dominant role in increasing the surface temperatures, while emissivity changes upon deposition contribute very less. The increase of surface temperature during growth is intrinsic to the chosen substrate–adsorbate combination. However, it is necessary to accurately control the surface temperature to achieve a homogeneous GST composition.

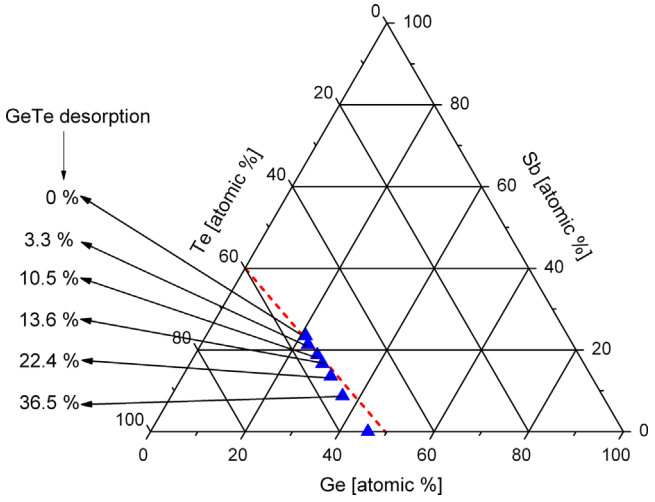

Fig. 3. Composition of the GST films in the Ge–Sb–Te ternary diagram and the corresponding GeTe desorption of each film during the growth.

To do that, the increase in desorption shown in Fig. 2(a) is fitted and a function which is inverse to the increase in desorption is used to control the thermocouple temperature in order to achieve a constant GeTe desorption signal during growth (see Fig. 2). Using the growth process described above a series of samples were grown at different constant desorption values. The composition measured for these samples is displayed in Fig. 3(a) in a ternary diagram and the corresponding GeTe desorption percentage is shown. A red dotted line shows the pseudobinary line. The end point on the ternary diagram corresponds to the composition of the epitaxially grown GeTe sample found to be $Ge_{0.46}Te_{0.54}$. Interestingly the composition variations of the GST samples follow a straight line leading towards the epitaxial GeTe composition, which is slightly off from the pseudo-binary line, but towards the $Ge_{0.46}Te_{0.54}$ composition point on the ternary diagram. A linear relationship exists between the percentage of desorption and the change in composition. Thus the GeTe desorption can be used as a measure of the sample composition, after calibration with a conventional technique.

With an increase in desorption, Sb concentration decreases while Ge increases and Te remains almost constant. GST exhibits a metastable NaCl type of crystal structure with Te atoms occupying one sublattice and Ge/Sb/vacancies occupying the other one [33,34]. Thus, one can infer that the Te concentration is unaffected by the surface temperature used for growth as it completely fills one sublattice. However, a strong competition between the Ge and Sb atoms in occupying the other sublattice is revealed. Fig. 4(a) shows the specular $\omega-2\theta$ scans of the GST epitaxial film shown in Fig. 3(a). A clear trend in the shift of the GST peak is observed. With an increase in Ge concentration, the peak positions move towards low Q_z values, indicating an increase in the out-of-plane lattice spacing. Fig. 4(b) shows the out-of-plane lattice constant with respect to Sb and Ge atomic percentage. With an

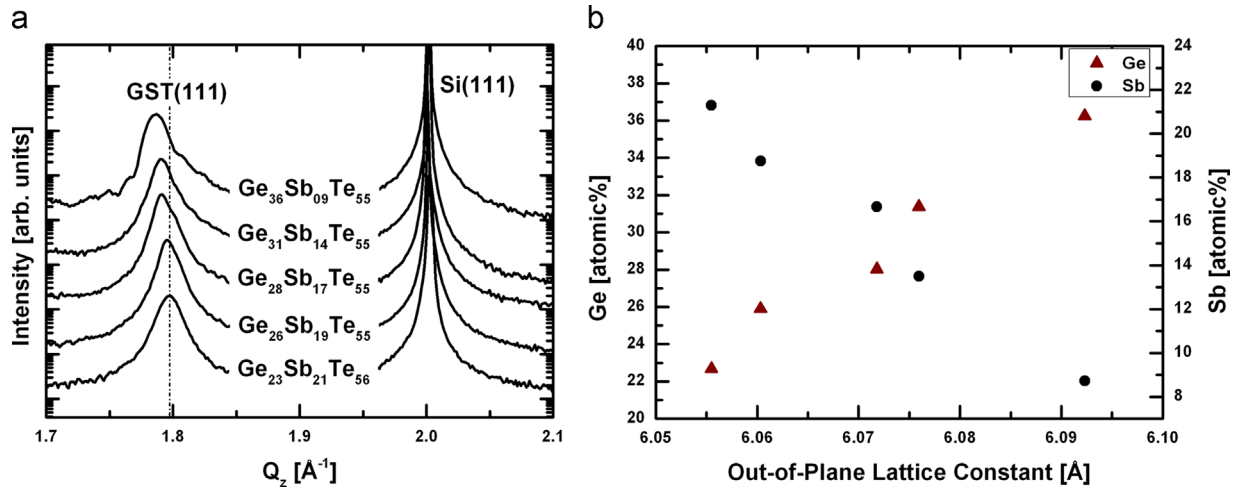

Fig. 4. (a) Specular $\omega-2\theta$ scan for samples of a different composition. (b) Ge and Sb atomic % with respect to out-of-plane lattice constant.

increase in Ge/Sb concentration, the out-of-plane lattice constant increases/decreases linearly. In the assumption that the layers are fully relaxed, the GST out-of-plane lattice constant can be used as a measure of the composition. This assumption is fairly reasonable as the lattice mismatch between Si(111) and GST is about 10.8%.

4. Conclusion

GST film composition is shown to be highly dependent on the growth temperature. The inaccuracy in measuring the right substrate temperature poses a serious problem in reproducibility of the film composition. From the initial results on QMS desorption and thermocouple temperature as a function of composition, it is shown that desorption percentage as a reference for growth calibration is more reliable than the thermocouple temperature. During the growth, an increase in desorption which in turn is directly proportional to the surface temperature is observed. The thermocouple fails to sense this increase in surface temperature resulting in a compositional gradient along the film's surface normal. The increase of GeTe desorption due to increase in surface temperature is compensated by reducing the thermocouple temperature so as to keep the desorption constant throughout the growth. We demonstrate that by changing the surface temperature, GST epitaxial films with composition varying along the technologically important GeTe–Sb_2Te_3 pseudobinary line can be fabricated. The specular $\omega-2\theta$ scans show an increase in out-of-plane lattice spacing with change in composition. This might be used as a reference for determining the composition of the GST epitaxial film grown under similar flux conditions.

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