

Desorption kinetics of GeTe deposited on Si(111)

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ABSTRACT

To develop a model for the growth of epitaxial phase change materials, it is very important to investigate the different kinetic adatom processes such as adsorption, desorption, and surface diffusion. Especially desorption is a key parameter which may significantly influence growth rate, material quality and composition, as well as surface morphology. Here, we present a detailed desorption study during deposition of GeTe thin films on Si(111) substrates taking into account the nucleation regime.

Key words: epitaxy, thin films, MBE, QMS

1. INTRODUCTION

In the last 20 years, optical discs such as CDs, DVDs, or even Blu-ray Discs, have been almost exclusively based on chalcogenide phase-change materials (PCMs) ¹. The success of these alloys is related to the rapid phase-change from the crystalline to the amorphous state, both exhibiting distinct dielectric functions and, thus, dissimilar optical contrast, allowing for different transmission and reflection of the read-out laser ². More recently, the technological importance of PCMs dramatically increased as they show potential to replace Flash memory, due to superior scaling characteristics, higher cyclability, and significantly faster read and write speeds ^{3,4,5}. These advantages spawn from the encoding of the information state using structure rather than charge. Among the PCMs, the most interesting compounds are Te-based PCM alloys, typified by Ge-Sb-Te (GST) ⁶. In GST, the metastable crystalline phase is utilized as the RESET state in the switching process, whereas the SET state is realized in the amorphous phase ². The stable configuration of the GST crystalline phase is trigonal, but amorphous thin films of GST grown by techniques such as sputtering crystallize into a metastable distorted rocksalt structure ⁷. It is very surprising that, despite the technological maturity of GST, the crystal structure of this metastable cubic phase has not been indisputably identified. In consequence, the fundamental physical mechanism underlying the switching process has not been fully understood, and several different models are currently discussed ^{8,9,10}. The different proposed switching mechanisms are strictly related to the structural properties of the material and its peculiar bonding nature, and hence the verification of these models would require a precise determination of the crystal structure. From this perspective the fabrication of epitaxial phase-change materials with perfect orientation and fine control of the growth kinetics would be beneficial. A method that allows epitaxial growth of phase-change materials is molecular beam epitaxy (MBE), which combines superior thickness control with ultrahigh purity and the possibility of using a variety of *in-situ* characterization tools ^{11,12,13,14}. However, the mechanism for the growth of GST by MBE is still not clear and there are very few investigations dealing with it.

Growth results on epitaxial GST previously reported ^{12,14} show that a narrow growth window exists for epitaxy, and that the growth rate decreases dramatically with temperature. This sharp drop can be explained as follows. Growth takes place as soon as the deposition flux exceeds the desorption. A single rise in growth rate is observed ¹², suggesting that the compound desorbs congruently. Observing GST growth by mass spectrometry we also observed that mainly GeTe molecules desorb (no Ge_nSb_m or Sb_nTe_m molecules are detected), thus indicating a strong bond between Ge and Te ¹⁴. For the growth of GeTe at temperatures for which we assume crystalline growth we might expect that either Ge_xTe_y or its constituent species such as Ge, Te or Te₂ desorb. This is confirmed by experiments as shown below.

2. EXPERIMENTS

The layers were grown in an MBE system dedicated to chalcogenides at the synchrotron BESSY II of the Helmholtz Center Berlin. The apparatus is equipped with separate effusion cells for the evaporation of elemental Ge, Sb, and Te, an *in situ* line of sight quadrupole mass spectrometer (LS-QMS) measuring species leaving the surface and high-energy electron diffraction (RHEED). Substrate preparation as well as the growth process were monitored by RHEED. A Hiden HAL IV QMS is used as it is capable of detecting atoms and molecules like Ge, Sb, Te, Sb₂, Sb₃, Sb₄, Te₂ and GeTe (scanning masses up to 512 amu). The QMS is located at a distance of 30 cm from the substrate at an angle of 20° to the substrate normal. The shutter in front of the quadrupole is closed and opened every 20 seconds to alternately measure the total and the background signal, which is subsequently subtracted from the signal. In order to reduce the amount of doubly ionized molecules and the splitting of large parent molecules into daughter fragments, the electron energy of the ionizer is kept at 20 eV and the emission current at 800 mA.

Si(111) wafers were prepared using a standard wet cleaning with solvents followed by a 10 minute HF dip and a deionised water rinse to produce the stable H-terminated Si(111) surface. The chemical treatment was followed by a subsequent introduction of the sample into the MBE chamber where it was heated to 700° C for 10 minutes to prepare the Si(111) (7 x 7) surface reconstruction.

3. RESULTS & DISCUSSION

Figure 1 displays a QMS signal (i.e. the beam equivalent partial pressure of the chosen atomic species or molecules) acquired during GeTe growth on a Si(111) substrate.

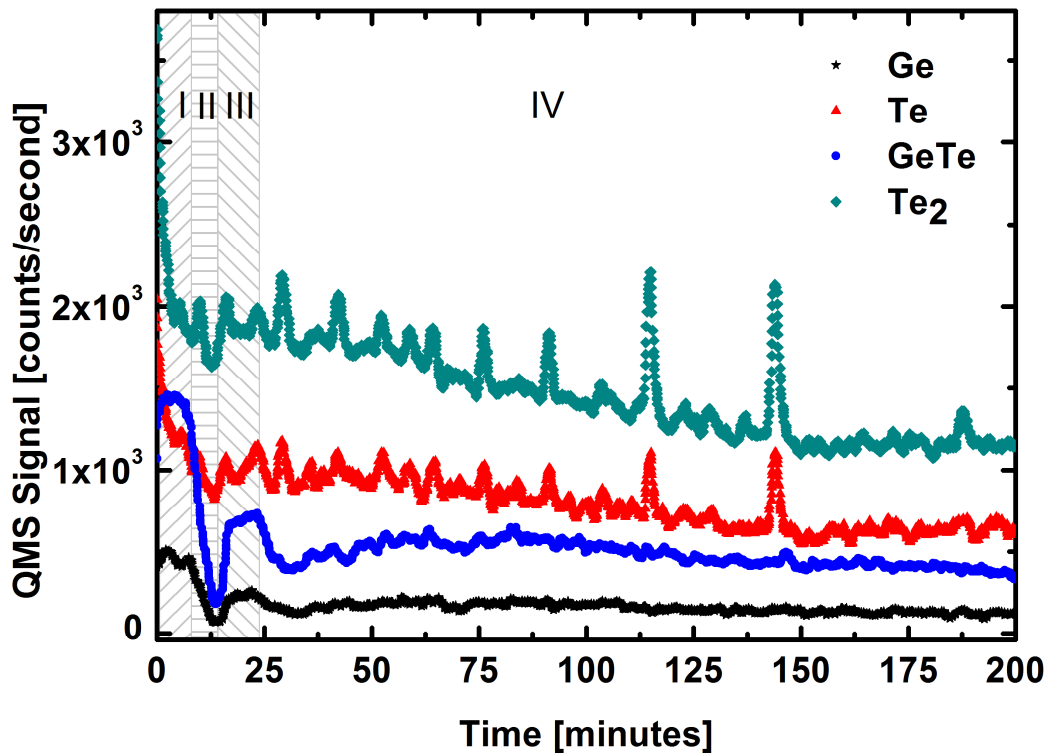


Fig1: Signal detected by the LS-QMS corresponding to the desorption of several species plotted versus growth time of GST on Si(111).

At the onset of deposition we set the growth temperature at an elevated value of 300° C, for about 10 min, such that no sticking of atoms on the surface is allowed, and all species completely desorb from the sample surface (region labeled I in the plot). The nominal ratio of the impinging Ge and Te fluxes was set to be 2:5.

The sample temperature is then decreased to 266°C at 0.1°C/s (area labeled II) and then set to the growth temperature of 250 °C for 235min (area III-IV). It has to be noted that the all signals and especially the GeTe do not stabilize immediately at the chosen growth temperature, thus first a rapid rise and then a decrease is monitored. This effect is associated to the stabilization of the proportional–integral–derivative controller of the substrate power supplier that performs a bounded oscillation. Additional to this technical aspect very often in the nucleation regime a high desorption of the constituents is reported ¹⁵, and can be assigned to a high energy barrier for nucleation, which inhibits wetting of the substrate and thus give rise to a high desorption rate. In other words the growth rate is reduced at nucleation and increases at equilibrium; this means that in the nucleation stage a thickness reduction occurs compared to the steady state growth regime. This should be taken into account if aiming at growing very thin layers or superlattice like structures.

In region IV, the Ge signal is stable, whereas Te and Te₂ slightly decrease, and GeTe has the tendency to a slight increase and then stabilization. These behaviors reveal that precise control of the substrate temperature during growth is mandatory as it affects the alloy composition along the growth direction. The procedure used to control the growth temperature will be described elsewhere.

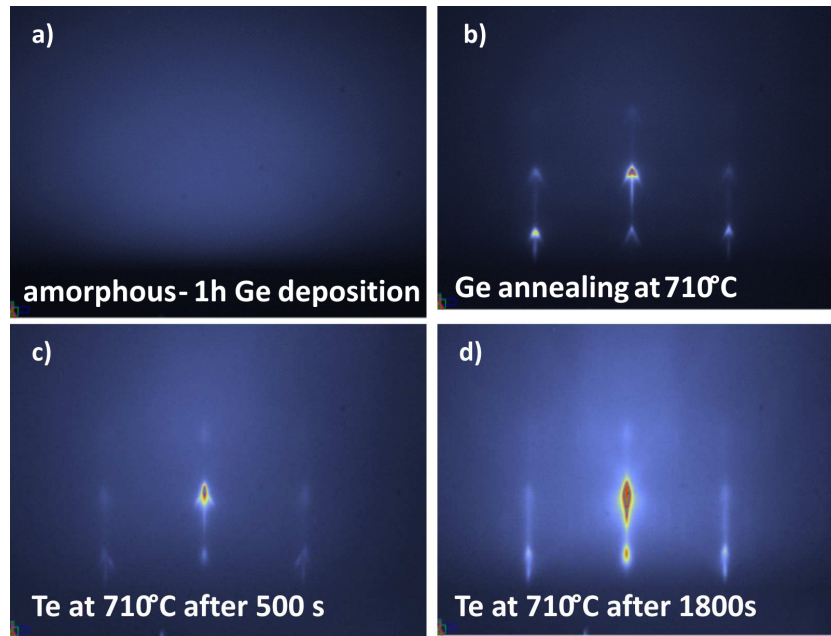


Fig.2: RHEED patterns acquired during a) amorphous Ge deposition, b) annealing of the Ge thin film c-d) Te deposition.

It is worth to recall that the desorbed flux is given by the following relation:

$$\Phi_{Des} = \Phi_{Sup} - (\Phi_{Dep} - \Phi_{Dec})$$

where Φ represents the flux and the different subscripts label desorbed (*Des*), supplied (*Sup*), deposited (*Dep*) adatoms and decomposed (*Dec*) material, respectively. Decomposition should then separately be taken into account as indeed the GeTe signal can be seen as being partly due to decomposition, which might even be enhanced under Te flux. The fact that most of the supplied Ge at the present growth temperature is desorbed in the form of stable GeTe

molecules in principle suggests that it would be even possible to completely etch away or decompose a Ge layer by Te deposition. This approach might be useful and relevant for selective area growth/etching experiments. To prove this assumption we performed the following experiment: A thin layer of Ge was deposited for about 60 min at room temperature with a growth rate of 0.2 nm/min. The Ge layer was then annealed at 710° C for crystallization, subsequently Te was deposited. At the chosen temperature Te only desorbs, while Ge does not.

With help of RHEED the experiment was monitored in situ. Fig. 2a, obtained after the deposition of Ge at room temperature, clearly displays a diffuse halo typical for an amorphous layer. During annealing at 710°C the RHEED pattern evolves into a spotty picture, which indicates the crystalline nature of the film (Fig. 2b). The intensity of the pattern diminishes during Te deposition suggesting Te etching of Ge (Fig.2c). At the end of the growth the RHEED pattern shown in Fig. 2d displays streaky features resembling the Si(111) 7x7 reconstruction. Not all the streaks are visible and highly intense, indicating a non perfectly clean surface, however a precise determination of the surface reconstruction should be investigated with further experiments.

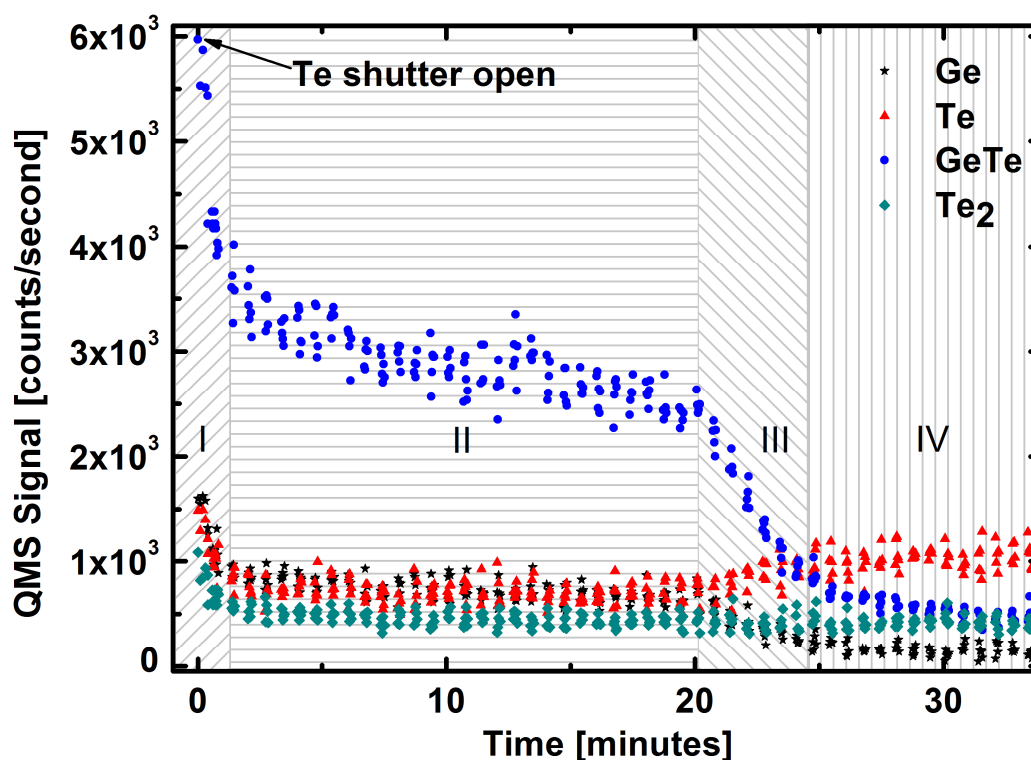


Fig.3: Signal detected by LS-QMS corresponding to the desorption of several species plotted versus the Te deposition time on a thin Ge layer.

Fig. 3 shows the QMS signal observed for Te, Ge, GeTe and Te_2 during the exposition to Te. The origin of the time axis was chosen to be the opening of the Te shutter. The graph of Fig.3 can be divided into four areas (I-IV). At time $t=0$ (area I), the QMS signal for all species suddenly increases, it is worth to note that the signal corresponding to the desorption of GeTe molecules increases by a factor of four with respect to the others. Afterwards, all signals rapidly decrease. The sudden increase and rapid decrease of the signals represents the first area. The increase of the signals at $t=0$ can be explained by attributing it to an sudden surface reaction between the deposited Ge and the incoming Te. Furthermore the rapid decrease of all signals indicates that the reaction rate also decreases, pointing at a stabilization of the surface temperature after the rise due to the heat from the effusion cell.

In the second area (II) the signals keep decreasing with two different slopes for about 20 min. The first slope accounts for a stronger desorption rate, whereas the second slope corresponds to a slower rate and this is an indication that the

reaction almost stabilizes and proceeds in a steady state. To conclude the GeTe signal is much higher than the others thus a preferred formation of GeTe molecules is favored, with small amounts of Ge and Te single atoms as well as Te₂ desorbe. Our previous findings of a strong bond between Ge and Te are substantiated¹⁴.

Within the third area (III) the GeTe and Ge desorption signals strongly decrease, whereas the signal of Te increases. The reason for the decrease of the signals is that the etching process comes to a halt as not enough Ge for the supplied Te is available. Simultaneously in fact it is possible to observe the rise of the Te signal which indicates an oversupply of Te. In the fourth (IV) and last area, all the signals except that of Te settle down to their background value.

4. CONCLUSION

In summary we have investigated desorption phenomena during molecular beam epitaxy of GeTe on Si(111) using a line of sight QMS. For the given growth conditions the growth rate is reduced at nucleation and increases at equilibrium, such a thickness loss is relevant for the growth of very thin layers or superlattice like structures. Sb desorbs in the form of single adatoms and does not form a stable molecule. Most of the supplied Ge is desorbed in form of a stable GeTe molecule, suggesting a strong Ge-Te bond and the relevance of decomposition mechanisms. A Ge layer can be etched by means of Te deposition and a preferred formation of GeTe molecules is observed, whereas a small amount of Ge and Te single atoms desorb, together with a small amount of volatile Te₂.

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Biographies

Karthick Perumal received M.Sc degree in physics in 2006 from Presidency College, Chennai and later M.Tech degree in Laser and Electro-Optical engineering in 2008 from Anna University, Chennai. Later he worked for six months as a senior research fellow at the Indian Institute of Science, Bangalore. Since 2009 he is with PDI, working towards his Ph.D on Epitaxial growth of Phase Change Materials.

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Henning Riechert received his M.Sc. degree in physics in 1982 from the Rheinische Friedrich-Wilhelms-Universität Bonn, Germany, and the Ph.D. degree in physics in 1986 from the University of Cologne, Germany. He was from 1986 to 1999 as scientist and project manager with Corporate Research & Development, Siemens AG, München, Germany. From 1999 to 2006 was as Project manager and photonics department head with Infineon Technologies, München, Germany. From 2006 to 2007 worked as Principal Senior Scientist in Materials Science at Qimonda AG, Dresden, Germany. Since 2007 he is Director of the Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany and Professor in Experimental Physics and Materials Science of the Humboldt-Universität zu Berlin, Germany.

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