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Growth study of $Ge_xSb_yTe_z$ deposited by MOCVD under nitrogen for non-volatile memory applications

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ABSTRACT

We report on the bubbler-type MOCVD growth of $Ge_xSb_yTe_z$ (GST) on SiO_2/Si substrates, potentially transferable to phase change memory (PCM) devices. Pure nitrogen was used as the process gas in order to reduce toxicity whilst increasing the simplicity of the process.

This systematic study allowed the modification of the growth parameters on SiO_2 to move through initial sub-micrometric crystalline grain deposition on to lateral island growth. Temperature was observed to play a critical role in film quality with strong morphology and island shape/size changes for small thermal variations. Eventually, continuous layers of GST in the hcp phase and composition close to the 2:2:5 were studied. The deposition on different substrates was also investigated. Although crystal nucleation is still far from achieving the target step coverage required for uniform coating of patterned substrates, the electrical sheet resistance of GST films exhibited values corresponding to those expected for chalcogenide materials suitable to be integrated into PCM devices.

1. Introduction

Chalcogenides compounds, such as $Ge_xSb_yTe_z$ (GST), especially with the 2:2:5 composition, are very attractive materials for phase change memories (PCMs), in which information can be stored (set) and cancelled (reset) by inducing crystal phase or amorphization transitions [1].

Among the GST deposition methods, the MOCVD has in principle several advantages, in particular a better step coverage for deposition on patterned substrates, industrial scaling and high compositional control. Up to now, only a few works report on different MOCVD-related methods; however, they suggest that the GST deposition (mainly the precursor pyrolysis) needs to be somehow activated. For this reason, nanoV-CVD^{TM} and spinCVD^{TM} [2], ALD/MOCVD [3,4], cyclic PECVD [5], hot-wire and liquid injection MOCVD [6] have been employed to obtain more or less homogeneous and smooth films. On the contrary, for conventional (bubbler-type) MOCVD deposition under H_2 gas mixtures [7], rather rough GST layers are reported, formed by hexagonal micrometric crystals along with vertical crystals. In the only case of a prototypal PCM device based on the MOCVD [8], the GST was deposited by a similar H_2-based process to fill up a cell structure. To our knowledge, there is no report of standard MOCVD GST growth which employs pure N_2 (to reduce dangerousness and device production costs) as a process gas. In this work, the MOCVD deposition of GST under pure N_2 is studied in terms of growth parameters for a range of substrates, aiming at the achievement of a continuous layer with proper structural, compositional and electrical properties, in view of future applications for PCM devices.

2. Experimental procedure

The GST deposition was performed using a new horizontal low-pressure MOVPE AIXTRON reactor (based on AIX200/4). Electronic-grade tetrakisdimethylaminogermanium ($[N(CH_3)_2]_4Ge$, TDMAGe), trisdimethylaminoantimony ($[N(CH_3)_2]_3Sb$, TDMASb) and diisopropyltelluride ($(C_3H_7)_3Te$, DiPTe) were used as Ge, Sb and Te precursors, respectively. Such precursors were selected and synthesized by SAFC^{TM} to ultra-high purity using proprietary techniques. Precursor choice was based on volatility and transport compatibility to ensure that GST stoichiometric control could be maintained. Furthermore, toxicity and reactivity were considered to reduce process hazards and minimize unwanted pre-reactions. Finally, thermal stabilities of the sources were matched to avoid

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depletion effects and so aid uniformity. Electronic-grade purified N_2 was used as the carrier/process gas.

The substrates were n^+ Si(0 0 1), 4″ wafers, covered with a 50-nm-thick layer of SiO_2. Since the final substrates to be employed for memory applications contain a pattern of micro-trenches (to be filled with GST), formed by a combination of SiO_2, TiN and Si_3N_4, in some runs also TiN (40 nm)/Si and Si_3N_4 (70 nm)/Si substrates were loaded alongside the SiO_2/Si ones, to investigate the effect of different chemical surfaces on the GST nucleation mode. A minimum precursor partial pressure in the range of 10^{-2} mbar was needed for the deposition of GST, so that growth pressures in the range of 250–450 mbar and total flows between 4 and 6 L/min were used; the growth was performed in the temperature range of 350–400 °C. Thickness analysis was performed with a Woollam M2000 spectroscopic ellipsometer. Morphological analysis was based on scanning electron microscopy (SEM) observations, performed by a Zeiss Supra 40 field-effect microscope at an accelerating voltage of 15 kV.

X-ray diffraction (XRD) experiments, both in grazing incidence and Bragg Brentano configurations, were carried out by means of an ItalStructures HRD3000 diffractometer. The experimental XRD curves were analysed by a best-fit procedure based on the Rietveld method [9]. Compositional analysis was performed by total reflection X-ray fluorescence (TXRF) spectra. X-ray fluorescence measurements were done using a Italstructures XRR-TXRF 3000 system. X-ray photoelectron spectroscopy (XPS) was provided by a standard Mg K_α radiation source (1253.6 eV) and an Omicron EA 125 HR analyzer. Electrical characterization of the samples was obtained by sheet resistance vs. temperature measurements, using the *van der Pauw* 4-probe method (from RT up to 260 °C).

3. Results and discussion

The nucleation of GST on SiO_2 turned out to generally proceed via the formation of sub-micrometric crystallites. Subsequently, the substrate surface is progressively occupied by the crystal lateral growth, until it is covered by a more or less uniform GST layer, whose average thickness is of the order of hundreds of nanometres, along with a variable density of 3-D microcrystals.

To identify the conditions leading to the complete surface coverage, different pre-growth surface treatments were thus investigated, namely leaving the SiO_2 substrate in the presence of TDMAGe, TDMASb and DiPTe vapours, for 5 min at the growth temperature of 375 °C. The precursor concentrations employed for the surface treatments were the same as those used during the subsequent GST deposition. The ternary GST compound was deposited immediately after the surface treatment.

Fig. 1 shows the effects of different surface treatments in GST samples grown at 375 °C, 450 mbar, total flow = 6 L/min, TDMAGe partial pressure = 2.68×10^{-2} mbar, TDMASb partial pressure = 0.715×10^{-2} mbar, DiPTe partial pressure = 20.4×10^{-2} mbar and deposition time = 30 min. It appears that in the sample without pre-treatments only isolated crystals can be observed (Fig. 1a). Notably, the TDMAGe treatment dramatically increases the density of flat crystals (Fig. 1b) and, when TDMAGe+TDMASb are used, islands are bigger and tend to coalesce, indicating a good pre-disposition to the full surface coverage (Fig. 1c, sample A1). To this respect, it is reported that the MOCVD deposition of Ge films on TiAlN/SiO_2/Si substrates is catalysed by the presence of Sb vapours [10].

The situation is worse when TDMASb or DiPTe precursors are separately delivered, since isolated crystals are again obtained (Figs. 1d and e). Fig. 1f shows the TXRF analysis of the MOCVD-deposited GST without pre-treatments (medium spectrum), which appears comparable to that obtained from a reference

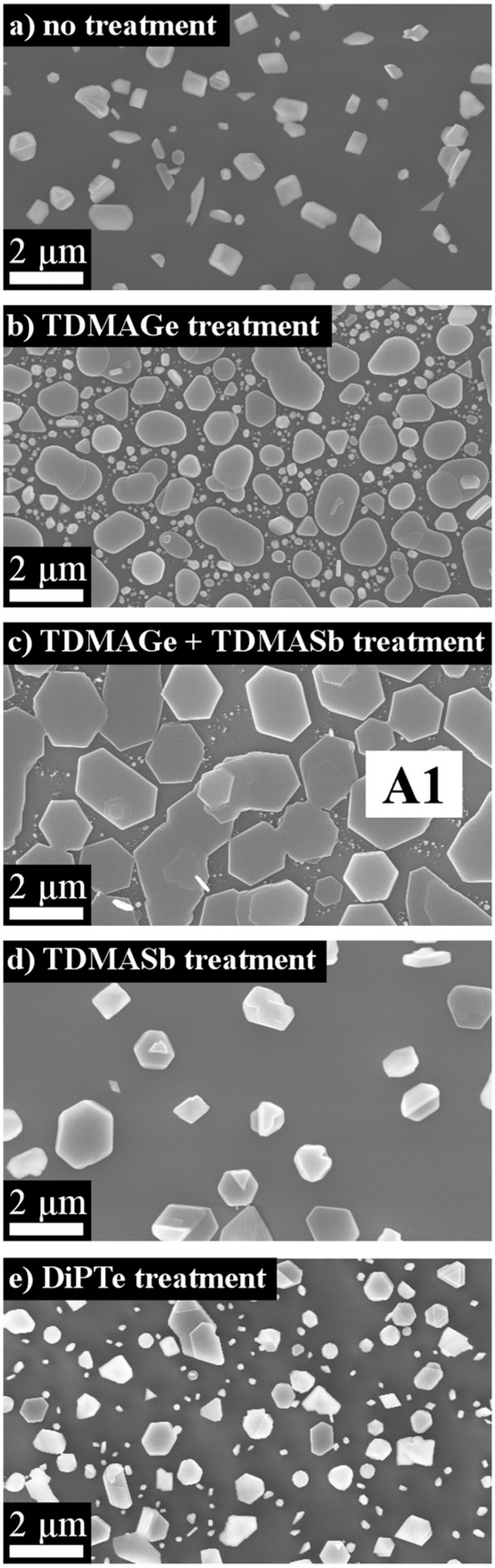

Fig. 1. (a–e) SEM plan views of GST samples grown at 375 °C, for 30 min with different pre-growth treatments under the indicated precursor vapours. (f) TXRF spectra of sputter-deposited GST (from STMicroelectronics), MOCVD–GST without any pre-growth treatment (as in (a)) and MOCVD–GST with TDMAGe pre-growth treatment (as in (b)); TXRF compositions are also reported.