Crystallization study of $GeSb_4$ phase change material thin films

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ABSTRACT

$GeSb_4$ is a promising material for phase change random access memories. In this work, X-Ray synchrotron radiation diffraction, time resolved reflectivity measurement and Transmission Electronic Microscopy are used to study crystallization behaviour of amorphous films of $GeSb_4$. Films with thickness as low as 10 nm are studied. When temperature increases, Sb and Ge phases sequentially crystallize. It's shown that both the crystallization temperature and microstructure evolution are strongly dependent on the film thickness.

Key words: nucleation, growth, $GeSb_4$, PCM.

1. INTRODUCTION

Te free high Sb content phase change materials have been recently investigated as promising materials for Phase Change Memories due to their very high crystallization temperature [1, 2]. Recently Krusin *et al.* [3] demonstrated a composition closed to $GeSb_4$ offers the best performances in terms of crystallization speed and reliability for cycling properties.

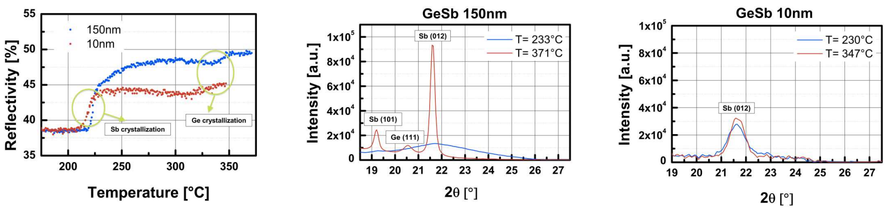
For GeSb two different crystallization steps are present: one corresponding to the crystallization of the rhombohedral Sb phase and the other one, at higher temperatures, corresponding to the cubic Ge one. In this work the influence of film thickness on the crystallization behaviour of initially amorphous $GeSb_4$ is studied by reflectivity measurements, X-Ray Diffraction using Synchrotron Beam and TEM observations.

2. EXPERIMENTS

Thin films of $GeSb_4$ (10 and 150nm), initially deposited in the amorphous state by Physical Vapor Deposition (PVD) and capped with 10nm of ZnS-SiO_2, have been submitted to various annealing treatments under Ar ambient monitored by in-situ reflectivity. Then they were studied by ex-situ X-Ray Diffraction using synchrotron radiation (beamline D2AM at ESRF). Thanks to the high flux of synchrotron radiation and 2D detection, grain sizes and textures are measured for films as thin as 10nm.

High Resolution Transmission Electron Microscopy (HREM) observations are carried out in order to obtain a complete insight into the crystalline structure.

3. RESULTS & DISCUSSION



(a) (b) (c)

$GeSb_4 150nm$		$GeSb_4 10nm$	
$233C$	$371C$	$230C$	$347C$
$\approx 2nm$	$\approx 30nm$	$\approx 8nm$	$\approx 9nm$

Table 1

Fig 1: (a) Reflectivity measurements of 10nm (red line) and 150nm (blue line) $GeSb_4$ layers, (b) and (c) XRD measurements on 150nm and 10nm respectively $GeSb_4$ films, annealed at temperatures above $T_{c(Sb)}$ (blue line) and above $T_{c(Ge)}$ (red line). Table 1: Crystallites size in 10 and 150nm $GeSb_4$ samples obtained with Scherrer's law on Sb(012) peak.

The crystallization temperature for the 150nm $GeSb_4$ sample obtained from the reflectivity measurements (Fig.1a) is 223°C, while for the 10nm sample is slightly lower, 218°C, in agreement with literature [4]. The XRD measurements performed on the 150nm $GeSb_4$ sample (Fig.1b) annealed at 233°C show a wide peak with a low intensity associated to Sb (012), corresponding to a grain size of a few nanometers (Tab.1). On the contrary, when annealing at 371°C, narrow and intense peaks are evidenced, corresponding to Sb (101), Ge (111) and Sb (012). In this case, the calculated grain size for Sb crystallites is about 30nm. This result suggests that Sb phase crystallizes following a nucleation process, with the presence of a large density of very small Sb crystallites for temperatures just above the crystallization temperature. These crystallites subsequently grow after Ge precipitation (Fig.2). Indeed, at this temperature, the cross-sectional TEM images show a polycrystalline layer of 155nm, composed of Sb and Ge grains (Fig 2a and 2b). The grain sizes observed through cross sectional TEM observations is consistent with XRD measurements, while larger grains (54nm in average diameter) are measured in the plane (Fig.2d). As can be seen in Fig.1c, the 10 nm layer shows a peak characteristic of Sb (012) after annealing at 230°C that remains unchanged even after annealing at 347°C. This result suggests that in this case, at $T_{c(Sb)}$+10°C the Sb crystallites have already reached their final dimension (Tab.1).

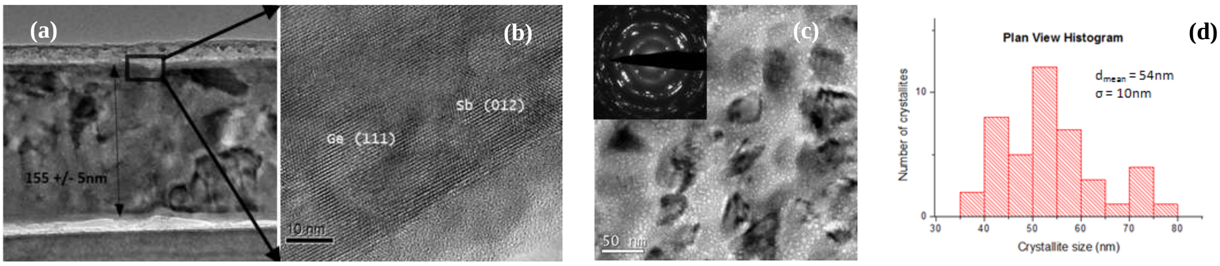


Fig 2: TEM observations of $GeSb_4$ layers annealed at 371°C. (a) Cross section (XS) observation in Bright Field conditions for the 150nm layers, (b) Associated HREM image in XS, showing Sb and Ge grains, (c) Plan-view observation, with in inset the associated diffraction pattern for the 10nm film, (d) Associated size distribution of the grains measured in the plan-view images.

4. CONCLUSION

For 150nm $GeSb_4$ films, it was evidenced the nucleation of a high density of small crystallites for temperatures just above the crystallization temperature of Sb. These grains grow up to the size of 30nm after Ge crystallization. The grain size measured on cross-sectional TEM observations is in good agreement with the one measured by XRD (30nm) while the grains in the plane, measured in plane-view specimen are significantly larger. On the contrary, for the 10nm films, the grains have already reached their final dimensions after the Sb crystallization. This size is around 10nm, independently from the subsequent Ge segregation.

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Biographies

Audrey Bastard is a PhD student working in partnership with CEA-LETI, ST Microelectronics and CEMES Toulouse. Her research area is the study of material crystallization mechanism for application to non-volatile access memory. She received a Master Degree in the Departement of Material Sciences of Engineering School in Luminy, Marseille in 2008.

Giada Ghezzi is a PhD student at CEA, LETI, MINATEC. She got her Master Degree at the Politecnico di

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Jean-Paul Simon, “Directeur de Recherches” au CNRS, shares his time between the University of Grenoble SIMaP* Laboratory and the D2AM** french beamline in ESRF. He mainly checked the theories of phase separation or ordering by neutrons and X-ray scattering experiments and, to differentiate atomic species, developed the resonant techniques.
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Françoise Hippert is professor at Grenoble Institut Polytechnique and doing research in Laboratoire des Matériaux et Génie Physique (CNRS and Grenoble INP). She obtained her PhD in 1983. Her fields of interest is condensed matter physics: magnetism (frustrated systems, Kondo effect), quasicrystals (link between properties and structure), ferroelectricity, liquids and recently phase change materials.

Caroline Bonafos (40 years-old) has obtained the Dipl-Ing. Degree in Solid State Physics in 1993 and then her PhD in 1996, both from the National Institute for Applied Sciences (INSA) of Toulouse. The subject of her PhD thesis was the "The role of End-Of-Range defects on the boron anomalous diffusion She spent 2 years (1997-1999) in post-doctoral position at the Electronics Department of University of Barcelona as a Marie Curie fellow to study the growth of semiconducting nanocrystals ion beam synthesised in silica for opto-electronics. Since 1999, she is Staff Scientist (Chargée de recherche) in the Nanomat group of CEMES an autonomous laboratory of the National Centre for Scientific Research, where she performs work on TEM study and modelling of the growth kinetics of nanoparticles for electronics (charge storage), opto-electronics and plasmonics application. She is the author and co-author of over 110 publications in international journals and conferences. In 2004, she was awarded for her research results by the “Médaille de Bronze” of CNRS. She obtained her “Habilitation à Diriger les Recherches” in february 2007. She is actually the coordinator of a French ANR project (“NOMAD”) dealing with the fabrication of nanocrystal based non volatile memories implying high k matrix.

Jean-Pierre Gaspard is professor of Condensed Matter Physics at the University of Liège (Belgium). His fields of research include: the theoretical study of disordered systems (liquid and amorphous materials), matter under extreme conditions (high temperatures and high pressures), electronic instabilities and symmetry breaking mechanisms, total energy calculations and computer simulation of liquids, neutron and X-Ray scattering and X-ray absorption under pressure (EXAFS).

Frederic Fillot, PhD, is research engineer at CEA, LETI, MINATEC. His research focuses on gate stack in CMOS devices and more recently on ion beam and X-ray characterisation.

Sylvain Maîtrejean has been in the staff of CEA LETI Minatec since 2000. Before joining LETI, he hold a master's degree in physics and material science at the Grenoble National Engineering School for Physics (ENSPG) in 1996. In 2000, he received a Ph.D. in physical metallurgy from the National Polytechnic Institute of Grenoble (Grenoble-INP).
Within CEA Leti minatec, his first activities involved metallic thin film process and characterization for CMOS devices with special focus on metal gate. Later on, he was in charge of the BEOL integration group and participated to the development of advanced interconnects such as Cu/ULK interconnects, 3D integrated circuit, Carbon nanotube interconnects. His actual research field concerns the development of material and integration processes for phase change memories. His main research interests are the mechanical reliability of narrow devices and the impact of nano-confinement on microstructure evolutions and materials properties.
He is the author or co-author of over 80 publications in international journals and conferences.