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On angle resolved RF magnetron sputtering of Ge–Sb–Te thin films

J. Gutwirth [a,*], T. Wágner [a], P. Bezdička [b], M. Hrdlička [a], Mil. Vlček [c], M. Frumar [a]

[a] University of Pardubice, Faculty of Chemical Technology, Research Centre LC 523 and Department of General and Inorganic Chemistry, Legions' sq. 565, 53210 Pardubice, Czech Republic

[b] Institute of Inorganic Chemistry, Academy of Sciences of Czech Republic v.v.i., 25068 Husinec-Rez, Czech Republic

[c] Joint Laboratory of Solid State Chemistry of Institute of Macromolecular Chemistry of Academy of Sciences of Czech Republic v.v.i. and University of Pardubice, Studentska 84, 53210 Pardubice, Czech Republic

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ABSTRACT

Thin amorphous films of Ge–Sb–Te were deposited from $Ge_2Sb_2Te_5$ target by RF (f = 13.56 MHz) magnetron sputtering in argon plasma. Composition and chemical homogeneity of target and prepared thin films were traced by Energy Dispersive X-ray Analysis coupled with Scanning Electron Microscope (SEM-EDX). SEM technique was also used for surface morphology observation. Crystallinity of target and prepared thin films was studied by X-ray Diffraction (XRD). Optical parameters of prepared thin films (spectral dependence of refractive index, optical band gap energy E_g^{opt}) and film thicknesses were established via Variable Angle Spectroscopic Ellipsometry (VASE) supported by UV–Vis–NIR spectroscopy. Influence of deposition conditions (RF power, Ar pressure, angle divergency from normal direction) to composition, crystallinity, optical properties and deposition rate was established.

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1. Introduction

Several non-volatile rewritable data storage technologies exist parallel nowadays [1]. One of the possible and currently applied data storage technology is based on reversible phase change between amorphous and crystalline state. The phase change is realized via optical pulses or electrical pulses, whereas detection consists in difference of optical reflectivity or electric resistance of both phases [2]. Firstly mentioned system is commercially realized as rewritable optical discs (i.e. CD-RW, DVD±RW, DVD-RAM, HD DVD-RAM and BD-RE discs), while second system newly approach markets as phase change random access memory systems (i.e. PC-RAM/P-RAM/C-RAM/OUM® devices).

Active materials in phase change based memories are currently chacogenide materials [3]. The benefit of these materials consists in possibility of easily feasible reversible phase change. In addition, the rates of phase changes are high and stability of both phases in ambient conditions are relatively good. The most favorable systems are currently based on Sb–Te binary system with addition of some other elements such as Ge, In, Ag, etc., e.g. one of the commercially widely used composition is $Ge_2Sb_2Te_5$ material [4,5].

Although phase change based data storage systems are widespread, the theoretical aspects of high crystallization rates resulting in huge change of physical (namely optical and electrical) properties is not still elucidated. Thus, the research on field of

* Corresponding author. Tel.: +420 466 037 265; fax: +420 466 037 311.
E-mail address: Jan.Gutwirth@upce.cz (J. Gutwirth).

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phase change materials is focused on experimental as well as theoretical studies. The experimental research is focused on development of new phase change materials [6] as well as improving of materials currently applied [3]. The theoretical research deals with relationships between the composition, structure and properties of both phases as same as with mechanism of crystallization processes [7–12].

2. Experimental

Vacuum deposition system Tesla UP 858 equipped with 1 in. magnetron Kurt J. Lesker Torus 1 was used for thin film deposition. The system is pumped down by rotary and diffusion pump, whereas vacuum is monitored by Penning and triode gauge in pre-evacuation level and by Pirani gauge Lavat VPR 1 recalibrated for Ar during the deposition. The system is designed for three off-axis substrate holders (angle divergencies from normal direction: position A – $\alpha_{DEP} = 2.4°$, position B – $\beta_{DEP} = 18.0°$, position C – $\gamma_{DEP} = 24.0°$); target–substrate holders configuration is plane-parallel in normal distance $l = 12$ cm. Substrate holders rotate at a speed of 20 rpm. Microscope slides, silica glasses and silicon wafers 1.5×1.0 cm were used as substrates. The system is equipped with RF power source Advanced Energy RFX 600 operate at frequency 13.56 MHz coupled with matchbox Advanced energy ATX 600. One inch target of $Ge_2Sb_2Te_5$ composition fixed to copper backplate supplied by Umicore was used. System was pre-evacuated to background pressure $\sim 3 \times 10^{-4}$ Pa and subsequently flushed by argon at deposition pressure before deposition. Particular deposition conditions (RF power, Ar pressure and deposition time) are summarized in Table 1.

Target was studied by several techniques before it was used for deposition. Composition and chemical homogeneity was checked by SEM-EDX technique, while crystallinity was studied via XRD.

Composition and chemical homogeneity of target and prepared thin films were studied by SEM-EDX using Jeol JSM-5500 LV apparatus equipped with analyzer IXRF Systems and detector Gresham Sirius 10. Ge Kα, Sb Lα and Te Lα lines were utilized for analysis. Silicon and silica glass substrates were used to eliminate interferences namely of Sb L-lines (comes from deposited thin films) and Ca K-lines whose comes from standard microscope glass substrates. Accuracy of EDX analysis is better than ±0.5 at.%, however, in case of Sb and Te is negatively influenced by overlapping of Sb L- and Te L-lines. Moreover, decrease of technique accuracy with decrease of film thickness should be expected. The same apparatus was used for observation of surface morphology of prepared thin films. Accelerating voltage $U = 20$ kV, SE signal, high vacuum mode (target) or low vacuum mode (thin films) were applied.

The character (crystalline/amorphous) of target and prepared thin films was studied by XRD. Measurement was realized via diffractometer PANalytical X'PertPRO with Co Kα X-ray tube ($U = 40$ kV, $I = 30$ mA) and Fe β filter. Primary as same as secondary optics was Soller slits (0.04 rad). Multichannel semiconductor detector PANalytical X'celerator with anti-scatter shield was used for detection. Monocrystalline Si substrates of 100 orientation were used to avoid amorphous background of glassy substrates. Qualitative analysis was performed with HighScore software package (PANalytical, The Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, Germany, version 8.0) and JCPDS PDF-2 database [13].

Optical properties of prepared thin films were studied by UV–Vis–NIR spectroscopy using the double beam dispersive spectrophotometer Jasco V-570. Measurement was carried out in range 300-2300 nm with band width 2 nm and scan speed $400 \text{ nm} \times \text{min}^{-1}$. Obtained transmission spectra were used as a support for evaluation of ellipsometric measurements, which were carried out on J.A. Woolam V-VASE apparatus equipped with NIR extender and focusing windows. Measurement range was 300–2300 nm with measuring angles $\alpha = 60°$, 65° and 70°. For evaluation of ellipsometric data, software W-VASE (v. 3.445) and Tauc-Lorentz dispersion formula [14,15] were used. Maximum possible errors of evaluation [14,15] were $\Delta n = \pm 0.001$, $\Delta E_g^{opt} = \pm 0.01$ eV and $\Delta d = \pm 1$ nm.

3. Results

Target was found to be chemically homogeneous with stoichiometry close to $Ge_2Sb_2Te_5$ within the technique accuracy. Some crystalline structures were observed on target surface by SEM, nevertheless chemical homogeneity in terms of SEM-EDX technique was not negatively influenced. Target was used as calibration standard instead pure individual elements to reach maximum possible accuracy of thin films analysis. Differences of thin films compositions caused by calibration of EDX to target material instead to individual elements are generally within the technique accuracy on behalf of calibration to target.

Target crystallinity was determined by XRD technique. X-ray Diffraction pattern of target is presented in Fig. 1. It is clearly visible that the target is crystalline in origin. Moreover, three different crystalline structures (i.e. hexagonal $Ge_2Sb_2Te_5$, rhombohedral $Ge_{0.95}Sb_{2.01}Te_{4.00}$ and rhombohedral $Ge_1Sb_2Te_4$) were detected as could be seen in Fig. 1. However, any quantification is difficult due to overlapping of three most intensive peaks in diffractogram.

Table 1
Deposition parameters and composition of prepared thin films.

Sample	Ar pressure (Pa)	RF power (W)	Deposition time (min)	Composition (at.%)	
				Si substrate	SiO_2 substrate
1 A	2	20	60	$Ge_{24.1}Sb_{21.8}Te_{54.1}$	$Ge_{25.0}Sb_{20.7}Te_{54.3}$
1 B				$Ge_{25.4}Sb_{22.1}Te_{52.2}$	$Ge_{24.1}Sb_{23.1}Te_{52.8}$
1 C				$Ge_{18.8}Sb_{25.8}Te_{55.4}$	$Ge_{26.9}Sb_{20.7}Te_{52.4}$
2 A	2	10	60	$Ge_{22.0}Sb_{22.1}Te_{55.9}$	$Ge_{19.6}Sb_{24.0}Te_{56.4}$
2 B				$Ge_{27.2}Sb_{19.9}Te_{52.9}$	$Ge_{29.7}Sb_{19.2}Te_{51.1}$
2 C				$Ge_{39.1}Sb_{14.2}Te_{46.7}$	$Ge_{23.8}Sb_{22.7}Te_{53.5}$
3 A	1	20	60	$Ge_{26.3}Sb_{22.4}Te_{51.3}$	$Ge_{23.0}Sb_{22.4}Te_{54.6}$
3 B				$Ge_{24.0}Sb_{21.3}Te_{54.7}$	$Ge_{24.5}Sb_{22.0}Te_{53.5}$
3 C				$Ge_{25.7}Sb_{21.3}Te_{53.0}$	$Ge_{23.3}Sb_{22.4}Te_{54.3}$
4 A	4	10	60	$Ge_{25.6}Sb_{18.6}Te_{55.8}$	$Ge_{27.7}Sb_{19.6}Te_{52.7}$
4 B				NA	$Ge_{26.2}Sb_{17.1}Te_{56.7}$
4 C				NA	$Ge_{30.4}Sb_{22.2}Te_{47.4}$

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