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Structural and optical properties of optimized amorphous GeTe films for memory applications

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ABSTRACT

Chalcogenide amorphous materials, such as GeTe, are known to exhibit deposition dependent optical and structural properties. The formation of a single and homogeneous amorphous GeTe (a-GeTe) phase is questionable since the deposited films can be mixtures of monoelemental nanoclusters. In this work, we employed two deposition techniques, pulsed laser deposition from a polycrystalline GeTe target and co-sputtering from two distinct Ge and Te targets, respectively, to obtain a-GeTe films. To improve the homogeneity of the amorphous phase obtained by magnetron sputtering, the substrate temperature was varied from room temperature up to 180 °C. The samples were investigated by X-ray diffraction, X-ray reflectometry, X-ray photoelectron spectroscopy and spectroscopic ellipsometry. It was found that the film mass density, optical bandgap, refractive index and absolute reflectivity become progressively larger with increasing substrate temperature, due to the minimization of voids fraction and the number of dangling bonds in the amorphous structure. Moreover, X-ray photoelectron spectroscopy results prove the formation of Ge-Te bonds and therefore of the GeTe alloy at the optimal substrate temperature of 180 °C. This study reveals the importance of optimizing the deposition conditions for obtaining a specific amorphous phase, which enables the atomic rearrangements responsible for fast phase-change needed in memory applications.

1. Introduction

Germanium telluride, GeTe, is an important phase change material (PCM), which shows a reversible transition between crystalline and amorphous states, when an optic or electric pulse is applied. Since the amorphous and crystalline phases have significantly different optical properties and switching between them is very fast, GeTe is suited for rewritable optical data storage [1], such as: compact discs - CDs (using a 780 nm laser to read, write and erase the data), digital versatile discs DVDs (650 nm) and Blu-ray discs - BDs, (405 nm). Due to its higher crystallization temperature than its more well-known counterpart $Ge_2Sb_2Te_5$ (GST) [2], GeTe was also proposed to be used in the automotive industry as a high temperature memory (automotive systems require data retention above 125 °C). Moreover, GeTe shows a pronounced difference in resistivity between the two phases and nanosecond switching speed [3], which makes it appropriate for non-volatile memories (NVM). There are several GeTe properties such as optical and resistance contrast, transition speed between amorphous and crystalline state and crystallization temperature that are critical for the mentioned applications and they are ultimately related to the material structure in the two states.

The physical properties of various vapour-deposited amorphous semiconductor films are dependent on the deposition parameters and post-deposition annealing, mainly due to changes in the microstructure, voids and dangling bonds [4] known to exist in amorphous films due to positional disorder. In addition, compositional fluctuations or compositional disorder amplify this dependence, leading to a microstructure which displays density fluctuations [5]. If the voids and dangling bonds are reduced, the physical properties of amorphous films are expected to exhibit a stable behaviour. Annealing is usually used for decreasing the number of such defects and to reach a reproducible amorphous state [6]. According to Messier et al. [7] the structural differences depend on the structure of the target material and the deposition method. It is also believed that non-crystalline films deposited by sputtering are non-uniform in composition, with Te-rich and Ge-rich regions [8], while the sputtering power controls the degree of disorder and films structure. It was observed that increased pressure during magnetron sputtering leads to increased crystallization temperature [9]. Ageing is another issue in phase change amorphous materials, also related to structural changes, with an effect on the off-state resistivity. This phenomenon is

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known as resistance drift, which was correlated in some studies with the increase in the number of Ge-Ge homopolar bonds [10]. In GeTe, the existence of Ge-Ge bonds and therefore of Ge dangling bonds are considered to be the origin of the localized states [6].

Crystallization temperature is an important property of phase change materials that is directly influenced by the deposition conditions and post deposition heat treatments. Kumar et al. [11] observed a decrease of the crystallization temperature with the annealing temperature, the as-deposited sample having the highest transition temperature. Vapour-quenching techniques can lead to very unstable non-crystalline solids which transform readily at very low temperatures to crystalline phases [12]. In these cases, an irreversible exothermic process is observed, corresponding to structural relaxation and disappearance of defects, incorporated during deposition in a metastable amorphous phase. In other cases, a vapour-deposited non-crystalline film will crystallize or phase separate quickly such that a homogeneous glass phase will not be formed. The initial metastable amorphous phase usually has a higher energy than a homogeneous glass, the atomic mobility is increased, which can lead to diffusions that result in structural relaxations. During atomic motions, crystallites are formed and further serve as growth centres during crystallization, producing a decrease of the crystallization temperature. In GeTe, the structural mismatch between the amorphous and the crystalline phases increases the atomic mobility at the interface between the two phases which will elevate the rate of crystallization after surpassing the nucleation barrier.

Differences between the properties of amorphous phase and between transitions from amorphous to crystalline reported so far have been related to the metastable nature of amorphous phase. It is important to comparatively investigate the amorphous films fabricated by different techniques with an accent on sputtering deposition, which is the most used deposition technique in industry. Each technique has its advantages when it comes to chalcogenides. For instance, pulsed laser deposition (PLD) is known for the relatively good stoichiometric transfer of the material from the target to the substrate [13], while thermal evaporation produces films with intermediate range order due to the existence of the first-sharp-diffraction-peak (FSDP), which is rarely observed in magnetron sputtered films [14]. Of course, annealing can be used post deposition, but there is a finite atomic mobility in solid a-GeTe [4] films, which is increased with annealing temperature, so a better solution to obtain homogeneous films is to increase substrate temperature. The differences in the amorphous structure are critical for predicting device behaviour and lifetime.

In most covalent alloys the optical contrast between the crystalline and amorphous phase is small, mainly attributed to the fact that the short range order remains nearly unchanged. This is not the case for GeTe, where the local structure around Ge atoms changes from a six-fold coordination in the crystalline state to a four-fold coordination in the amorphous state [15], which leads to volume changes between 6% and 10% [16]. The origin of the contrast in optical properties between amorphous and crystalline phases in phase change materials is still not fully understood. One explanation might be the existence of resonant bonding in the crystalline phase [17,18]. Since each atom has an average of three *p* electrons for bonding and it should be covalently bonded to six nearest neighbour atoms, resonances between bonding and nonbonding states occur. The resonance bonding leads to a strong electron delocalization and a high electronic polarizability, resulting in a high optical dielectric constant and high refractive index in the crystalline phase, while structural distortions suppress resonant bonding in the amorphous phase [17].

In this article, in order to test the formation of a homogeneous amorphous phase in GeTe films, we have compared amorphous films deposited by PLD from a polycrystalline GeTe target, with amorphous films obtained by magnetron sputtering (MS) from two different Ge and Te targets on a heated substrate at increasing temperatures. The structure and optical properties of each film are carefully analysed and compared with literature data.

2. Materials and methods

Thin films of GeTe were prepared on silicon substrates by pulsed laser deposition using a KrF* laser source ($\lambda = 248$ nm, $\tau_{FWHM} = 25$ ns), model COMPexPro 205, Lambda Physics-Coherent. A commercially available polycrystalline GeTe target (Testbourne Ltd., purity of 99.99%) was irradiated with a laser fluence of 1.5 J/cm^2 and repetition rate of 3 Hz. Depositions were carried out at room temperature while the pressure of the residual gas inside the chamber was 4×10^{-6} Torr. The target to substrate distance was 8 cm. The number of laser pulses for deposition was calibrated in order to obtain the desired film thickness. Additional GeTe films were prepared by *dc* magnetron sputtering. Ge and Te targets (2 in. in diameter) with a purity of 99.99% (Mateck Gmbh) and single side optical polished Si 100 substrates (ultrasonic cleaned in ethanol before deposition) were utilized. A base pressure of 6×10^{-6} Torr and a fixed argon flow of 20 sccm were used in all depositions. After the calibration of deposition rates by an Inficon Q-pod quartz crystal monitor, different magnetron powers were used on each target (51 W for Ge and 9 W for Te) in order to obtain the targeted film composition, while the deposition time was monitored to ensure the desired sample thickness. Substrate temperature was varied from 25 °C to 180 °C. The sample deposited by PLD, with the substrate kept at room temperature, was denoted S1, while the samples deposited by MS at different substrate temperatures (T_s) were denoted as: S2 (T_s = 25 °C), S3 (T_s = 120 °C) and S4 (T_s = 180 °C). The targeted thickness for each sample was 30 nm.

Grazing incident X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) measurements have been carried out with a Bruker D8 Advance, equipped with CuK_α target tube, scintillation counter and Göbell mirror. XRR and XRD patterns have been recorded over a range of 0°–6° (2θ) and 20°–50° (2θ), respectively. LEPTOS software from BRUKER has been employed to fit XRR patterns and to obtain the thickness and mass density of the samples.

Spectroscopic Ellipsometry measurements were performed using a Woollam Vertical-Variable Angle Spectroscopic Ellipsometer (V-VASE) at fixed angle of incidence (AOI) of 70°. The energy range was between 0.7 and 4.5 eV (275–1770 nm). The WVASE32 software was used to evaluate the dielectric constants ε_1, ε_2 and ε_∞, the index of refraction *n* and the extinction coefficient *k*.

X-Ray Photoelectron Spectroscopy (XPS) was performed with an AXIS Ultra DLD (Kratos Surface Analysis) setup using Al $K_{\alpha 1}$ (1486.74 eV) radiation produced by a monochromatized X-Ray source at operating power of 300 W (15 kV × 20 mA). The base pressure in the analysis chamber was at least 1.0×10^{-10} mbar. Sample neutralization was achieved using a flood gun. The detailed spectra were taken at 20 eV pass energy. Binding energies were referenced to the C1s peak standard value of 284.6 eV. For the XPS study, thin films (produced in the above described conditions) exposed to atmospheric air were measured in UHV as introduced.

Samples composition was computed from the XPS data showed stoichiometric compositions (Ge50Te50) with small deviations ± 3 at. % for both MS and PLD deposition techniques.

3. Results and discussion

3.1. X-ray diffraction (XRD) and X-ray reflectometry (XRR)

X-ray diffraction data (Fig. 1a) show that all the samples are amorphous. A broad peak is observed at 2θ ≈ 27.5°, which arises due to the short-range covalently bonded elements given by nearest neighbours. This peak is more prominent in the PLD sample, its position is shifted to lower angles for MS samples S2 and S3 and it returns to the original position for S4. It can be inferred that S1 is more covalently bonded (decrease in dimension of voids and reduction of dangling