Original article

Review of Microstructure and Magnetic Properties of GeTe Chalcogenide Material Doped with transition Metal ion

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Abstract

As a part of my study on the microstructural, magnetic, optical, and electrical properties of Chalcogenide materials doped transition metals thin films, this paper (Part I) presents a brief review on the microstructure and magnetic properties of GeTe phase change material with transition metal (TM) Doping. The deposition and characterization technique were demonstrated. The evaluation results Clearfield that the microstructure of GeTe doped transition metal was influenced by TM ions and the crystallographic phase structure was observed similar to the pure GeTe structure. The ferromagnetic property of GeTe was found strongly modified with some of the TM (Fe, Mn, and Cr) doping at temperature 2°K and at the same time is not much affected with some other TM (Ni, V, Ti and Co) doping. Moreover, the ferromagnetism of $Ge_{1-x}Cr_xTe$ thin film was dependent on the stoichiometric ratio, while the ferromagnetism of $Ge_{1-x}Mn_xTe$ films was influenced by the defects and dependent strongly on the hole concentration. The difference was attributing to the interaction of the ferromagnetic order. Unlike $Ge_{1-x}Mn_xTe$ in the long range RKKY ferromagnetic exchange interaction, short-range order such as a super exchange mechanism plays more important role in the ferromagnetism of the $Ge_{1-x}Cr_xTe$ films.

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1. Introduction

The past century has seen an enormous increase of novel technology used to store a very large amount of data (Wuttig and Yamada, 2007, Raoux et al., 2008, Wang et al., 2020). This rapid increase is motivated by new multimedia applications and the significant increase of knowledge, and information all over the world. Therefore, there are many commercial data storage technology meet this demand, one of the most successful among them being optical data storage (Meinders et al., 2006, Sun et al., 2006, Raoux et al., 2010, Yamada et al., 1987).

The history of phase change data storage materials research dates back to 1955; Kolomiets and Gorunova studied the semiconducting properties of chalcogenide glass, although they did not mention the phase transition of the chalcogenide glass, but they opened follow-up research on chalcogenide glass(Kolomiets, 1964). In the late of 1960s, Ovshinsky reported phase change memory based on reversible electrical switching phenomena in disordered semiconductor materials(Ovshinsky, 1968). Since that, there was a tremendous effort spent on understanding this phenomenon and nurturing this peculiar property of memory-switching effects into electronic memory applications. The first materials used for the electronics memory were glass formers(Anbarasu and Wuttig, 2011). Although these materials showed reversible electrical switching, but the crystallization time was in the order of microseconds. This short time imposed several limitations on device performance like speed, and repeatability. Hence, commercially viable development wasn't achieved until the mid-1980s. A major breakthrough was reached when the first materials called phase change materials were identified. According to the optical and electronic properties difference between the two states and a fast phase change induced by nanosecond pulse laser, phase change materials binary GeTe or ternary GST has been successfully used to produce rewritable optical data storage technology(Loke et al., 2012, Zhao et al., 2019, Jones, 2020).

Generally, in current semiconductor technologies, the current conduction in a semiconductor occurs via charge carriers (Eggenkamp et al., 1992, Fukuma et al., 2002a, Walsh et al., 1969). On the other hand, magnetic materials are used for information storage have been developed utilizing the electron spin(Wu et al., 2008, Yamada et al., 2020). To make use of both charge and spin of electrons in semiconductors, a high concentration of magnetic elements can be introduced in nonmagnetic II-VI, III-V and IV-VI semiconductors (Fukuma et al., 2003, Jungwirth et al., 2006, Burch et al., 2008). The material combining the charge and spin of the electron at the same time are the diluted magnetic semiconductors DMSs (Ohno, 1998, Ohno et al., 1996). DMS has charge and spin degrees of freedom in a single substance to realize a new class of spintronic devices (Liu et al., 2012). The potential advantages of spintronic devices will be higher speed, greater efficiency, and better stability, in addition to the low energy required to flip a spin Therefore, there are some special class of materials not only have all the characteristics of DMSs but also have the reversible phase change transition properties, called phase change magnetic materials (PCMM)(Song et al., 2011, Lee et al., 2011, Liu et al., 2013, Przybylińska et al., 2014).

PCMMs are considered as one of the most important and intensively studied group of materials used to develop new solid state data storage technology(Ovshinsky and Fritzsche, 1973, Wuttig, 2005), because they possess unique characteristics in appropriate temperature processing, which include the potential for externally reversible phase change controlled ferromagnetism and fast switching between amorphous and crystalline structures(Fukuma et al., 2001c, Tong et al., 2011).

First phase change magnetic materials exhibiting different magnetic properties between crystalline and amorphous phases as well as electrical and optical properties, has been theoretically and experimentally observed for Fe-doped Ge-Sb-Te (GST) (Li and Mazzarello, 2012), Mn-doped (Bi_2Te_3, Sb_2Te_3)(Choi et al., 2004) and TM-doped GeTe (TM refers for 3d transition metal atoms V, Cr, Mn, Fe, Co, Ni and cu)(Zhao et al., 2006, Ding et al., 2011) via different deposition methods. Moreover, first principle calculations show that many 3d-doped PCMs, such as Cr-doped GST, Mn-doped GST and Ni-doped GST, exhibit pronounced magnetic contrast between crystalline and amorphous states(Zhang et al., 2012). Upon doping each magnetic ion preferably substitutes a cation and introduces a local magnetic moment, as well as an extra hole due to the mismatch of the electronic structure of the two ions. These holes are loosely bound to the acceptor ions, thus propagate throughout the system. They interact with the magnetic ions, d orbitals, via the p – d hybridization. Therefore, the Doping of transition metal elements at PCMs modifies the magnetic, electrical, optical and to some extent structural properties, and opens up the possibility of exploiting this material for DMS functionality. Here, we present a brief review on the evolution of structure, microstructure and magnetic properties of GeTe, on doping with different TM elements.

2. Deposition and characterization techniques

Thin film deposition under different experimental conditions produces different results, depending on thin film preparation methods. currently, many methods can be used to fabricate phase change magnetic materials thin films including Pulse Laser Deposition(PLD)(Kamalianfar et al., 2013) Molecular Beam Epitaxial (MBE)(Lim et al., 2011) thermal evaporation(George and Menon, 2000), sputtering deposition system(Hoon et al., 1995, Meng and Dos Santos, 1997). The first part of this section focuses on the magnetron sputtering system, as example of deposition system widely used to fabricate thin film. The second part introduced the techniques used for thin film samples characterization. The microstructure of the films was studied using X-ray diffraction (XRD), Raman spectroscope; Scanning Electron Microscopy (SEM) and High Transmission Electron Microscope (TEM). The Magnetic properties for the most of thin films were mainly measured by Superconducting Quantum Interference Devices (SQUID) magnetometer.

Deposition techniques

There are various techniques and methods for depositing materials such as semiconductors, metals and ceramics onto substrates to form a thin film with a certain thickness. Among them, sputtering is of highly importance in the thin films processing field.

2.1 Deposition technique (Sputtering system)

The sputtering technique is considered as one of the most important and extensively used methods in the semiconductor industry in depositing thin films of various materials. Sputtering is a process where atoms are ejected from a solid target material due to bombardment of the target by energetic inert gas ions such as Argon (Ar+) generated in glow discharge plasma. These ions bombard the target or the source of the material to be deposited onto a substrate which is placed directly opposite to the target in a distance d and start to condense into a film.

The sputtering process can be done either in Direct Current (DC) or in Radio Frequency (RF) powers. A direct current (DC) power sputtering was used for the conducting materials while the RF sputtering for both conducting and non-conducting materials. Here, magnets are used to increase the percentage of electrons that take part in ionization of events and thereby increasing the probability of electrons striking the argon atoms as well as increase the length of the electron path, and hence increasing the ionization efficiency significantly.

The technique of RF sputtering uses an alternating voltage power supply at RF frequencies (13.56 MHz), so that the sputtering target is alternately bombarded by ions and then electrons as to avoid charge build-up. Hence, the insulators can be deposited by RF sputtering. In the case of RF sputtering, the plasma is mainly driven by ionization due to electrons which perform an oscillating motion in the plasma body. This kind of excitation is much more effective compared to ionization by non-oscillating secondary electrons (in the case of DC-sputtering), it also leads to lower target voltages in an RF discharge (Ellmer, 2000), and its operating pressure could also be practically extended down to 1mTorr(Shul, 2010). Because of the following advantages sputtering technique is widely used over other techniques. The sputtered materials show good stoichiometry and deposition rates uniformity over large areas. Moreover, the energy distribution of the sputtered atoms fell on the surface without being etched or damage in the early deposited layers.

2.2 characterization techniques

The aim of this part is to present a brief overview for XRD and SQUID system as the main characterization techniques which are used to investigate the microstructure and magnetic properties of GeTe Chalcogenide Material Doped with transition Metal ion.

2.2.1 X-Ray Diffractometer (XRD)

X-ray Diffractometer is a kind of electromagnetic radiation that can interact with the electrons in atoms (WENQIAN, 2009). It is an important and versatile technique used extensively to determine the crystalline and epitaxial quality of the nanostructured thin films grown under different deposition conditions, and to analyze their properties(Als-Nielsen and McMorrow, 2011). It's well known that a crystal lattice is a regular array of atoms in space. These are arranged in space to form a series of parallel planes separated from each other by distance d, which varies according to the nature of materials. The crystal planes oriented in different directions have different d spacing. Therefore, the diffracted waves from different atoms will interfere with each other and generate an intensity distribution. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) which have the same distribution as atoms. Bragg proposed a simple model for studying crystal structure whereby the crystal orientation and phase can be identified. In Bragg model the atomic levels of the atoms are organized in levels separated by a distance d (Weidemüller et al., 1995). when a monochromatic X-ray beam with wavelength λ is incident on the lattice planes in the crystal at an angle θ, diffraction occurs only when the distance travelled by rays reflected from successive phases differs by a complete number 'n' of λs. In general, each material produces unique x-ray spectrum of x-ray intensity as function of the scattering angle. Qualitative information could be obtained by comparing the X-ray diffraction pattern obtained from unknown sample with an internationally recognized database containing reference patterns for more than 70,000 phases. Furthermore, quantitative information's from the intensities ration can also be achieved.

2.2.2 SQUID System

Superconducting Quantum Interference Device magnetometer system (SQUID) is one of the most sensitive techniques for measuring magnetic flux of the materials which have extremely weak signals and investigates their magnetic properties. It uses the quantization of magnetic flux based on superconducting loops containing Josephson junctions to measure the magnetic field. The Josephson junction is a region of material that is not intrinsically superconducting, but is thin enough that tunneling effects cause the ring to behave as though it were composed entirely of a superconducting material. Therefore the Josephson junction can be described as two superconductors, divided by a thin insulating layer which electrons can pass through. SQUID magnetometer contains fine superconducting coil, obtained using a Josephson junction superposition: each electron moves along two directions simultaneously. The basic principle of SQUID magnetometer is the measurement of the magnetic flux change through the detection coil system. The output signal is proportional to the magnetic moment of the thin film, which is magnetized by the magnetic field from the superconducting magnet. Magnetic fields can be applied parallel or perpendicular to the sample so as to investigate both magnetization-applied field dependence and magnetization-temperature dependence.

3. Microstructure properties Review

It is well known that Chalcogenide phase change materials such as GeTe possess high capability of undergoing rapid and reversible switching between two phases namely amorphous (high electrical resistivity) and crystalline (low resistivity)(Feinleib et al., 1971, Adam et al., 2014). However, the amorphous and crystalline states have obvious different structural, microstructure, magnetic, optical and electrical properties. The structure and microstructure of pure and doped GeTe compounds for bulk and thin films have been intensely investigated experimentally and theoretically by using first principle calculations (ab initio simulations). Experimentally, the crystallographic phase structure of as-deposited and post-annealing binary GeTe doped with transition Metal ions were investigated using XRD, SEM and TEM techniques. Many authors reported that the crystallographic structure of GeTe doped with transition metals is similar to that for pure GeTe structure.

In the early years of this century, Y. Fukuma et al. published some papers on $Ge_{1-x}TM_xTe$ thin film (TM= Fe, Mn, Cr, Ni, V, Ti and Co) (Fukuma et al., 2001a, Fukuma et al., 2002b, Fukuma et al., 2008b). They successfully used rf sputtering and ionized-cluster beam methods to fabricate $Ge_{1-x}TM_xTe$

thin films on glass and a BaF_2 (111) substrate with TM composition ranging from 0.02 to 0.96 under certain process conditions(Fukuma et al., 2001b, Fukuma et al., 2007). They reported that the microstructure of $Ge_{1-x}TM_xTe$ thin films prepared at room temperature was amorphous while the annealed films are polycrystalline structure. At room temperature the crystal structure of $Ge_{1-x}TM_xTe$ has stable solid phase and below 450°C, however, the stable phase for GeTe is a distorted cubic structure or known as rhombohedral crystal structure with space group R3m, lattice constant a=5.98Ǻ and rhombohedral angle α = 88.35o. This structure can be viewed as a rock salt structure slightly distorted along (111) direction with a subsequent relaxation along the (111) direction. The rhombohedral distortion decreases rapidly with transition metal concentrations. At high temperature the crystal structure phase is a simple cubic NaCl structure. This structure is similar to the crystal structure of a large number of Chalcogenide compounds. Also, experimentally, it may be possible to grow both the rock-salt (RS) and zinc Blende (ZB) structures, even though the ground state structure appears to be RS. In the conventional unit cell of rock-salt GeTe structure, two types of atoms occupy alternate positions in a face-centered-cubic (FCC) lattice, i.e., one cation FCC lattice of Ge occupy (000) and one anion FCC lattice of Te occupy (1/2, 1/2, 1/2). Furthermore, from the theoretical viewpoint, the zinc blende (ZB) structure is highly interesting to study the phase change magnetic materials. Both RS and ZB structure are FCC-based, but differ in the distance between the Ge and Te atoms.

4. Magnetic Properties Review

Magnetism is a class of electronic phenomena exhibited by a magnetic field with an ordered state which is often stable to exceptionally high temperatures. The presence of magnetic order has a great impact on the magnetic properties of the material as well as electronic, electrical and optical properties

4.1 Experimental evaluation of magnetic properties

In 2006, Fukuma et al, prepared $Ge_{1-x}TM_xTe$ (TM = Cr and Mn) thin films of high quality (Fukuma et al., 2006), and found that the ferromagnetism such as spontaneous magnetization and Curie temperature of $Ge_{1-x}Cr_xTe$ thin film is strongly dependent on the stoichiometric ratio, while the ferromagnetism of $Ge_{1-x}Mn_xTe$ films was influenced by the defects and dependent strongly on the hole concentration. The difference was attributing to the interaction of the ferromagnetic order. Unlike $Ge_{1-x}Mn_xTe$ in the long range RKKY ferromagnetic exchange interaction, short-range order a super exchange mechanism plays more important role in the ferromagnetism of the $Ge_{1-x}Cr_xTe$ films. Further investigations on the $Ge_{1-x}Mn_xTe$ diluted magnetic semiconductors with different compositions have been done theoretically using first-principle calculations by (Xie et al., 2006). They confirmed Fukuma et al.'s spectroscopy results and found that Ge atoms and Mn atoms play competitive role in the occurrence of ferromagnetism. Therefore $Ge_{1-x}Mn_xTe$ with a moderate composition (x = 0.51) of Mn atoms is supposed to have highest Curie temperature, which is consistent with the experimental study.

In 2008, Chen et al studied the optical, magnetic, and transport properties of $Ge_{1-x}Mn_xTe$ ferromagnetic semiconductor grown by MBE. They found that the Curie paramagnetic temperature increased to 180 K(Chen et al., 2008). Consequently, in 2010, Lechner et al prepared further high-quality epitaxial $Ge_{1-x}Mn_xTe$ films. They were reported that the Curie temperature of $Ge_{1-x}Mn_xTe$ films can be reached to 200 K (Lechner et al., 2010). These results opened the door for the possibility to obtain the Curie temperature of these materials at room temperature.

In 2011, Song et al studied the relationship between the physical properties and phase change feature in transition of Fe doped GeSbTe thin film using PLD. They concluded that the Fe doped GST exhibited different magnetic, optical and electrical properties between amorphous and crystalline states (Song et al., 2011). Also at that year 2011, F. Tong et al were investigating the control of ferromagnetism by phase change in Ge0.98Fe0.02Te thin films(Tong et al., 2011). The author found that the magnetic property of Fe doped phase change material GeTe was varied with phase change between amorphous and crystalline states. They concluded that the fast control of ferromagnetism by phase change can be realized.

Accordingly, it can be reported that, phase change magnetic material $Ge_{1-x}TM_xTe$ is exhibiting pronounced magnetic properties contrast between crystalline and amorphous states as well as structural, electrical and optical properties. Experimentally and theoretically, the ferromagnetic property of GeTe is strongly modified with some of the TM (Fe, Mn, and Cr) doping and the same time is not much affected with some other TM (Ni, V, Ti and Co) doping. So that, to acquire phase change magnetic material (PCMM), a conventional chalcogenide phase change semiconductor material is doped heavily (doping 5%-10%) with magnetic ions (transition elements). Not only the dopants but also the form of the material decides the magnetic order in the host matrix. Powder GeTe exhibits room temperature ferromagnetism with Fe doping, superparamagnetism with Mn doping. On the other hand at temperature 2°K, GeTe thin films exhibit ferromagnetism with Fe, Mn and Cr doping.

Magnetic order of the $Ge_{1-x}TM_xTe$ samples is determined by the competition between the FM carrier-induced Ruderman–Kittel-Kasuya-Yosida (RKKY) (Chien, 2007) interaction and the antiferromagnetic (AF) superexchange interaction between

TM element spins.

4.2 Theoretical calculation of Magnetic properties

The literature mentioned in the above section clarified that there are many experimental studies were done to investigate the structural and magnetic properties of transition metal (TM)) doped chalcogenide materials (GeTe)(Adam et al., 2017), but regrettably there are no theoretical calculations to clarify the mechanism behind the change of ferromagnetic exchange interaction property during phase change of GeTMTe from amorphous to crystalline state. Therefore, in this section a theoretical calculation was done based on the experimental results to confirm the magnetic properties of $Ge_{1-x}TM_xTe$ thin films.

The crystal structure of $Ge_{1-x}TM_xTe$ thin films were constructed from the unit cell of the rock salts structure using spin- polarized version of CASTEP whose background framework based on density functional theory (DFT) plane-wave pseudopotential method, which allows you to perform first-principles quantum mechanics calculations. In this study we focused in three different Mn doping concentrations which are set as (25, 50 and 75%). The doping concentrations were obtained by substituting the Ge atoms at the face center-sites of the unit cell with the Mn atom. The Mn concentration 25and 75% have the same space group (PM-3M or 221) while the space group of Mn concentration 50% is (P4/MMM or 123). The space groups of all the doping concentrations are designate for the Rock-salt structure.

The magnetism calculations of $Ge_{1-x}Mn_xTe$ thin films (x= 0.25, 0.50 and 0.75) were carried out based on the framework of spin-polarized density functional theory (DFT), using the projector augmented plane-wave (Blöchl, 1994) method with a plane-wave basis set as implemented in the Vienna ab initio simulation package (VASP)(Kresse and Furthmüller, 1996). The electron-ion interactions were described by projector augmented plane-wave method (PAW), while the Perdew-Burke-Ernzerhof (PBE) functional was employed for the exchange-correlation energy between electrons. The energy cutoff is set to be 310 eV and the exchange-correlation functional was evaluated by Perdew-Burke-Ernzerhof form generalized gradient approximation. The convergence threshold for self-consistent field energy is set at (10^{-5}) eV. The Brillouin zone is sampled by 2×2×2 Monkhorst-Pack k-point grids for geometry optimizations and the self-consistent energy calculations. The structures model of the calculation method was optimized to be the lowest energy structure, which is the most stable structure closest to the real situation. The experimental lattice constants of the structures were employed as an initial input geometry. Therefore, the electronic properties such as density of states (DOS) energy band and the magnetic moments were calculated using the optimized geometries. Then a comparison between the total energy of the ferromagnetic state of the three cases was performed to determine whether the magnetic structure is ferromagnetic. Moreover, the density of states (DOS) of $Ge_{1-x}Mn_xTe$ thin films (x= 0.25, 0.50 and 0.75) were analyzed. The analysis of DOS provided a good understanding for the origin of ferromagnetism of $Ge_{1-x}Mn_xTe$ film.

Fig 1(a-c) presents the calculated DOS (d states) of ternary $Ge_{1-x}Mn_xTe$ thin film (x= 0.25, 0.50 and 0.75) in three structures of ferromagnetic state respectively. Therefore, the DOS plots analyses of $Ge_{1-x}Mn_xTe$ with various concentrations are performed to explain the origin of ferromagnetism in the $Ge_{1-x}Mn_xTe$ phase change magnetic materials. Many authors demonstrated that the origin of ferromagnetic phase of Mn doped III-V such as (Ga, Mn)As dominated by the carrier induced ferromagnetism, because the Mn atom in GaAs act as an acceptor, and it can bring the carriers and the localized spins at the same time. from Fig-1(a-c) it can be seen that the main part of spin up (d state) of Mn atoms in $Ge_{1-x}Mn_xTe$ for all the impurity concentrations are fall below the Fermi level and fully filled by the electron in position deeper in $Ge_{1-x}Mn_xTe$ films. However, the spin down states is partially occupied near the Fermi level. This means that the Mn atoms in such system can produce carriers. It was thought that the carriers are from Ge vacancies, which offer a large number of holes. These results are in good agreements with the experimental results previously reported in the literature for the origin of the carrier-induced ferromagnetism of $Ge_{1-x}Mn_xTe$ DMS. It can be concluded that the origin of ferromagnetic phase is (Ge, Mn) Te, the ferromagnetic interaction is mediated by the carriers, which is often explained by an RKKY interaction (Matsukura et al., 1998, Fukuma et al., 2008a). In RKKY interaction, the carrier density is quite important as well as the carrier mean free path.

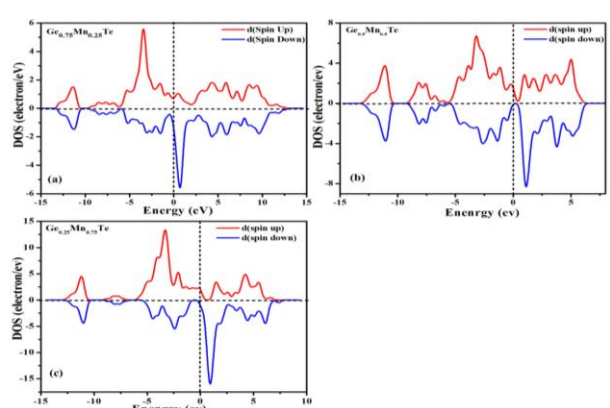

Figure 1 the DOS (d states) of ternary $Ge_{1-x}Mn_xTe$ thin film (a) x= 25%, (b) x= 50 % and (c) x= 75%.

Additionally, the calculated magnetic moments of $Ge_{1-x}Mn_xTe$ thin film were found to be 5.004, 9.946 and 14.513µB, while the Fermi energy were 5.282, 5.287 and 5.302eV. It was clearly observed that the values of the magnetic moments and the Fermi energy are increased with the Mn concentration increased.

5. Conclusions

In this article the microstructure and magnetic properties of GeTe on TM doing were carefully reviewed. The deposition techniques such as (Sputtering system) and characterization technique such as (XRD and SQUID) were demonstrated. In addition, it can be concluded that the microstructure of GeTe doped transition metal evaluation was influenced by TM ions and the crystallographic phase structure was observed similar to the pure GeTe structure. Moreover, the magnetic property of GeTe was strongly modified with some of the TM (Fe, Mn, and Cr) doping and the same time is not much affected with some other TM (Ni, V, Ti and Co) doping. Also the magnetic evaluation clarified that the ferromagnetism such as spontaneous magnetization and Curie temperature of $Ge_{1-x}TM_xTe$ (TM = Fe, Mn, Cr) thin film was dependent on the stoichiometric ratio, while the ferromagnetism was influenced by the defects and dependent strongly on the hole concentration.

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