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Study of Ag doped GeSbTe thin films using X-ray photoelectron spectroscopy

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Content

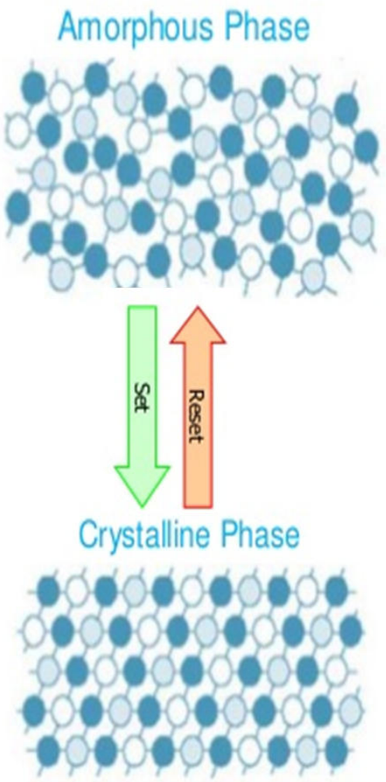
Introduction

In the modern era, materials having different structure under different conditions have unique importance from application point of view.

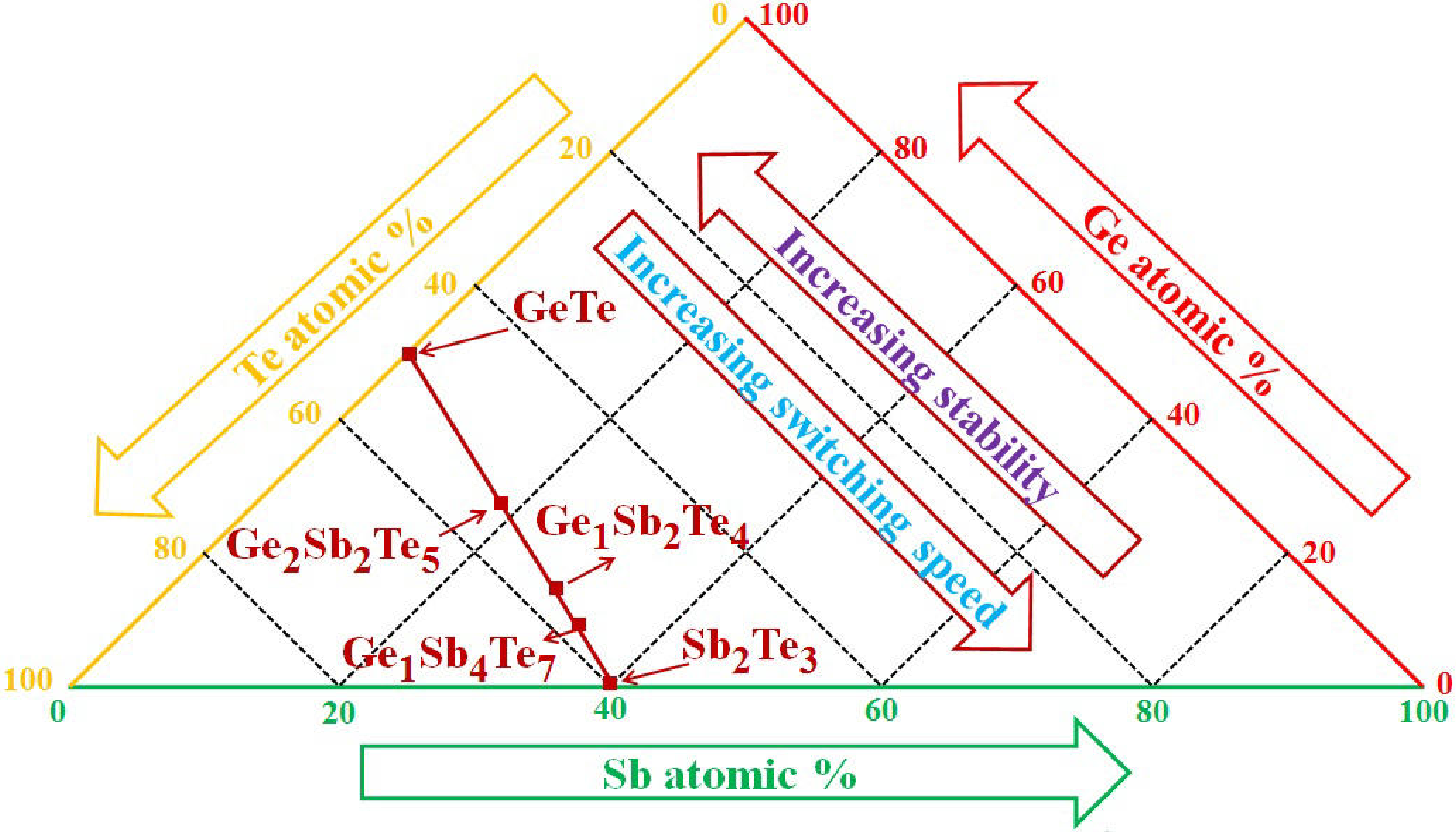
Phase change materials (PCMs), based on structural transition, are potential candidate for data storage, thermal storage, drug delivery, image recording.

Chalcogenide (ChG) based PCMs exhibit reversible structural phase transition from amorphous to crystalline, accompanied by a drastic change in optical and electrical properties, on the nanosecond timescale.

Alloys on GeTe-Sb_2Te_3 tie line and AgInSbTe are potential ChG based PCMs used for various technological applications.



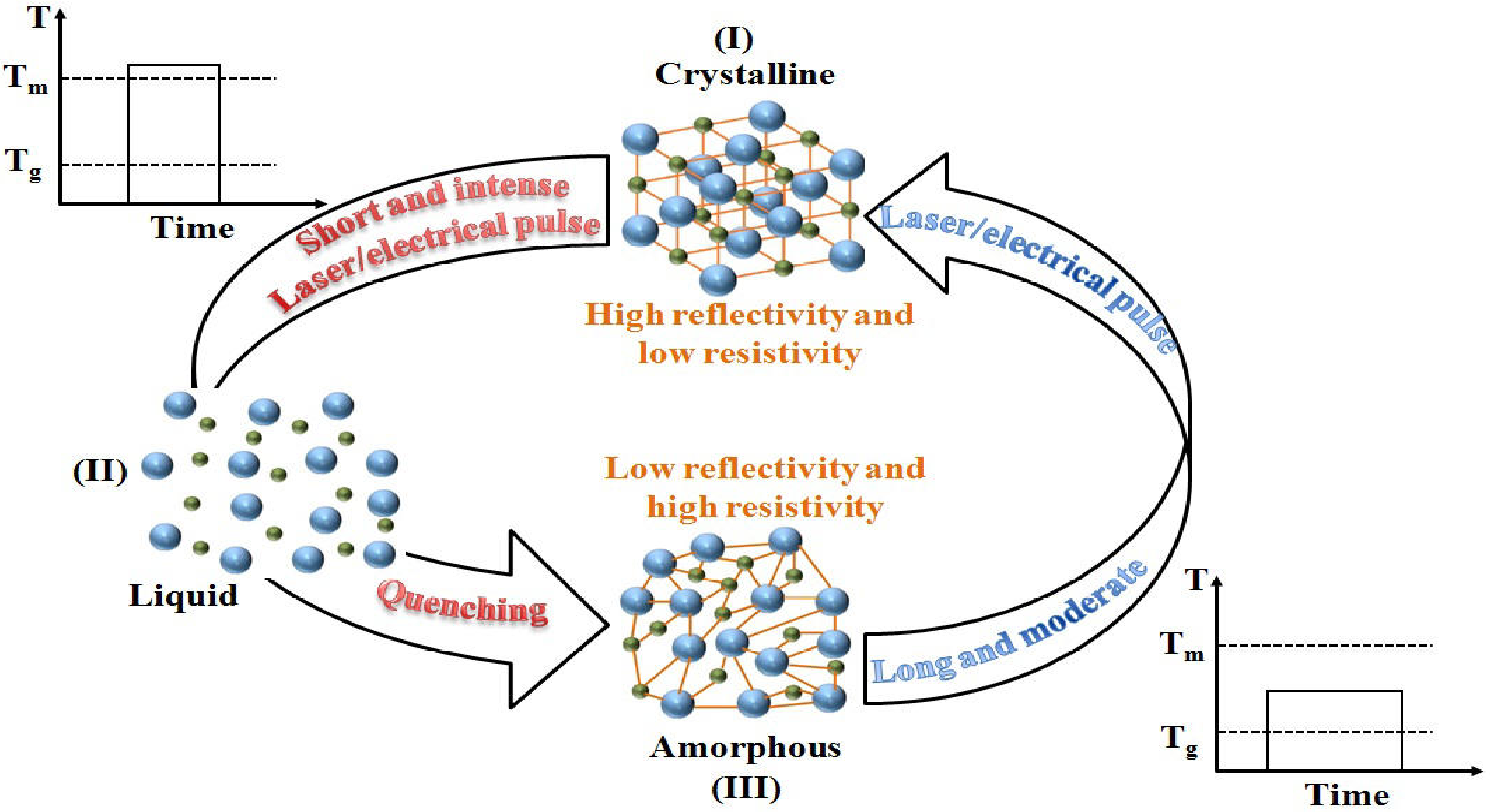
Nat. Photonics **11**, 465-476 (2017), *Adv. Opt. Mater.* **5**, 1700261 (2017), *Nat. Commun.* **8**, 1446 (2017), *Adv. Funct. Mater.* 1705563 (2018), *Sci. Reports* **7**, 42712 (2017).



- Among them, $Ge_2Sb_2Te_5$ (GST) is a potential candidate for phase transition technology due to its capability of phase transition on annealing and by applying current/voltage pulse and pressure owing to its versatile properties like fast crystallization speed, good thermal stability and better data retention.

Nat. Mater. **6**, 824 (2007), *Sci. Rep.* 5, 8050 (2015).

Phase change mechanism



Schematic of phase transition mechanism. State I is the crystalline phase having high reflectivity and low electrical resistivity. State I can be converted to State III (amorphous phase), having low reflectivity and high electrical resistivity, by applying short and intense laser/electrical pulse and with quenching of liquid (intermediate state II). Amorphous structure (state III) can be reconverted to crystalline structure (state I) by applying long and moderate laser/electrical pulse.

Nat. Mater. **6**, 824 (2007).

Properties of $Ge_2Sb_2Te_5$

As-deposited thin films are amorphous in nature.

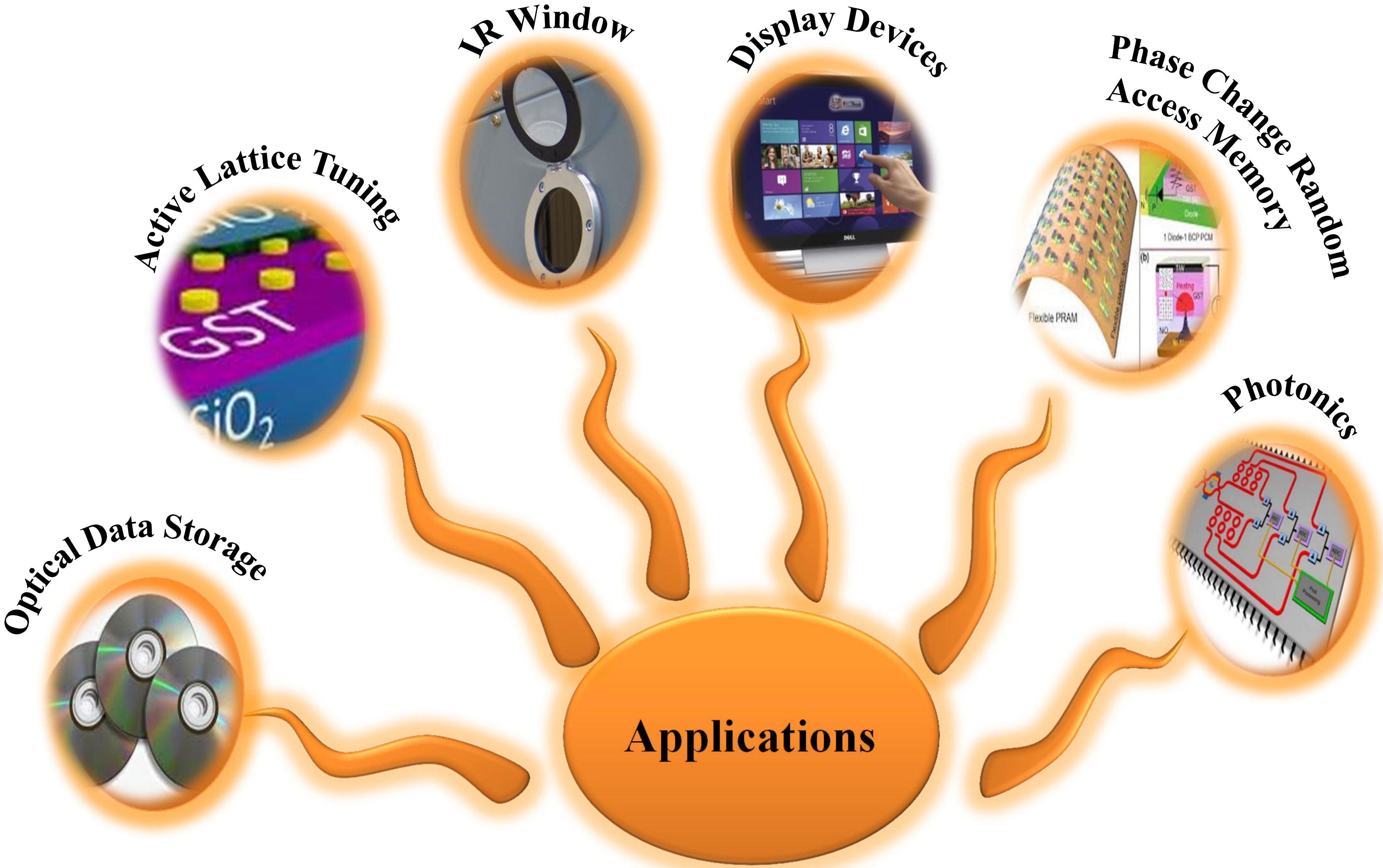
Face centered cubic (fcc) phase is achieved by annealing thin films above temperature of 150 °C.

Hexagonal close packed phase is achieved by annealing thin films above temperature of 250 °C.

20% contrast in optical reflectivity with phase transition from amorphous to fcc.

Three order of magnitude contrast in electrical resistivity with phase transition.

Nat. Mater. **6**, 824 (2007), *Chem. Rev.* ***110***, 240 (2010), *Sci. Rep.* 5, 8050 (2015).



Applications

Optical Data Storage

Active Lattice Tuning

IR Window

Display Devices

Phase Change Random Access Memory

Photonics

Nat. Mater. **6**, 824 (2007), Mater. Today **11**, 20 (2008), *Chem. Rev.* ***110***, 240 (2010), Nature 511, 206 (2014), *Sci. Rep.* 5, 8050 (2015), *Nat. Photonics* **11**, 465-476 (2017), Appl. Phys. Lett. **111**, 261102 (2017).

REVIEW ARTICLES | INSIGHT

Phase-change materials for rewriteable data storage

Phase-change materials are some of the most promising materials for data-storage applications. They are already used in rewriteable optical data storage and offer great potential as an emerging non-volatile electronic memory. This review looks at the unique property combination that characterizes phase-change materials. The crystalline state often shows an octahedral-like atomic arrangement, frequently accompanied by pronounced lattice distortions and huge vacancy concentrations. This can be attributed to the chemical bonding in phase-change alloys, which is promoted by p-orbitals. From this insight, phase-change alloys with desired properties can be designed. This is demonstrated for the optical properties of phase-change alloys, in particular the contrast between the amorphous and crystalline states. The origin of the fast crystallization kinetics is also discussed.

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attractive features[4,5], and we consider the potential of this storage concept as well as the unique material properties required.

In applications as a non-volatile memory, the pronounced difference in electrical resistivity is used. The amorphous state has a high resistance. Applying a long voltage pulse (set pulse) locally heats the amorphous region and leads to recrystallization. Applying

Nat. Mater. **6, 824 (2007).**

240 *Chem. Rev.* **2010,** *110,* 240–267

Phase Change Materials and Their Application to Nonvolatile Memories

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Received February 2, 2009

REVIEW

ADVANCED MATERIALS
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www.MaterialsViews.com

Design Rules for Phase-Change Materials in Data Storage Applications

*Dominic Lencer, Martin Salinga, and Matthias Wuttig**

***Adv. Mater.* 23, 2030 *(2011)* .**

nature photonics

REVIEW ARTICLE

PUBLISHED ONLINE: 1 AUGUST 2017 | DOI: 10.1038/NPHOTON.2017.126

Phase-change materials for non-volatile photonic applications

M. Wuttig[1,2,3]*, H. Bhaskaran[4] and T. Taubner[1,5]

Experimental details

$(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1, 3, 5 and 10) bulk alloys were prepared by **Melt Quenching technique.**

Thin films of prepared $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1, 3, 5 and 10) bulk alloys were deposited on glass substrate using **Thermal Evaporation technique.**

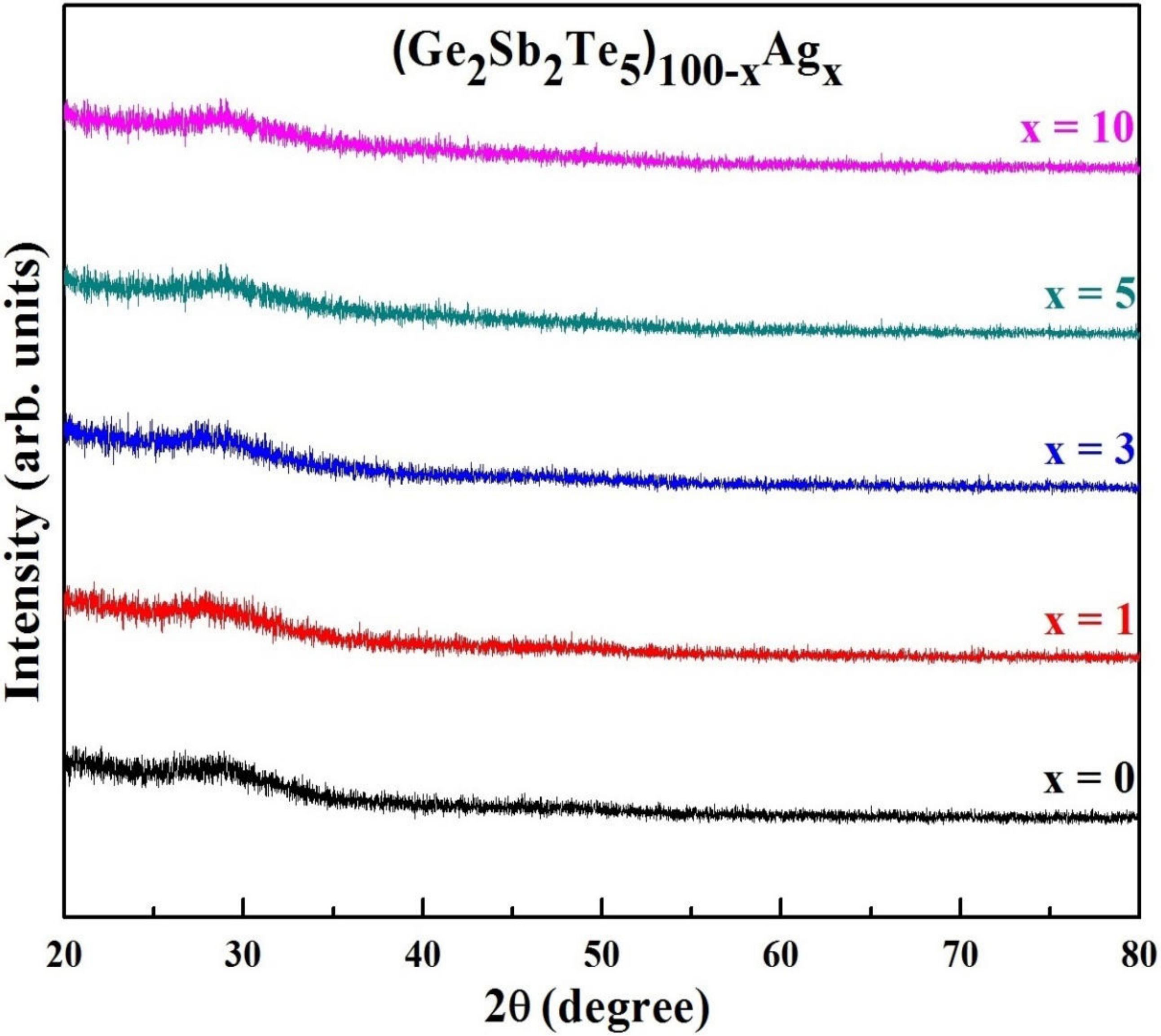
- As-deposited thin films were annealed in vacuum at 160 °C and 260 °C.

Singh et. al ; **Appl. Phys. Lett. 111, 261102 (2017) and Semicond. Sci. Technol. 32, 045015 (2017).**

Results and discussions

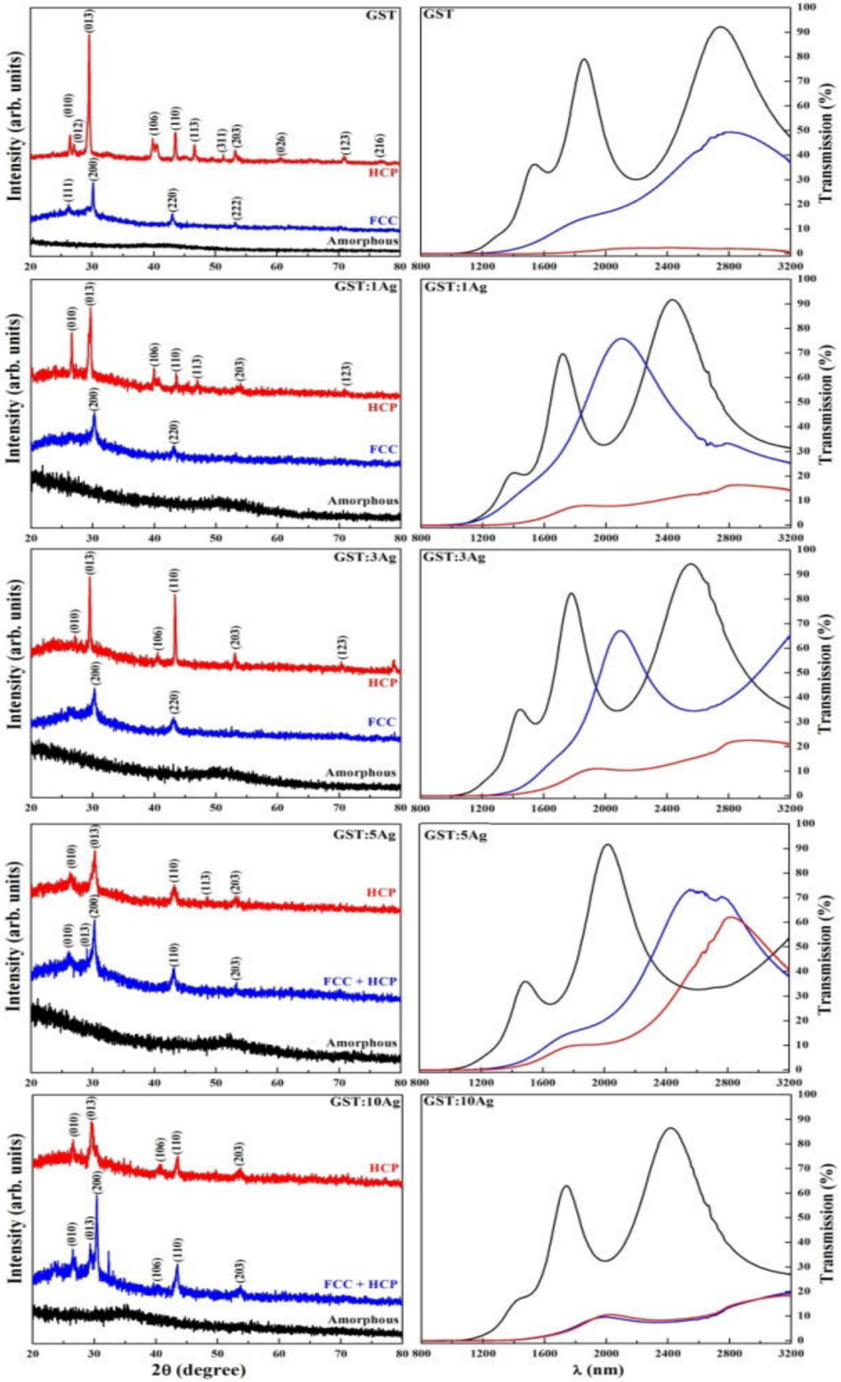
X-ray diffractometer (X'Pert PRO PANalytical) with radiation of Cu $K_{\alpha 1}$ (λ = 1.540 60 Å) was used for X-ray diffraction study.

As-deposited thin films of $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1, 3, 5 and 10) are amorphous in nature.



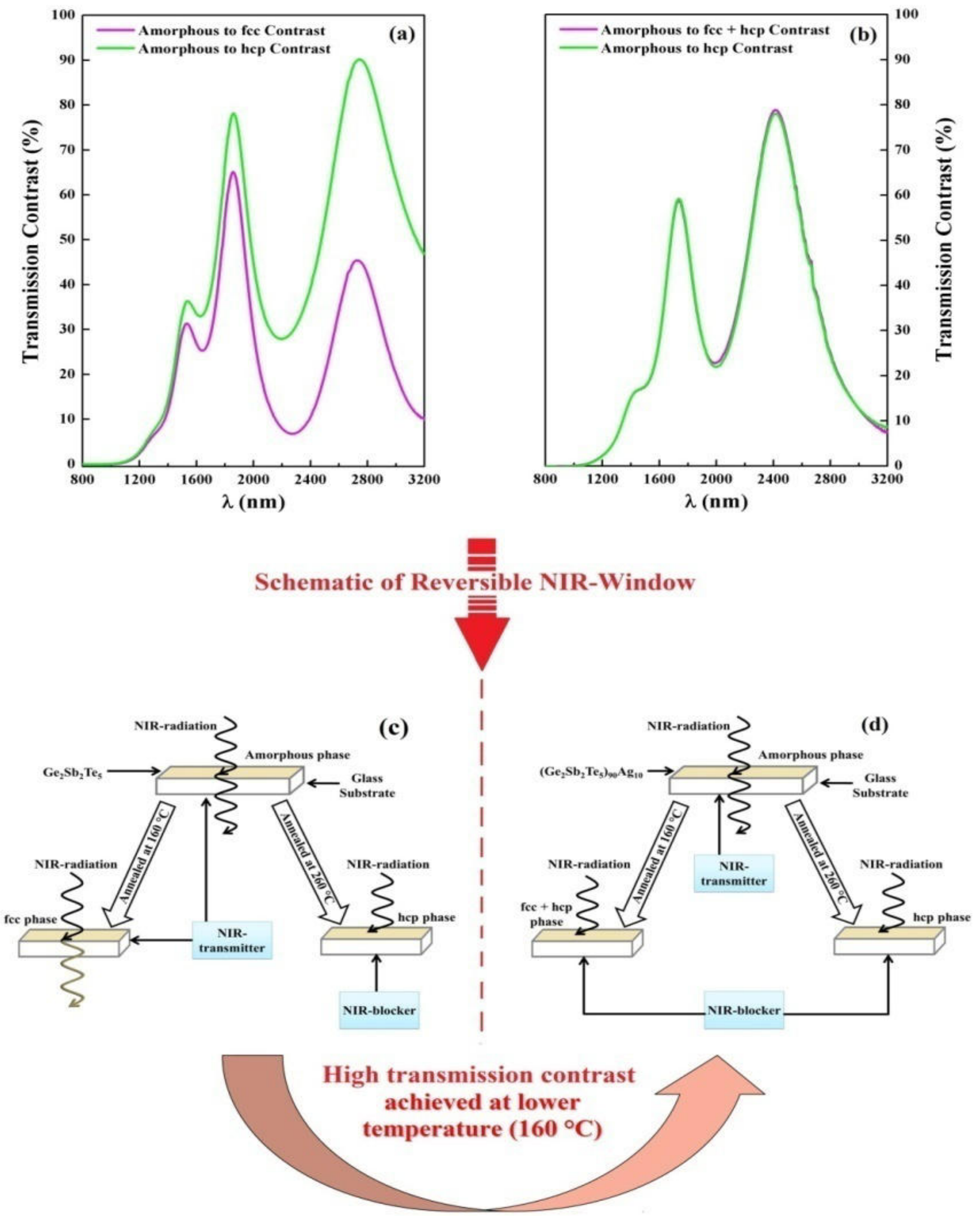
X-ray diffraction patterns of as-deposited thin films of $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1, 3, 5 and 10).

- Phase transition is achieved with annealing.
- $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1 and 3) thin films have fcc phase annealed at 160 °C and hcp phase at 260 °C.
- $(Ge_2Sb_2Te_5)_{95}Ag_5$ more fcc and minor hcp phase, on the other hand, $(Ge_2Sb_2Te_5)_{90}Ag_{10}$ has more hcp phase but minor fcc at 160 °C.
- Amorphous thin films are highly transparent in the NIR region; transmission sharply decreases with phase transition and it is negligible in the hcp phase.
- Transmission spectra of $(Ge_2Sb_2Te_5)_{90}Ag_{10}$ annealed at 160 °C and 260 °C almost overlaps



XRD patterns and transmission spectra of as-deposited (black), and annealed at 160 °C (blue) and 260 °C (red) $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 3 and 10) thin films.

- The transmission contrast can be used to fabricate transmission window in near-infrared (NIR) region.



(a-b) Transmittance contrast between amorphous-FCC and amorphous HCP phases in $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0 and 10) as-deposited and annealed thin films. (c-d) Schematic of reversible NIR-window.

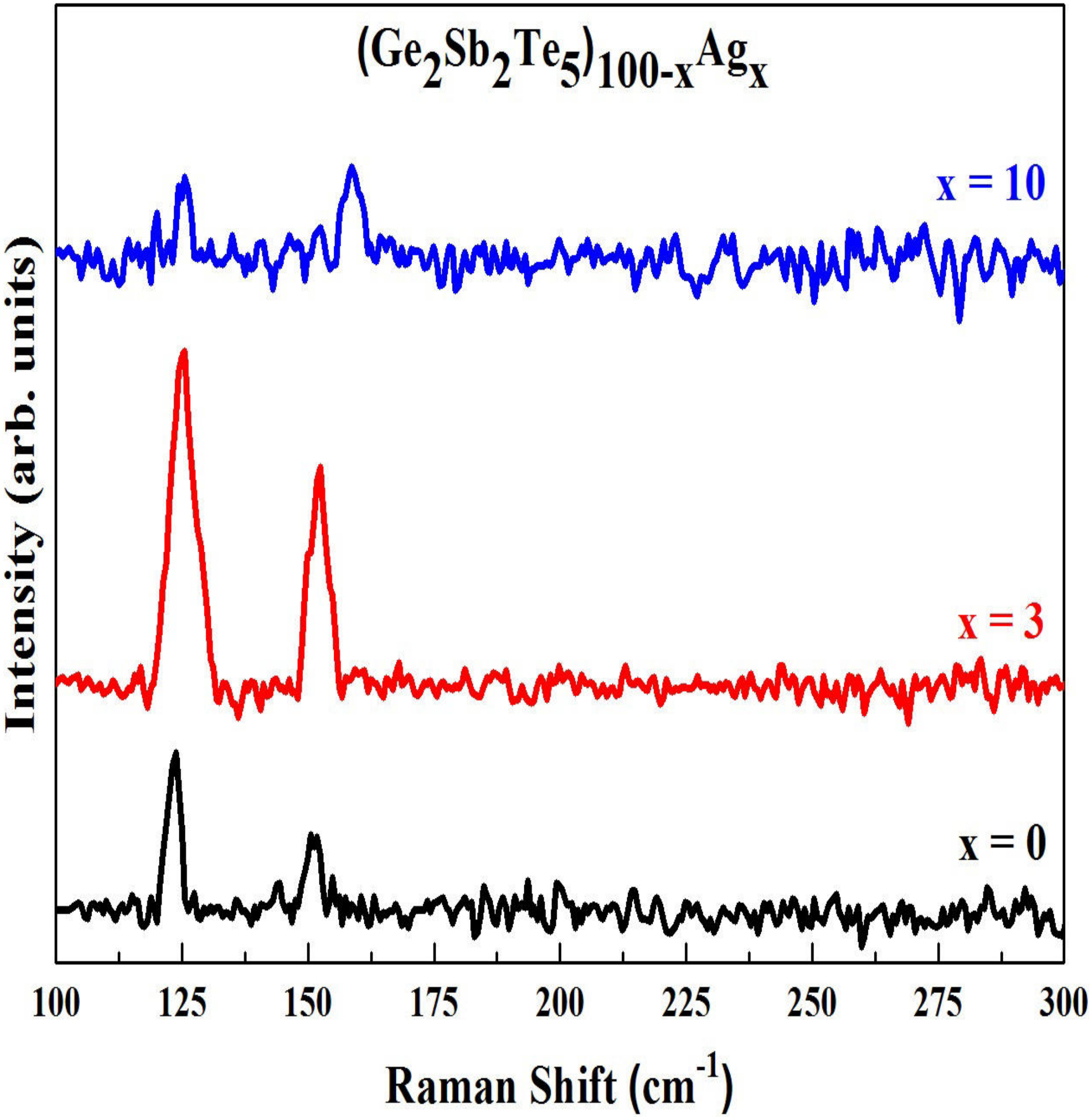
Raman spectroscopy

- Raman scattering spectra were measured at room temperature by a Micro-Raman spectrophotometer (LabRAM HR800, JY).

- The Raman band at ~124 cm^{-1} with A_1 mode is assigned to $GeTe_{4-n}Ge_n$ (n=1, 2) corner sharing tetrahedral and band at ~152 cm^{-1} to be associated with Sb-Te vibrations in $SbTe_3$ unit or from defective octahedral coordination of Sb atoms.

- With Ag doping upto 3% the intensity of these bands improves but with 10% Ag the intensity of these bands starts decreasing, which confirms the structure modification and distortion in the system.

Mater. Chem. Phys., **136**, 935 (2012).

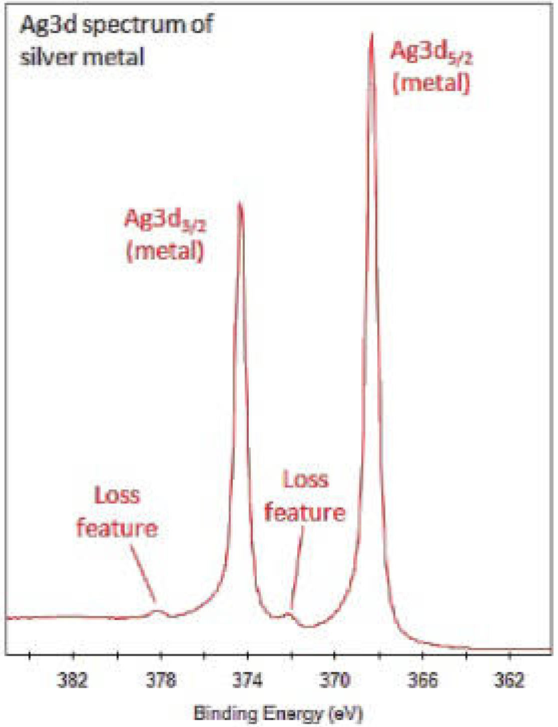


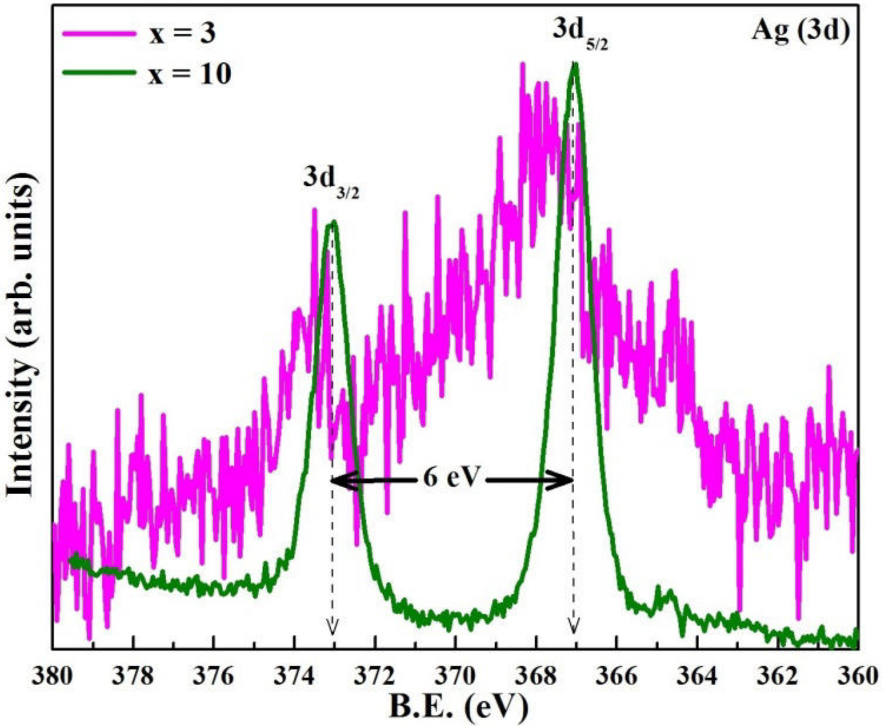
Raman spectra of as-deposited $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 3 and 10) thin films.

X-ray photoelectron spectroscopy

Omicron Multiprobe Surface Analysis (Scienta Omicron, Germany). A Mg K_α radiation source (1253.6 eV) along with a seven channel detector was employed for XPS data acquisition. The surface contaminants were removed by means of the mild sputtering method using 500 eV Ar^+ ions for 10 min. **Valance band and core level spectra was measured**.

Core level of Ag (3d):

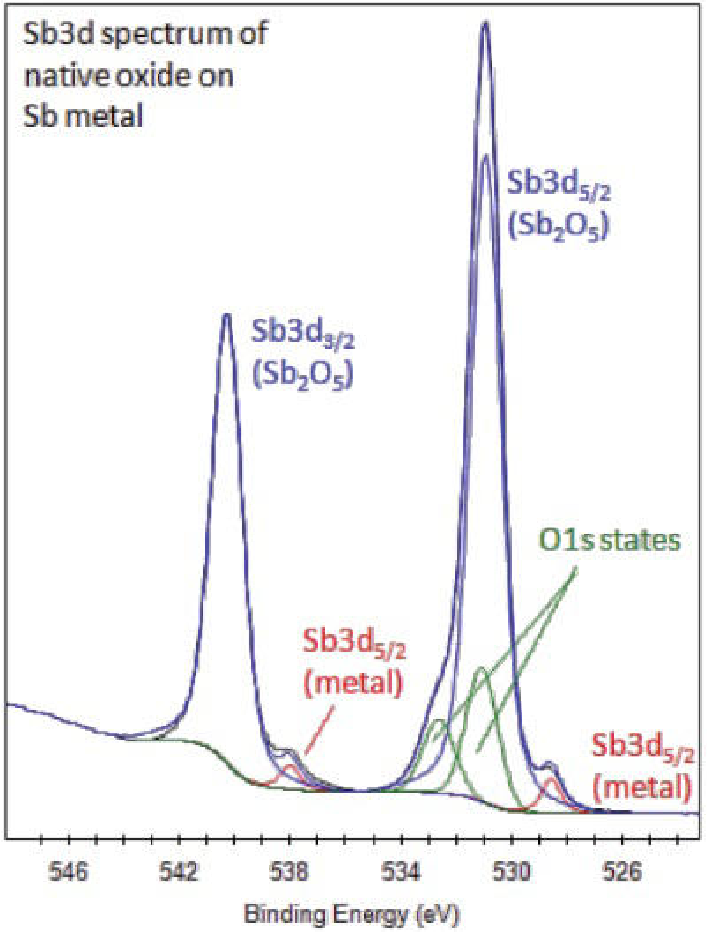


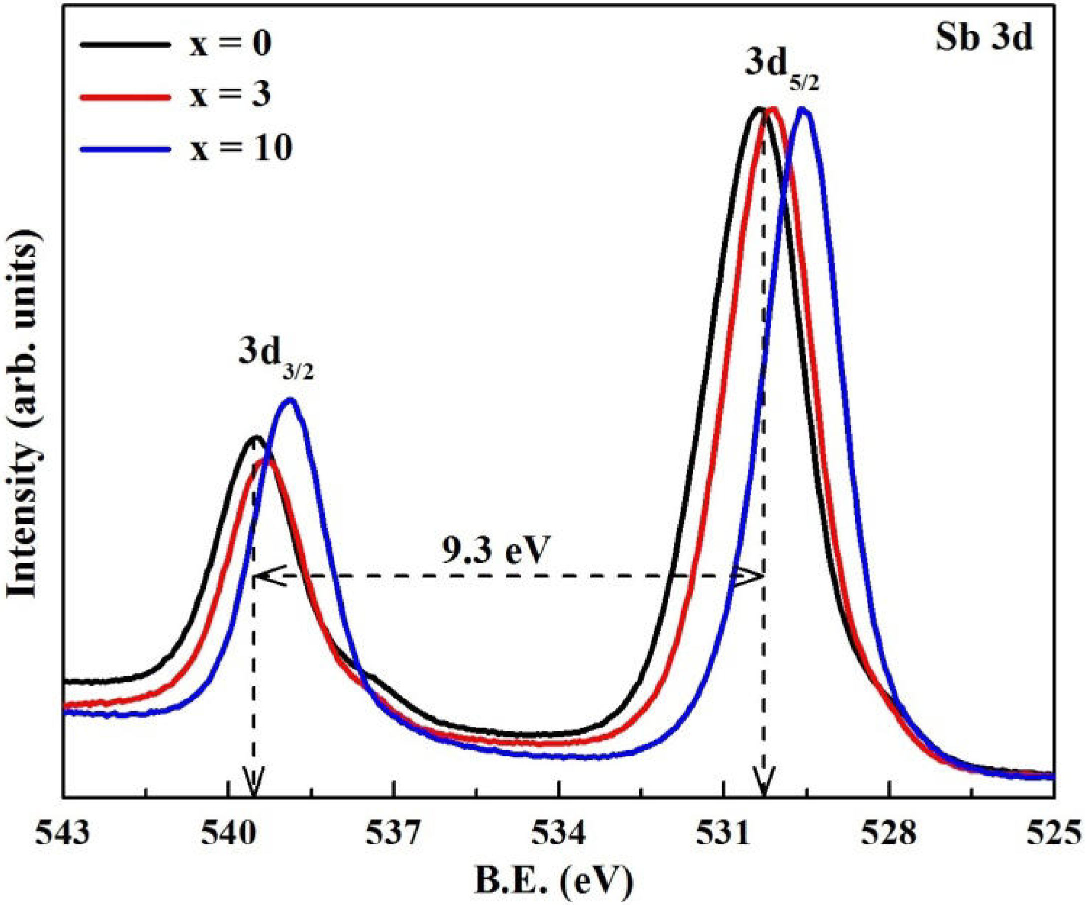


Silver metal ($3d_{5/2}$) = 368.2 eV

Ag (3d) region has well separated spin-orbit components (Δ_{metal}= 6.0eV)

Core level of Sb (3d):

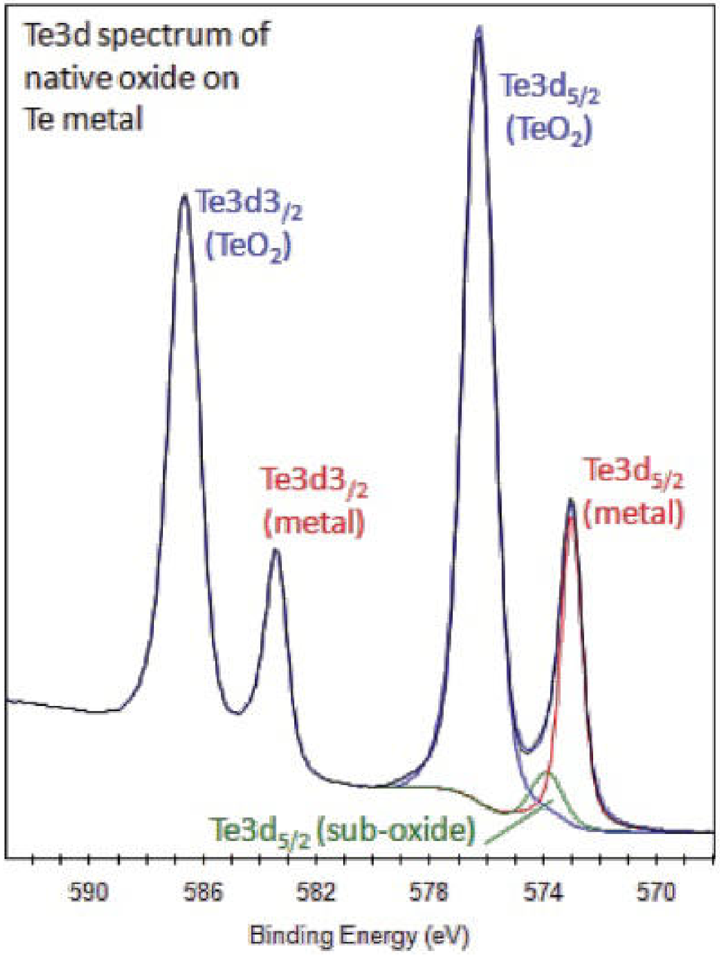


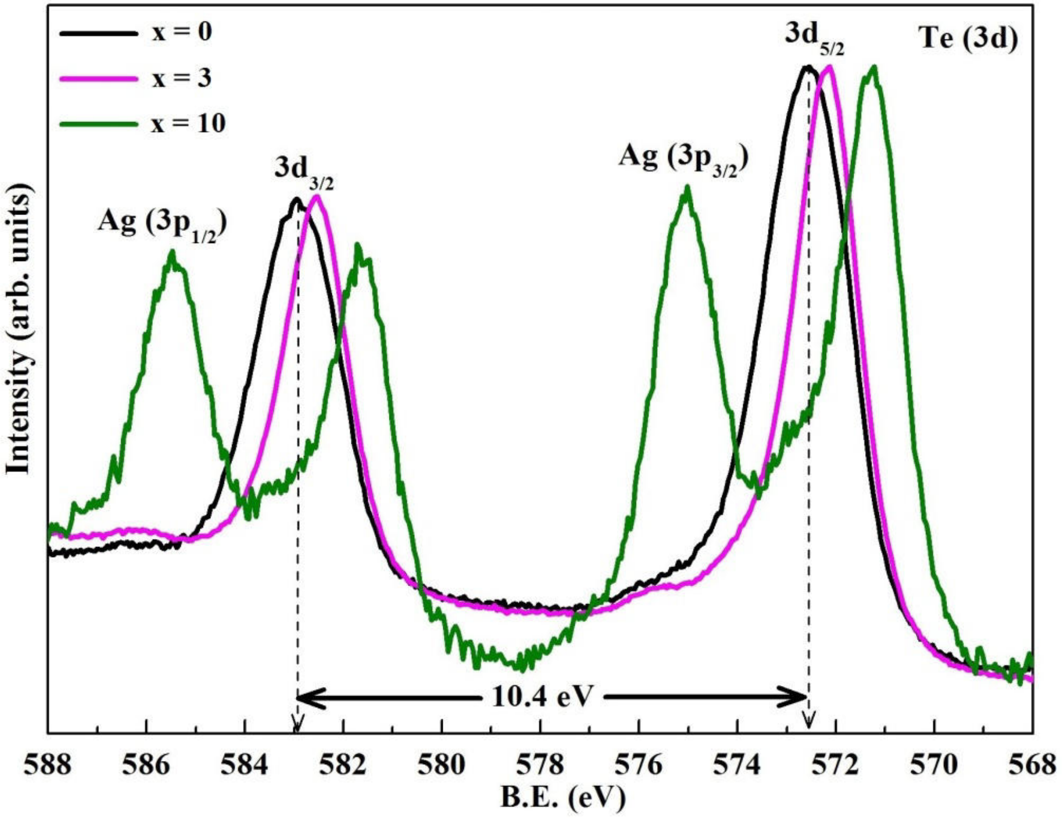


Sb metal ($3d_{5/2}$) = 528.3 eV

Sb (3d) region has well separated spin-orbit components (Δ_{metal}= 9.3 eV)

Core level of Te (3d):

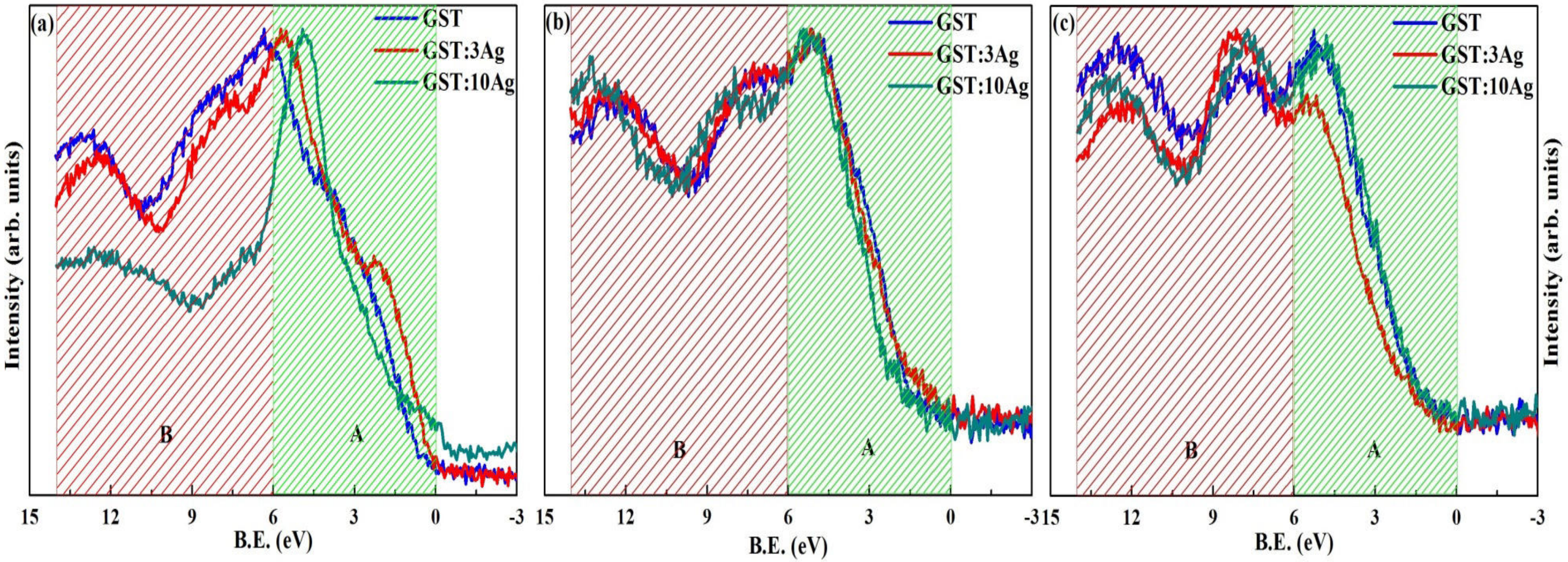




Te metal (3d$_{5/2}$) = 573 eV
Te (3d) region has well separated spin-orbit components (Δ_{metal}= 10.4 eV)

Valance band spectra:

- The Valence band spectra (VBS) can be divided into two main parts, Region A contains the *p*-bands of Ge 4*p*, Sb 5*p*, and Te 5*p*, while region B is due to the Ge 4*s*, Sb 5*s*, and Te 5*s*.
- The VBS of GST and GST:3Ag has same shape but an additional feature around 2 eV was appeared with Ag addition because of increase in metallic character.
- The drastic change in density of valence state is observed with 10% Ag content. This may be due to the distortion in the host lattice



Valence band spectra of $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 3 and 10) thin films: (a) as-deposited, (b) annealed at 160 °C and (c) annealed at 260 °C.

Summary

- $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1, 3, 5, 10) bulk alloys are prepared using melt quenching technique.
- $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1, 3, 5, 10) thin films are deposited on glass substrate using thermal evaporation method.
- Deposited thin films are amorphous in nature.
- $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ (x = 0, 1 and 3) thin films annealed at 160 °C and 260 °C have face centered cubic (fcc) and hexagonal closed packed (hcp) structures, respectively.
- $(Ge_2Sb_2Te_5)_{90}Ag_{10}$ has more hcp phase but minor fcc annealed at 160 °C.
- Transmission spectra of $(Ge_2Sb_2Te_5)_{90}Ag_{10}$ films annealed at 160 °C and 260 °C almost overlap.
- This is a significant result in phase change technology that hcp phase is achieved at lower temperature.

$(Ge_2Sb_2Te_5)_{90}Ag_{10}$ is the potential candidate for reversible near infrared window.

Acknowledgment

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THANKS