Laser-induced crystallization in $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ chalcogenide thin films

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Abstract . $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ chalcogenide thin films having thickness 300 nm, prepared by vacuum evaporation technique were crystallized by Nitrogen Laser for 10, 20 and 30 min. As-synthesized and laser-crystallized films were analyzed by X-ray diffraction, field emission scanning electron microscopy (FESEM), UV/VIS/NIR spectroscopy and dc conductivity measurements. The observed optical band gap becomes smaller by inducing laser-crystallization period 0 to 30 min, which is due to the crystallization of amorphous films. The lowering of band gap by laser-crystallization is an interesting behavior for a material to be used in various electronic devices. The dc conductivities of as-synthesized and laser-crystallized films were analyzed at different temperatures from room temperature to 400 K. We have noticed that the dc conductivity becomes larger at different temperatures under investigation at different laser-crystallization time. Similar to behavior of optical band gap, the dc conductivity activation energy is also observed to become slower with increasing laser-crystallization time and there is a good compliance between these two values.

Keywords: Thin films, optical constants, dc conductivity

1. Introduction

For the last few decades, chalcogenide thin film has drawn a great attention due to their technological importance in various optoelectronic devices^[1-3]. Amorphous and crystalline phases in chalcogenide thin films can be taken as the two bit binary storage data and could be detected optically. Several researchers have analyzed chalcogenide thin films as suitable materials for phase change optical storage. Optical, electrical and structural alterations between disordered (amorphous) and ordered (crystallized) states inspired scientists to investigate the use of these materials for information technology and also for high resolution display appliances^[4-7]. The working of re-writable phase change recording is based on the sensitivity and stability of amorphous-crystalline phase change. Now days, Chalcogenide Random Access Memory (C-RAM) is one of the best candidature as 21st century nonvolatile memory. Its principle deals with the reversible change among amorphous and crystalline state by thermal annealing or laser-irradiation. Amorphous material has a larger resistivity while the polycrystalline has a smaller resistivity, which can be considered as 1 and 0 states. Recently chalcogenides have drawn the attention as promising candidates for optoelectronic applications^[8]. The pompousness of these materials is due to their interacting optical, electrical and thermal properties which ensure their possible use in optical fibers^[9-10], X-ray imaging^[11-13] etc. Laser-induced crystallization in glassy thin films is governed by the variation in optical constants. The identification of different crystallized states with

laser-irradiation can be observed in ternary alloys. The modification in optical constants can be associated with the transformed state from amorphous to crystalline and vice-versa.

Due to importance of these materials several researchers directed their work to chalcogenides. A significant amount of research work ^[14-16] has been cited on laser-irradiation, annealing, γ -irradiation etc on the optical, electrical and thermal behavior of chalcogenides. Huajun et al ^[17] have done laser radiation effect on structure of Ge-Sb-Te while Bahishti et al ^[18] have observed the laser irradiation on selenium–tellurium alloys. Nemec et al ^[19] prepared the As-S thin films and studied the irreversible photo induced changes in it. Yue et al ^[20] have observed the annealing effect on physical properties of SnS films and in a similar way Abdalla ^[21] has reviewed the role of heating films on the optical constants in Ge-Se. The study on the optical properties by gamma and UV irradiation by Balboul ^[22], ion irradiation-induced changes in Ge-Se-Bi by Sharma et al ^[23], photovoltaic applications on annealing films of Cd-Zn-S by Chavhan et al ^[24], ion- beam irradiation on thermal stability in Ge-Sb-Te by Bastiani et al ^[25] also deserve to be mentioned here.

The presented work is devoted to understanding the phenomena of amorphous to crystallized phase transformation of $Ga_{15}Se_{81}Zn_4$ chalcogenide thin films by laser-irradiation.

2. Experimental

Melt-quenching method was used to synthesize the bulk amorphous $Ga_{15}Se_{81}Zn_4$ chalcogenide. We have used materials like Ga, Se, Zn with 99.999% purity to prepare bulk amorphous alloys. With atomic

percentage, the materials were placed and packed in quartz ampoule at high vacuum (10^{-5} Torr.). This packed ampoule was then heated in a computerized Muffle Furnace, in which temperatures was continuously raised up to 1173 K and leave the furnace at 1173 K for 16 hours with rotating arrangement of the ampoule attached with the furnace. The ampoule was then dropped into an ice water tank. The glassy as well as amorphous nature of the quenched $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ was verified by non-isothermal measurements using Differential Scanning Calorimetry (DSC). High vacuum evaporation techniques were used to prepare thin films with thickness 300 nm onto glass/Si wafer substrates under a pressure of 10^{-6} Torr, at a rate of 4 nm/s. As-prepared thin films were then crystallized by a Transversely-Excited Atmospheric-pressure (TEA) nitrogen laser for 10, 20 and 30 min. The identification of transformed phases was done by XRD and Field Emission Scanning Electron Microscope (FESEM). The optical absorbance of the films was observed by a double-beam spectrophotometer (A JASCO, V-500). The dc conductivity measurement was done on thin films of $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ glass using with initially-deposited indium electrode with planer geometry. The film thickness is ca 4000 Å. We have applied a fixed dc voltage on the film and the corresponding current at various temperatures was observed by Keithley-6517 electrometer. The dc conductivity studies were done under a high vacuum furnace Neytec Qex, in which the vacuum was about 10^{-4} Torr during the measurements.

3. Result and discussion:

3.1. DSC, X-ray diffraction and FESEM studies:

Figure 1 presents the thermograms obtained from non-isothermal DSC measurements recorded at heating rate of 20 K/min for bulk $Ga_{15}Se_{81}Zn_4$ glass. It indicates that the synthesized sample has only one endothermic sharp peak which belongs to glass transition temperature, the other exothermic peak corresponds to crystallization temperature and the last sharp endothermic peak represents the melting temperature of $Ga_{15}Se_{81}Zn_4$ glass. These sharp peaks in the DSC thermogram confirm the glassy as well as amorphous behavior of the synthesized sample.

The behavior of the as-synthesized and laser-crystallized $Ga_{15}Se_{81}Zn_4$ thin films was investigated using a Philips (Model-PW1710) XRD with Cu target as source of X-rays having wavelength $\lambda=1.5406 \text{ \AA}$ ($CuK\alpha_1$). Angle of scan was from 20–70 degrees with scan chart speeds of $2^\circ/\text{min}$ and $1\text{cm}/\text{min}$ respectively. Figure 2 displays the XRD of as-synthesized and laser-characterized $Ga_{15}Se_{81}Zn_4$ thin films. The amorphous state of as-synthesized film is verified by the nonappearance of intense structural peaks while the laser-crystallized films depict the sharp peaks representing the polycrystalline nature of irradiated films.

Fig. 1. DSC plot for $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ glass at 20 K/min heating rate.

Fig.2: X-ray pattern for as-prepared and crystallized $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films.

The intensity of peaks becomes higher with increasing the laser-crystallization time, which suggests that the crystallinity of films increases and the sample becomes more polycrystalline.

Fig. 3 (a & b): FESEM of as-synthesized and laser-crystallized (30 min) thin films of $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ deposited on Si (1 0 0) wafer.

The morphology of as-deposited and laser-crystallized (30 min.) thin films of $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ glasses prepared on Si (1 0 0) wafer were studied by Field Emission Scanning Electron Microscope (QUANT FEG 450, Amsterdam, Netherlands) and are represented in Figs. 3 (a) and (b). The accelerating voltage of 20 kV and 10 mm working distance has been taken for the operation of FESEM. It is seen that the as-prepared films show film like morphology with the grains of size of the order of few micrometers on the surface. With laser irradiation, these grains increase in size from few micrometers to tens of micrometers and the crystallinity of films also improves with the increase in laser irradiation time.

3.2. Optical studies:

The optical constants of as-synthesized and laser-crystallized $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films can be obtained from the measurement of the absorbance determined from the spectro-photometric experiments. Absorption coefficient (α) can be determined from the absorbance versus wavelength curve as ^[3-7]

Absorption coefficient (α) = Absorbance (Optical Density)/thickness of the film

$$(1)$$

Using Eq. (1), we have calculated the absorption coefficient at different wave lengths and found to be in the order of 10^4 cm^{-1} . These values are in the range with the observed values of absorption coefficients mentioned by several research groups ^[4-6] for ternary chalcogenide thin films. The following relation has been used to calculate the optical band gap energy:

$$(\alpha h\nu)^{1/r} = B(h\nu - E_g)$$

$$(2)$$

where ν represents the frequency ($\omega = 2\pi\nu$), B is proportionality constant and r is a parameter which depends on several types of transition and may be direct or indirect. The linear plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for as-synthesized and laser-crystallized $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films are provided in Fig. 4.

TABLE- 1: Coefficient of absorption (α), optical band gap (E_g), dc activation energy (ΔE_c), and dc conductivity in $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films

$\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$	As-Prepared	Laser-crystallized (10 min)	Laser-crystallized (20 min)	Laser-crystallized (30 min)
(α) (cm^{-1}) at 520 nm	2563	4164	4772	6793
E_g (eV)	2.08	1.86	1.69	1.54
ΔE_c (eV)	1.79	1.67	1.54	1.38
σ_{dc} ($\Omega^{-1}\text{cm}^{-1}$) at 346 K	8.04×10^{-7}	6.62×10^{-6}	6.22×10^{-5}	5.22×10^{-4}

The figure indicates that a non-direct transition is responsible during the absorption mechanism. The indirect optical band gaps can be determined from the x-axis cut of $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots and are tabulated in Table 1. It is obvious from this table that the optical band gap becomes lessens with increasing laser-crystallization time.

The creation of some defects in the amorphous material is due to the dangling bonds. These defects create localized phase in the amorphous thin films. The existence of high density of localized states in the band structure is the cause for lowering the optical band gap.

Fig. 4. $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) for as-prepared and laser-irradiated thin films of $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ deposited on glass substrate.

The transformation of absorption edge towards lower energies can be discussed on the concept of increased tailing of the band edge into the gaps. Laser-crystallization on amorphous thin films produces crystallization in the thin films. The large variation in E_g , after laser-

irradiation is an indication of amorphous to crystalline phase transformation.

3.2. Study of Electrical Conductivity:

The transport phenomenon of the materials can be analyzed by the electrical conductivity measurements. Chalcogenides thin films generally represent the excited temperature changeable dc conductivity (σ_{dc}) and is given by the relation,

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{\Delta E_c}{KT}\right) \quad (3)$$

where, σ_0 represents pre-exponential factor, K is the Boltzman constant, T is the temperature of the sample and ΔE_c is the dc activation energy. The dc activation energy can be calculated from the slope between $\ln(\sigma_{dc})$ against $1000/T$ graph.

Fig. 5 shows the temperature dependent dc conductivity at various temperatures in $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films. It is observed from the figure that σ_{dc} becomes larger exponentially with increasing temperature. It indicates that the conduction in $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films is through an excited process which also represents the semiconducting properties of the prepared alloys.

Fig. 5. Temperature dependence of dc conductivity for as-prepared and laser-irradiated thin films of $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ deposited on glass substrate.

The laser-irradiation time dependence of σ_{dc} is shown in Table 1. For all laser-crystallized time, the variation of $\ln(\sigma_{dc})$ against $1000/T$ are found to be straight lines representing that the conduction in $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films is through thermal excitation. The calculated values of σ_{dc} at temperature 346 K are tabulated in Table 1. An increase

in dc conductivity has been obtained by orders of magnitudes with increasing the laser-irradiation time. These changes in σ_{dc} with corresponding decreases in ΔE_c are due to the change in Fermi level. The lowering in activation energy by enlarging the laser crystallization time can be described in terms of crystallization in amorphous chalcogenide films. It can be associated to increase in orderedness in the system which gives the amorphous to crystalline phase transformations.

4. Conclusion:

Optical and electrical parameters associated with amorphous to crystallization phase transformation have been investigated in $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films. The XRD of as-synthesized $\text{Ga}_{15}\text{Se}_{81}\text{Zn}_4$ thin films indicates the amorphous state while the laser-crystallized films depict the polycrystalline state. The optical band gap is observed to be slower with increasing laser-crystallization time. The crystallization states in these films by laser are associated with the variation in optical constants. The amorphous to crystalline phase transformation was also verified by FESEM analysis. The temperature dependence of dc conductivity indicates that the conduction is responsible for the thermal excitation tunnel of charges in band tails of the localized states. The lowering of activation energy by laser-crystallization time can be interpreted in terms of inducing crystallization which represents the amorphous to crystallization phase transformation.

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التبلور المستحث بالليزر في افلام الشالكوجينية ($Ge_{15}Se_{81}Zn_4$) الرقيقة

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المستخلص: تم تحضير افلام الشالكوجينية ($Ge_{15}Se_{81}Zn_4$) الرقيقة ذات سمك 300 نانومتر بواسطة تقنية التبخير في الفراغ حيث تم بلورتها باستخدام ليزر النيتروجين لفترات زمنية 10، 20، 30 دقيقة. تم تحليل الأفلام المخلقة والمبلورة بالليزر باستخدام حيود الأشعة السينية، المجهر الإلكتروني الماسح ذو المجال الانبعاشي، طيف الأشعة فوق البنفسجية/ الطيف المرئي/ طيف الأشعة تحت الحمراء القريبة، الموصلية الكهربية للتيار المستمر. حزمة الفجوة الضوئية المرصودة أصبحت أصغر بواسطة التبلور المستحث بالليزر خلال الفترة من صفر إلى 30 دقيقة ويعزى ذلك إلى تبلور الأفلام غير المبلورة. انخفاض حزمة الفجوة باستخدام التبلور بالليزر سلوك مثير للاهتمام للمواد التي تستخدم في الأجهزة الإلكترونية المختلفة. الموصلية الكهربية للتيار المستمر لهذه الأفلام المحضرة تم تحليلها عند درجات حرارة مختلفة تبدأ من درجة حرارة الغرفة وتنتهي عند درجة حرارة 400 كلفن. لقد لوحظ أن الموصلية الكهربية للتيار المستمر أصبحت أكبر عند درجات الحرارة المختلفة. وبصورة مشابه لسلوك حزمة الفجوة الضوئية فقد لوحظ انخفاض في طاقة التنشيط للموصلية الكهربية للتيار المستمر كذلك بزيادة زمن التبلور بالليزر وهناك توافق جيد بين هاتين القيمتين.