Synthesis and study the optical properties of $Ge_{20}Bi_xSe_{80-x}$ thin films

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Abstract

The optical properties of $\mathrm{Ge_{20}Bi_xSe_{80-x}}$ thin film at $x = 0, 0.2$ and 0.6 deposited on glass substrate with thickness of $(205 \pm 50\ \mathrm{nm})$ was prepared using thermal evaporation technique. X-ray diffraction has been study and show amorphous crystalline for the films prepared with different concentration of Bismuth and annealed at temperatures 373 K and 473 K at one hour. A study of the absorption spectrum in the wavelengths (300-900) nm has been used to calculated the optical energy ($\mathrm{Eg^{opt}}$) of the samples. The results show a decrease in the value of the optical energy with increase in Bismuth concentration in the sample, while increase (1.5-2)eV with increase of the temperature of annealing from 373 K to 473 K.

Key words

Optical properties, $Ge_{20}\,Bi_x\,Se_{80-x}$ thin films, thermal evaporation technique.

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تحضير ودراسة الخواص البصرية لأغشية $Ge_{20}Bi_xSe_{80-x}$

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الخلاصة

الخواص البصرية لغشاء $Ge_{20}Bi_xSe_{80-x}$ عند x=0, 0.2 و 0.6 والتي رسبت على قواعد من الزجاج بسمك 205 nm والذي حضر باستخدام طريقة التبخير الحراري. من خلال فحص حيود الاشعة السينية تبين لنا ان الغشاء المحضر نوع عشوائي لكل الاغشية والتي حضرت باختلاف نسب البزموث والتي لدنت بدرجة حرارة 373k و 473k لمدة ساعة. ومن دراسة امتصاصية الطيف الموجي بول موجي (300-900)nm استطعنا ان نحسب فجوة الطاقة البصرية والنتيجة كانت كلما زادة نسبة البزموث كلما قلت فجوة الطاقة البصرية في العينات المحضرة، ولاحظنا زيادة في فجوة الطاقة تتراوح بين (1.5-2)eV مع زيادة درجة التلدين من 373k الى 743k.

Introduction

The importance in the study of the physical features of the thin films of the random semiconductors has attracted the attention of many researchers. This is because of their great importance in many applications and modern technological techniques. Besides, they have a high efficiency close to the efficiency of crystalline semiconductors. In addition, their preparation is easy and economic. However, amorphous semiconductors are divided into two major groups [1]:

1. Elements: they are semiconductors of quarterly bonds (tetrahedrally bonded like C, Ge, Si).
2. The random compounds such as chalcogenidge (i.e. CdSe, CdTe) and glass oxides (i.e.SiO_2, GeO…) [2].

The compound Ge_{20}, Bi_x, Se_{80-x} is considered one of the important compounds in the glass of chalcogenidge group which attracted the attention of some researchers to study its properties because of its ability to form the glass of extent scope of concentration. As for Selenium (Se), it is considered in itself an important element in the formation of the glass. In addition, it has several applications in the field of manufacturing solar cells and opening and closing memory semiconductors devices [1, 3, 4].

Thin film can be prepared by physical method like thermal evaporation [5]. This method is considered one of the oldest and most widely used methods in the preparation of films. The evaporation of the material has been done by placing it in a boat of Tungsten (W) or molybdenum (Mo). (it can be done by using the appropriate boat depending on the type of material under consideration) and the melting degree of the boat which is much more than the degree of the fusion of the material under study.

The formation process of the prepared film in this way includes the following stages [6]. a) Evaporate the material (the boat should have been heated by an electrical current to the degree of material boiling). b) Transfer of atoms from the source of evaporation to the substrate in vacuum. c) Deposited the material on the substrate.

The process of preparing films by thermal evaporation is influenced by several factors, the most important of which are:

1. The vacuum in the Chamber.
2. The type of the materials.
3. The distance between the boat and the substrate.
4. The deposition rate.

The electrical and optical properties have been studied by many researchers. Sastry and Reddy [7] have studied thin films of InTe and InSe obtained by evaporation of pure material from a tantalum boat in a onto well cleaned glass substrates. The deposition temperature was varied from 303 to 573 K. Optical absorption of the films was recorded in the range 13000 to 3000 cm^{-1} and the data was used to deduce optical energy gap of the films. Alwany etal [8] have studied the conductivity type of $Ge_{20}\,Bi_4\,Se_{76}$ films. They indicated that films was n- type and they compared it with $Ge_{20}Se_{80}$ which were p- type. They also proved that the Ge_{20}, Bi_4, Se_{76} films were increase in electrical conductivity by several degrees from the $Ge_{20}Se_{80}\,films$ at the room temperature. The optical energy gap decreases from 1.9eV $for\ Ge_{20}Bi_4Se_{76}$ films to 1.5eV for $Ge_{20}Se_{80}\,films$.

The objectives of this study

1. Prepare the compound $Ge_{20}Bi_xSe_{80-x}$ in the laboratory at the values (x=0, 0.2 and 0.6).
2. Prepare thin films from this compound by the thermal evaporation vacuum method.
3. Studying the structural features of the compound.
4. Studying the optical properties of the compound at the room temperature at wavelengths (300-900) nm to find out the energy gap.
5. Studying the effect of the thermal treatment (annealing) on the optical properties at different temperatures (373K), (473K) and for one hour to indicate the effect of this process on the energy gap.

The experimental procedure

The alloy $Ge_{20}Bi_xSe_{80-x}$ has been prepared by mixing certain ratios of the elements with purity (%99.99) of Germanium (Ge) at molecular weight (72.59), Bismuth (Bi) at molecular weight (208.98) and Selenium (Se) at molecular weight (78.96). The weights of the mixture and the weight of Germanium, Bismuth, and Selenium have been determined at the value of (x). The weights of the mixture for ratios x (x=0, 0.2 and 0.6) have been put in tubes of quartz. The Pyrex-type was cleaned well by water, washing powder; then by distilled water, and after that by alcohol and the device of the ultrasounds and it was dried and become ready to use.

Results and discussion

The analysis of the X-ray diffraction spectrum of the powder compound $Ge_{20}Bi_xSe_{80-x}$ at all the suggested values of (x) that this powder show no peak had been appeared in the structure of these three compounds as indicated in the Figs.(1a), (2-a) and (3-a) respectively. The amorphous state of all the values of (x) can be interpreted on the base that method of preparation by the rapid cooling of molten method decreases the possibility of the arrangement of atoms long extent (in crystal case). This supports has been confirmed by Tace and Menth [9] Biswaw [10] and Choudhuri et al. [11]. Besides, Salman [12] indicted that the compound $Ge_{20}Bi_xSe_{80-x}$ is structurally random.

Same result also have been shown for as deposited $Ge_{20}\,Bi_6\,Se_{74}$, $Ge_{20}\,Bi_2\,Se_{78}$, $Ge_{20}\,Se_{80}$ films (for Figs. (1b), (2b), and (3b)) and when the films annealed at temperature (373k) and (473k) for one hour as shown in the Figs. (1c), (1d), (2c), (2d), (3c), and (3d).

This indicates that adding and annealing process at these temperatures did not affect the nature of these films structure.

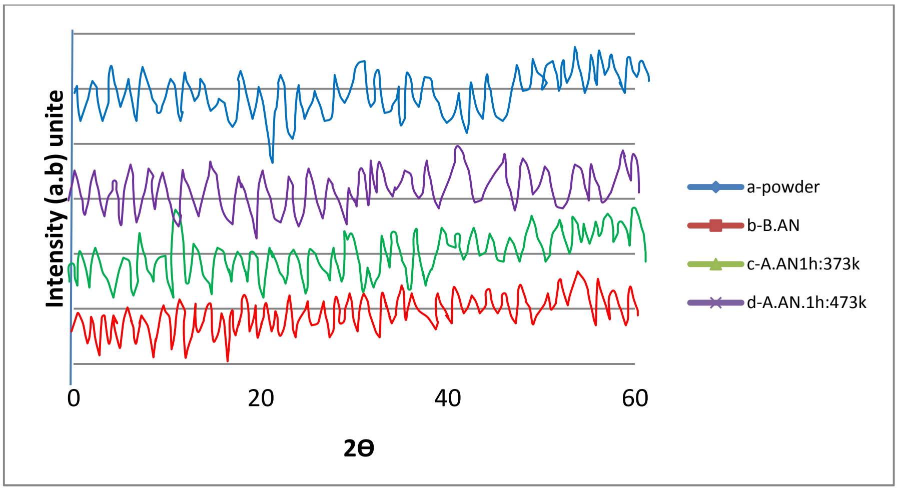


Fig. 1: X-ray diffraction of $Ge_{20}Se_{80}$ powder and films before and after annealing at different temperature.

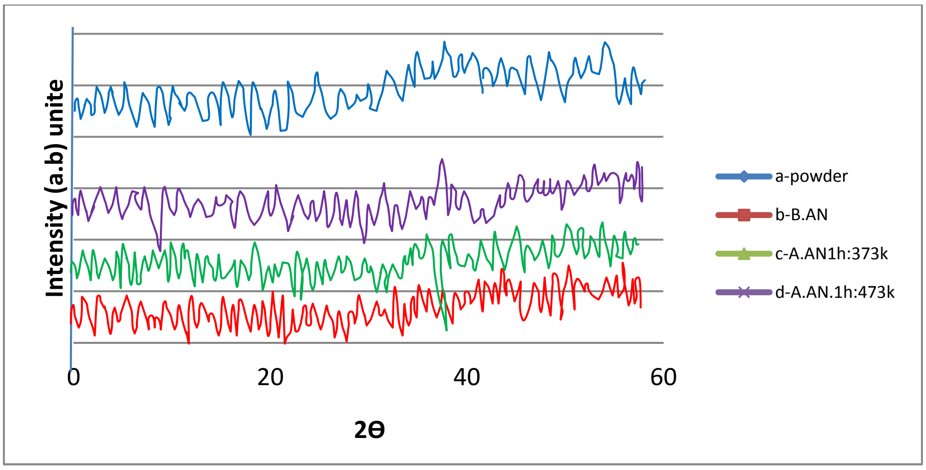


Fig. 2: X-ray diffraction of $Ge_{20}Bi_2Se_{78}$ powder and films before and after annealing at different temperature.

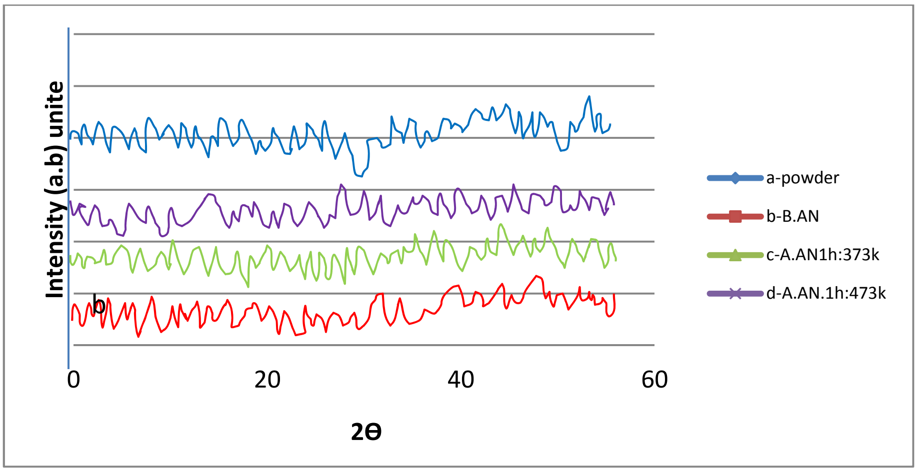


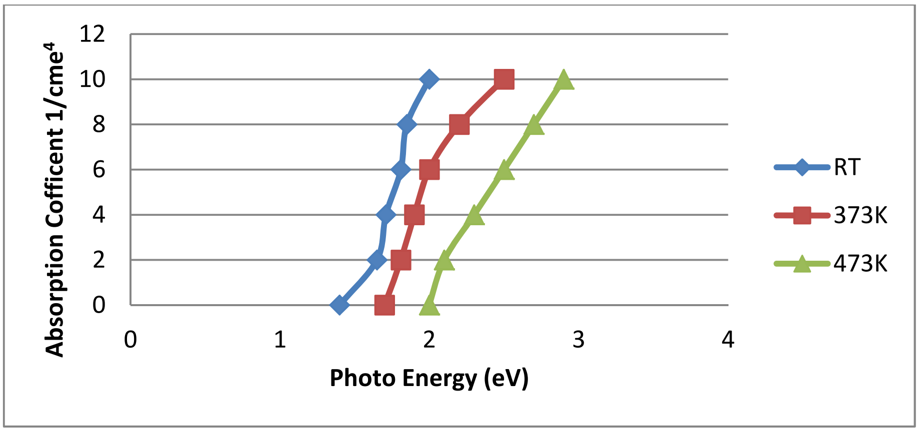
Fig. 3: X-ray diffraction of $Ge_{20}Bi_6Se_{74}$ powder and films before and after annealing at different temperature.

The absorption coefficient (α) was calculated from the transmission spectrum by the following equation:

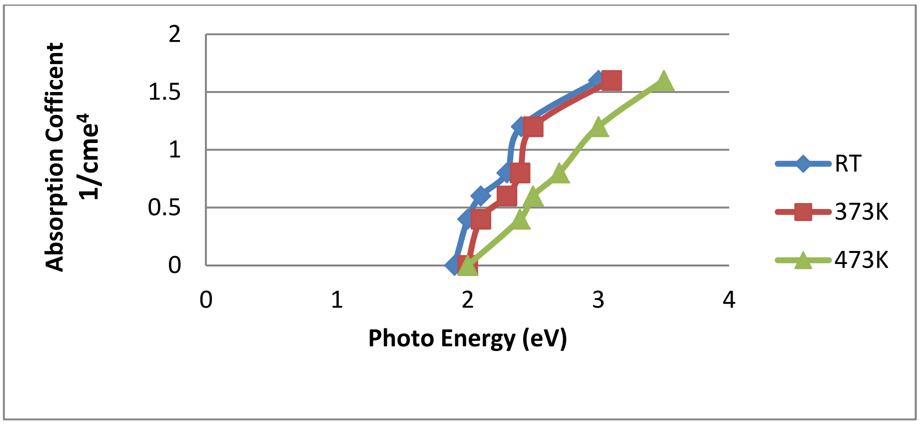
$$\alpha = \frac{2.303}{t}\log\left(\frac{1}{T}\right) \qquad (1)$$

where t: is the thickness of the films and T: is the transmission.

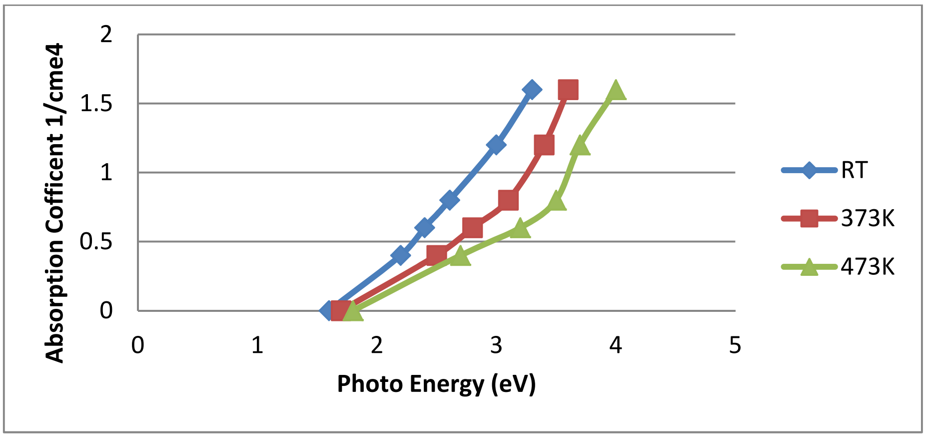
The Figs. (4a), (4b) and (4c) indicate absorption coefficient as a function of Photon energy of the thin films of $Ge_{20}Bi_xSe_{80-x}$ at different values of x (x=0, 0.2 and 0.6) before and after annealing at temperature (373k) and (473k) for an hour. It was also noticed that the values of absorption coefficient with an extent from $10^3\ cm^{-1}$ to $10^5\ cm^{-1}$. It was found that the change of the absorption coefficient and the photon energy of all the films was weak at the low energies and increased nearby the optical absorption edge. It was also noticed that the annealing process deviate the absorption edge towards the high energies and a more decrease of the absorption coefficient than it was before the annealing [7, 8]. This could be attributed to reason that the process of annealing which led to the reduction of the defects existence in trap centers. This led to an increase of the optical energy gap. Besides, it was noticed that the absorption coefficient increased in relation to the increase of the ratio of Bismuth in the films before and after annealing.



a-$Ge_{20}Se_{80}$



b- $Ge_{20}Bi_2Se_{78}$



c- $Ge_{20}Bi_6Se_{74}$

Fig. 4: Absorption coefficient $Ge_{20}Bi_xSe_{80-x}$ films before and after annealing.

The relation between $(\alpha hw)^{1/2}$ and the photon energy (hw) which represents an indirect transition. This can be indicted in the following equations [4]:

$$ahv = B(hv - Eg^{opt})^r \qquad (2)$$

where α: the absorption coefficient $(cm)^{-1}$, hv: the photon energy (eV), B: constant depends on the nature of material $(cm, ev)^{-1}$, r: represents an exponential coefficient depending the nature of electronic transitions and it takes the values (2, 3, 1/2, 3/2) in this case r=2, and Eg^{opt} optical energy gap.

The relation between the photon energy ((hν) and $(\alpha h\nu)^{1/2}$ was drawn. When extending the straight part of the curve to cross the photon energy axis at the point, $(\alpha h\nu)^{1/2} = 0$ we got the value of the optical energy of this transition.

The Figs. (5a), (5b), and (5c) represent the values of the optical energy gap of all the films at room temperature.

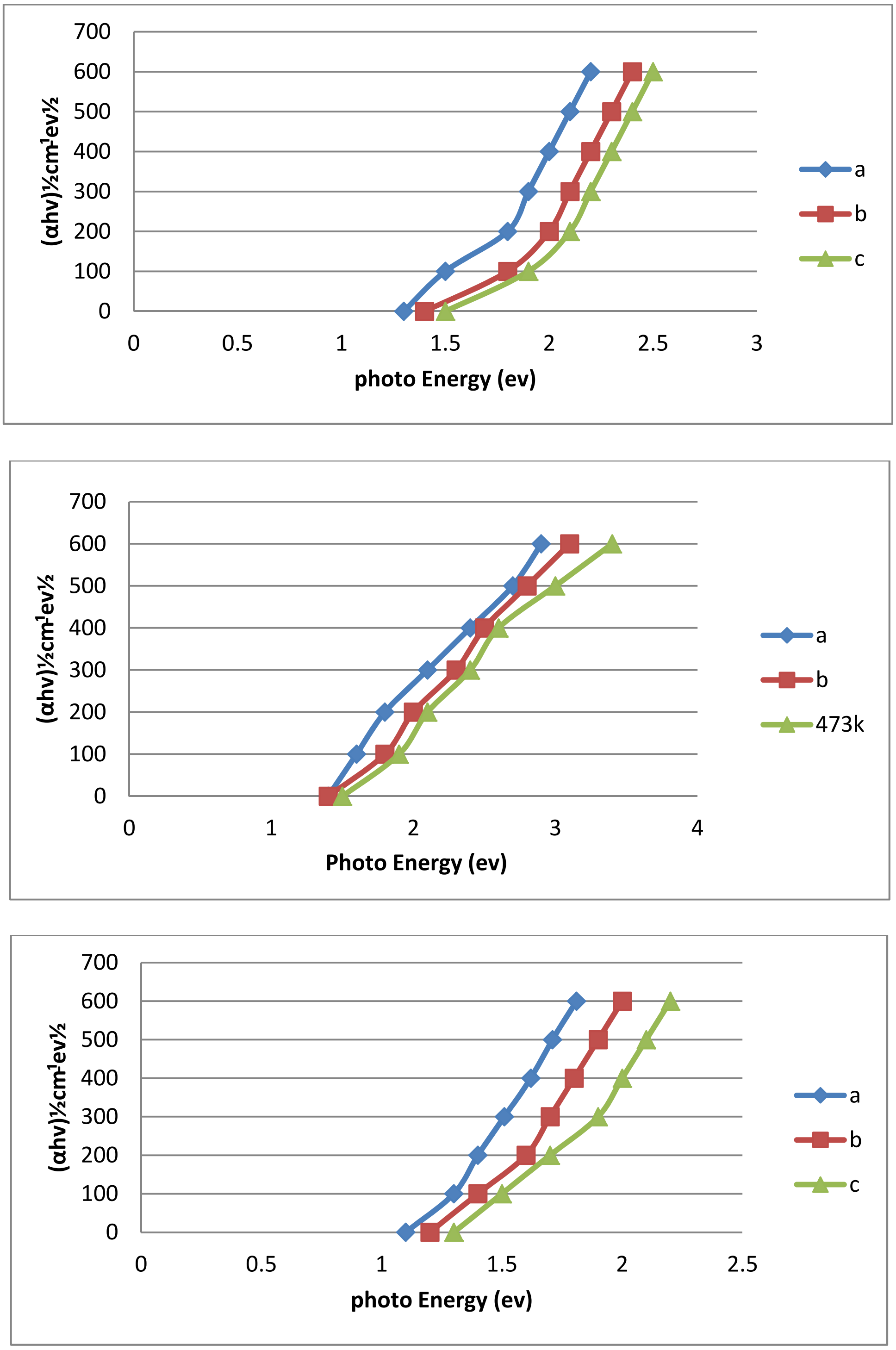


Fig. 5: Optical energy of $Ge_{20}Bi_xSe_{80-x}$ films before and after annealing at 473K for an hour a-$Ge_{20}Se_{80}$ b- $Ge_{20}Bi_2Se_{78}$ c- $Ge_{20}Bi_6Se_{74}$.

It was found that the optical energy gap decreased with the increase of Bismuth in the films. This might be due to the increase of the width of tails (E_t) or the increase of the density of the topical cases inside the motor gap resulting from the increase of the randomization in the film structure [10]. It also showed that the values of the energy gap decreased with the increase with the increase of annealing temperature [11]. This could be attributed to the annealing process which led to a reduction in the topical levels nearby the packs of valence and conduction [12, 13].

Conclusions

X-ray diffraction has been study and show amorphous crystalline for the films prepared with different concentration of Bismuth and annealed at temperatures 373 k and 473 k at one hour. The values of absorption coefficient increased with the increase of Bismuth ratio. The value of optical energy decreased with the increase of Bismuth ratio concentration in the sample, while increase with increase of the temperature of annealing from 373 K to 473 K.

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