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INVESTIGATION OF OPTICAL PROPERTIES OF X-RAY IRRADIATED GaSe THIN FILMS GROWN BY ELECTRODEPOSITION

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ABSTRACT

The optical properties of X-ray irradiated GaSe thin films grown at electrolytic bath temperatures of 60 and 80ºC have been studied in this work. The results for the as-deposited GaSe revealed the films grown at 60 and 80 ºC have energy band gaps of 2.80 and 2.20 eV respectively. The absorption/extinction coefficients of the deposited materials were found to be 3.72 × 10^4 cm^{-1} and 4.44 × 10^4 cm^{-1} / 0.12 and 0.15 respectively. The films were later exposed to X-ray for ~10 seconds. Upon exposure of the films to X-ray radiation, the energy band gaps of the samples increased to 3.00 and 2.35 eV, the absorption coefficients of the GaSe thin films decreased to 3.52 × 10^4 cm^{-1} and 3.97 × 10^4 cm^{-1} respectively, for the films grown at 60 and 80 ºC. The elimination of the noise effects at the ultra-violet region of the absorption spectrum of the investigated samples was noticed after X-ray irradiation. Thus, X-ray irradiation could serve as a post-deposition treatment of thin films.

1.0 INTRODUCTION

Gallium selenide is a group III-VI semiconductor [1], with a hexagonal layer structure [2], similar to grapheme [3-5]. GaSe is made up of covalent bonds between the Ga and Se atoms, with the Se atoms stacking the top and bottom layer while Ga ions are in the middle, that is, the Se-Ga-Ga-Se order [4]. GaSe crystallizes into four polytypes namely ε, γ, δ and β [3] and all the polytypes can be found in a single crystal [6]. In application, GaSe has shown great potential in nonlinear optical applications because of its capability to convert frequency from near-IR into mid-IR and further into the THz-range, due to their high birefringence and nonlinear optical properties [7 – 9], as well as broad low-loss transmittance [8]. According to[3], GaSe has a transparency range 0f 0.65 to 18 μm with optical absorption not exceeding 1 cm^{-1} in the wavelength range and can satisfy phase matching for parametric conversion in the 1 to 18 μm wavelength range.

Despite some outstanding qualities of GaSe as extensively discussed in [3], some of its poor qualities arising from growth and mechanical properties still limit application [8]. Several efforts have been reported as attempts made in improving the weak hardness and fabrication at low temperatures or tuning the linear optical parameters of GaSe. These include the doping of GaSe with Mn and Cr which resulted in prominent peaks in photoluminescence and photoconductivityspectra for high doping levels [10,11],while Ni-doped GaSe showed a dominant linearabsorption [12].

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According to [8], GaSe doped with In of varying concentrations showed that optical absorption and micro-hardness of the doped GaSe increased with increasing concentration of In.

On the other hand, the exposure of different materials to different types of radiation has been reported to have varying effects depending on the exposed materials. As reported in [13], the exposure of $Mn_{0.5}Zn_{0.5}Sm_xFe_{2-x}O_4$ ceramic nanocrystal to varying doses of γ radiation completely vanished the magnetic anisotropy, with the irradiated sample behaving as super-paramagnetic ceramics, with some variation in saturation magnetization. A gel resistance to gamma irradiation was reported by [14] as no effect was found beyond 3 Gy when magic polymer gels were exposed to gamma radiation. Also, gamma irradiated Cr_2O_3 showed an increased crystallite size, a red shift in the absorption edge and a decrease in the resistance of the material [15]. According to [16], the effect of gamma irradiation on the optical and structural properties of aqueous CdS quantum dots showed that photoluminescence degradation of the quantum dots is strongly dependent on concentration, with low concentration yielding the fastest degradation. With the reported varying effects of ionising radiation exposure on different materials, this work, therefore, seeks to investigate the effect of X-ray irradiation on the optical properties of electrodeposited GaSe.

2. EXPERIMENTAL DETAILS

Gallium Selenide (GaSe) thin films were prepared from an electrolytic bath containing 0.1 M $GaCl_3$ and 0.02 M SeO_2 in 400 ml of de-ionized water. The bath pH was adjusted to 2.50 ± 0.02 by making use of a diluted ammonia solution. The stirring of the solution was carried out for a few hours to aid the quick dissolution of the chemical compounds in the de-ionized water. Electrodeposition of GaSe films was done at a cathodic potential of 1400 mV at two different bath temperatures of 60 and 80^{o}C. A growth duration of 15 minutes was used in this work for all deposited GaSe layers. An electric heater which contains a built-in magnetic stirring unit was used for heating up the electrolytic bath to the desired temperatures. A micro-controller-based potentiostat was utilised as a power supply to carry out the GaSe thin film electrodeposition. The optical properties of GaSe thin films were investigated by using the UV – Visible spectrophotometer available at the central research laboratory of the Federal University of Technology, Akure (FUTA) Nigeria.

3. RESULTS

Table 1 shows the summary of the optical parameters obtained for both as-deposited (AD) and X-ray irradiated (XRI) GaSe thin films at different deposition temperatures. The absorption spectrum of AD – and XRI – GaSe thin films deposited at two different growth temperatures (T_g) of 60 and 80^{o}C are shown in Figures 1 and 2 respectively. Figuress 3 and 4 reveal the optical graphs used for energy bandgap estimation of as-deposited and X-ray irradiated GaSe thin films respectively.

Table 1: Summary of optical parameters obtained for AD – and XRI – GaSe thin films grown at deposition temperatures of 60 and 80^{o}C.

Sample	Energy bandgap (E_g±0.02) (eV)	α (cm^{-1})	k (arb. unit)	n (arb. unit)
AD-GaSe_60^{o}C	2.80	3.72×10^4	0.12	1.86
AD-GaSe_80^{o}C	2.20	4.44×10^4	0.15	2.20
XRI-GaSe_60^{o}C	3.00	3.52×10^4	0.11	1.93
XRI-GaSe_80^{o}C	2.35	3.97×10^4	0.13	2.13

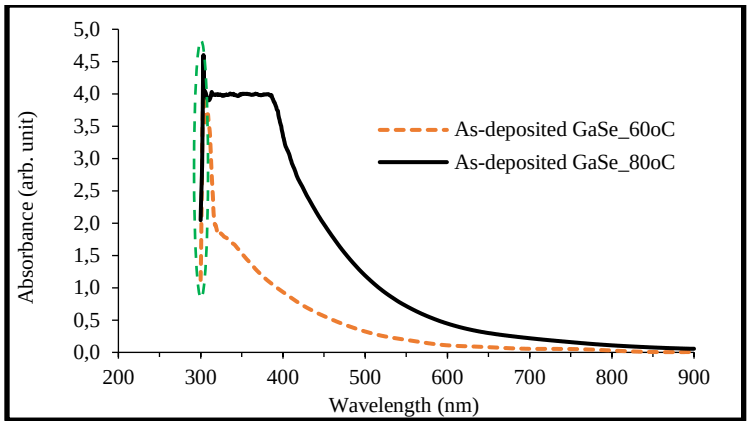

Figure 1: Optical absorbance graphs for as-deposited GaSe thin films. (Note that the dotted circled section represents the noise level at the ultraviolet region of the UV-visible spectrum)

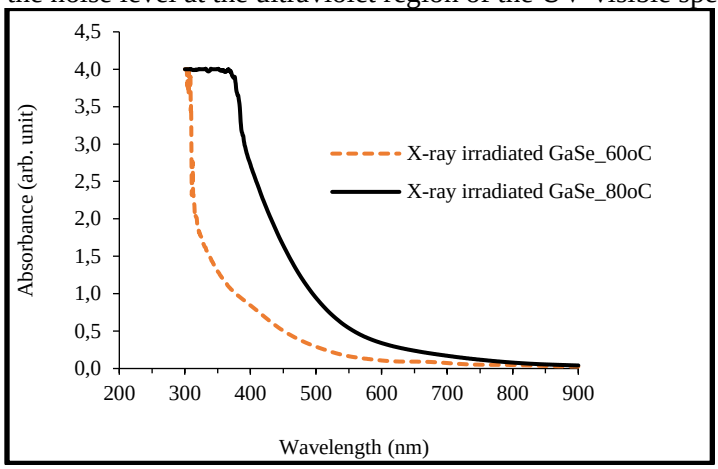

Figure 2: Optical absorbance graphs for X-ray irradiated GaSe thin films. (Note that the noise level at the ultraviolet region of the UV-visible spectrum has been eliminated as a result of the surface treatment of GaSe films via exposure to X-ray radiation).

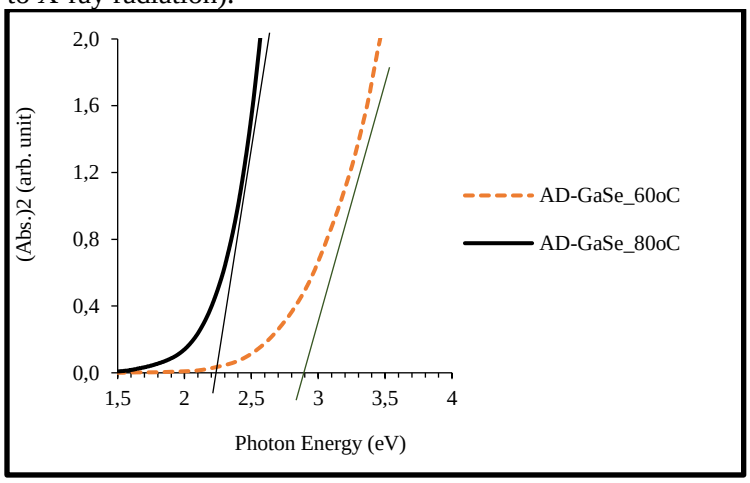

Figure 3: Energy bandgap estimation of as-deposited GaSe thin films grown at 60 and 80°C.

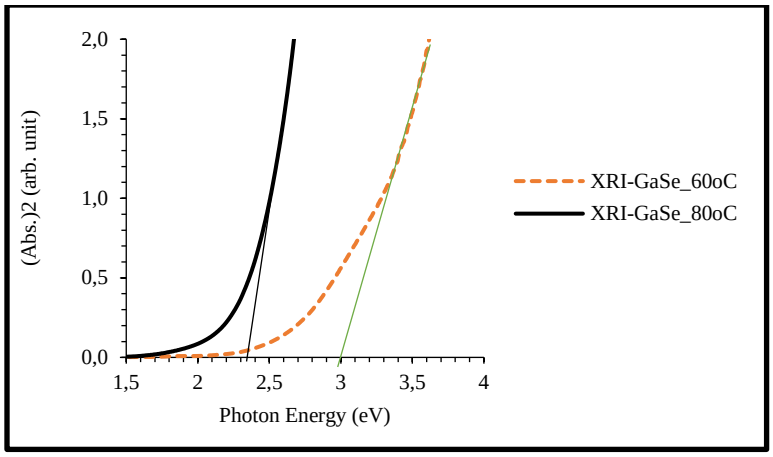

Figure 4: Energy bandgap estimation of X-ray irradiated GaSe thin films grown at 60 and 80°C.

4. Discussion of Results

The effects of X-ray irradiation on the optical properties of electrodeposited (ED) GaSe thin films grown at two deposition temperatures have been investigated and presented in this work. Even though the films were grown at the same duration of 15 minutes, a variation in the thin film thickness was observed. This variation was due to the fact that deposition current densities observed from the potentiostat were higher in films grown at 80°C than the ones grown at 60°C. The average deposition current densities are ~ 0.69 and 1.60 mAcm^{-2} for films grown at 60 and 80°C respectively. Using Faraday's law of electrolysis [17], the thicknesses of the thin films grown at 60 and 80°C were estimated to be ~271 and 630 nm respectively.

Before exposing the films to X-ray radiation, the experimental results revealed that the growth temperature influenced the optical parameters. The optical constants of the films namely extinction coefficients (k) and refractive index (n) are stated in Table 1. Table 1 also shows the values of the absorption coefficients (α) and energy bandgap (E_g). As revealed in Table 1, before and after exposure to X-ray; GaSe film grown at 80°C had higher absorption and extinction coefficients than the GaSe film deposited at 60°C. This, therefore, shows that GaSe films grown at 80°C have the ability to absorb more photons from the solar spectrum. The films with higher α also have higher k values; this result agrees with the theory since α and k are directly related according to Equation (1) [18].

$$k = \frac{\alpha\lambda}{4\pi} \qquad (1)$$

The lower value of n seen in GaSe films grown at 60°C before and after exposure to X-ray radiation shows that light can propagate more in the GaSe semiconductor materials grown at 60°C than 80°C. The faster propagation of light is due to the fact that GaSe films grown at 60°C have higher transmittance and lower absorbance than GaSe films grown at 80°C.

After the exposure of the films to X-ray radiation, the absorption coefficient of the films decreased from 3.72 × 10^4 cm^{-1} to 3.52 × 10^4 cm^{-1} for the film grown at 60°C. For the GaSe film grown at 80°C; α decreases from 4.44 ×10^4 cm^{-1} to 3.97 ×10^4 cm^{-1}. It should be noted that GaSe single crystals have been reported to have absorption coefficients as low as 1 cm^{-1} [3]. The reason for this low value is that it is an indirect bandgap semiconductor. Generally, indirect bandgap semiconductors have low values of α as seen in the case of Si mono crystal [19]. The higher absorption coefficient values of the order of 10^4 cm^{-1} seen in this work is remarkable and it reveals that the transition of electrons from the valence band to the conduction band is a direct type of transition thus showing that the ED-GaSe semiconductors possess the nature of a direct bandgap material. These results thus showed that preparatory techniques can influence the nature of the bandgap of semiconductors. While GaSe single crystals grown by the vertical Bridgman method [20] can be an indirect bandgap semiconductor, ED-GaSe layers can be a direct bandgap semiconductor as evident in this work.

Figures (1) and (2) show the absorption spectrum of AD – and XRI – GaSe thin films respectively. As seen in Figure 1, noise effects at the ultraviolet (UV) region of the wavelength range (shown with a dotted circle) were observed in the GaSe films that were not exposed to X-ray radiation. After exposure to X-ray radiation as illustrated in Figure 2,

elimination of the noise effects was observed. The presence of noise effects at the UV region reveals the possibility of defects in the semiconductor material. These results thus showed the possibility of treating surface defects in a material by exposing them to X-ray radiation.

The optical spectra used for energy bandgap estimation of AD – and XRI – GaSe thin films are illustrated in Figures (3) and (4) respectively. The graph was achieved by plotting A^2 (the square of absorbance) versus *hv* (photon energy). Extrapolation of the line of the best tangent of optical spectra to the axis of photon energy (at $A^2 = 0$) gives the energy bandgap of the material. The shape of the spectra showed that the GaSe binary compound semiconductors have a direct bandgap nature. As stated in Table 1 and illustrated in Figure 3, AD – GaSe thin films have bandgaps of 2.80 and 2.20 ± 0.02 eV for films grown at 60 and 80^{o}C respectively. Figure 4 shows that XRI – GaSe films possess energy bandgaps of 3.00 and 2.35 ± 0.02 eV for films grown at 60 and 80^{o}C respectively. In both cases of AD – and XRI – GaSe films, the energy gaps were found to decrease with increasing temperature. It was also observed that exposure of the films to X-ray radiation enhanced the energy bandgaps. For instance, the bandgap of GaSe films grown at 60^{o}C increased from 2.80 to 3.00 ± 0.02 eV. This increment shows that the exposed materials grown at 60^{o}C can serve as buffer layers in solar cell fabrication as a result of its increased bandgap. It has been established in the literature that a reduction in particle sizes can cause an enhancement in energy bandgap as a result of the quantum confinement effect [21, 22].

5. CONCLUSION

GaSe thin films have been successfully electrodeposited on fluorine-doped tin oxide conducting glass substrates. The effect of exposing the GaSe films grown at two different temperatures to X-ray was studied. The high absorption coefficient of the GaSe films before and after exposure to X-ray radiation coupled with the shape of the absorption spectra used for energy bandgap estimation revealed the direct bandgap nature of the electrodeposited GaSe semiconductor. The optical results obtained by plotting absorbance as a function of wavelength explain the possibility of treating surface defects in the GaSe materials via exposure of the films to X-ray radiation. The increase in the energy bandgap after exposure to X-ray radiation could be from the impact the X-ray has on particle sizes of the thin films.

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