



Modified Optical Properties of Arsenic Selenide Thin Film at Low Temperatures

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p-ISSN: 1608-9391
e-ISSN: 2664-2786

Article information

Received: 14/10/2022
Revised: 7/11/2022
Accepted: 14/11/2022

DOI: 10.33899/rjs.2023.178575

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ABSTRACT

With the simultaneous thermal spraying of glassy arsenic selenide (As_2Se_3), a significant influence of the introduced Indium (In) and Selenium (Se) on the films' structural and photovoltaic properties was established. The glassy As_2Se_3 and In or Se were deposited simultaneously at up to 60 nm/s on cooled substrates at different temperatures ranging from 70 to -50°C , layers with a thickness of 0.5 to 1 μm in a vacuum 10-3 Pa. Films produced on low-temperature substrates result in structural modifications that can be utilized for lithography and electrically active defects. The energy necessary for the As_2Se_3 annealing technique, according to the results, is equal to 0.57 eV of high-temperature energy. When Se is supplied at a temperature of -50°C , we saw that the photocurrent increases at low temperatures. The image is minimally affected by Se increases greater than 7%. The solubility time of the non-irradiated segment is 5 seconds, the rest layer dissolves in 12 seconds, and the thickness of the rest layer is above 75%.

Keywords: Thin film, X-ray fluorescence, photovoltaic

INTRODUCTION

There are a variety of techniques to manufacture charged defect states in CuGaSe₂ (CGS), which essentially change their electrical characteristics. Without external impurities, it is substitutional doping and chemical + modification (Iba and Lüth, 2009) (Nissa *et al.*, 2020) (Jafari *et al.*, 2018). To avoid self-compensation and create unusual electronic configurations of defects, it is desirable that chemical and thermal modification occur under non-equilibrium conditions. (Böer and Pohl, 2018). The potential for introducing impurity and intrinsic defect states into layers formed in a vacuum on a substrate that has been cooled below room temperature is present in glassy arsenic chalcogenides (Coleman, 2019). In this regard, the purpose of the research is to determine how the simultaneous deposition of As₂Se₃ with doping In and Se by this technique affects the photoelectric and structural characteristics of these layers (Todorov and Tsankov, 2011).

MATERIALS AND METHODOLOGY

The simultaneous deposition of glassy As₂Se₃ with In or Se at a rate of up to 60 nm/s on cooled substrates at various temperatures (T) ranging from 70 to -50 °C, produced layers with a thickness of 0.5 to 1 µm in a vacuum on the order of 10⁻³ Pa. Poor adherence to substrates, usually polished amorphous quartz, hindered experiments at lower temperatures. The acquired layers' composition was investigated using XRF analysis. XRF analysis was used to determine the composition of the layers that were produced. When utilized in fields up to 1000 V/cm, aquadag—a trading name for a water-based colloidal graphite coating commonly used in cathode ray tubes (CRTs)—planar contacts were ohmic. A Unipan 237 selective nano-voltmeter was used in a cryostat with a nitrogen atmosphere to measure the photoconductivity after it was modulated by light (14.8 Hz). The selective solubility of the layers was studied from the change in transmission upon irradiation of HeNe with a laser after or without irradiation (40 min) with a halogen lamp.

At different temperatures of the substrate up to -50°C, layers made only of As₂Se₃ were investigated. T_p (various temperatures, ranging from 70 to -50 °C) is thermally changed, comparable to the layers produced at T=25° in (Jafari *et al.*, 2018), where T_p is much less than the glass transition temperatures (T_g).

It is important to note that two activation energies are often indicated prior before the commencement of a typical decline in thermal activation at low temperatures. Studying the characteristics of selective solubility is important because a rise in charged defects could be linked to a loss of ordered structure.

EXPERIMENTAL RESULT

It was observed that there are no significant differences between As₂Se₃ deposited at low temperatures (-30, -50°C) and deposited at 20°C; the layer appears as a weak negative photo-resist that transforms into a positive one after being annealed to T=T_g; following thermal polymerization, light has a photo-destructive effect.

Experiments were conducted with the introduction of 1 - 5 wt.% of natural T_p to examine the effect. It was discovered in (Jafari *et al.*, 2018), that the neutral states grow with the addition of in up to 0.1 eV above the transport states under equilibrium conditions, T_p = T_g.

For a sample collected at T=-50 °C, Fig. (1), Curve 1, illustrates the relationship between photo-conductivity and temperature. The observed dependence will follow the typical theoretically predicted curve if we assume, in accordance with (Darwish and Hamdalla, 2021), that the electrons remain trapped in the C₃⁺ states serving as recombination centers.

The temperature dependence of the photo-current at T_p = -10 °C causes a rise in photo-conductivity at low temperatures (curve 4), which could be caused by the emergence of a defect charged in+ state following compensation for the C₃⁺ states, which serve as a shallow recombination center. For a-CdS (Morigaki and Oghihara, 2006) and a-Si (Nicoara *et al.*, 2022), the thermal quench

of slow recombination sites is related to a similar pattern of photo-conductivity. For a-CdS (Morigaki and Ogihara, 2006) and a-Si (Nicoara *et al.*, 2022) thermal quench of slow recombination sites is related to a similar pattern of photo-conductivity

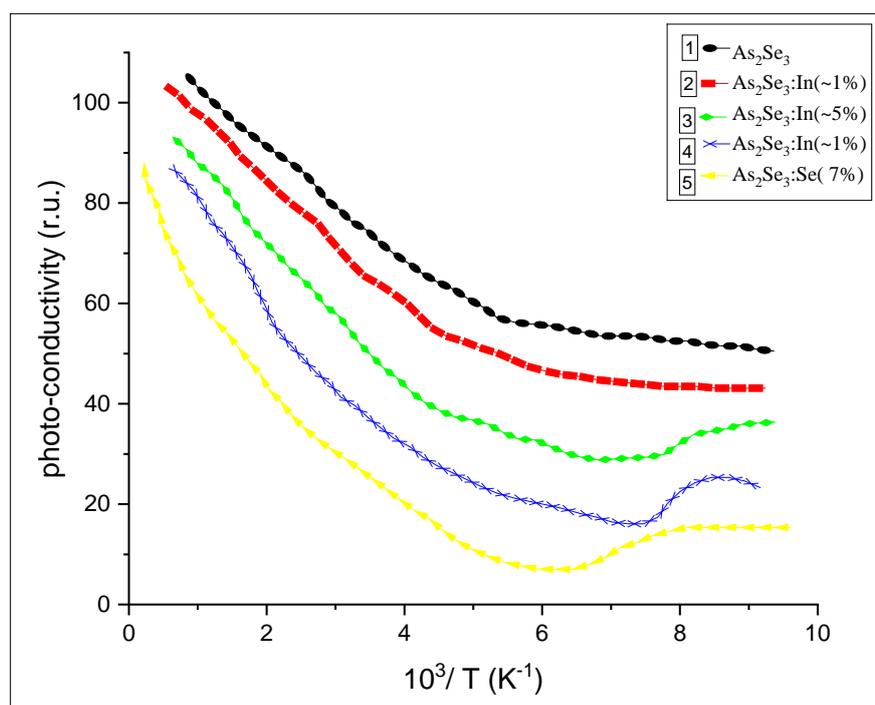


Fig. 1: The photo-current of As_2Se_3 layers changed at low temperatures ($T = -50^\circ\text{C}$, curves 1, 2, 3 and 5) and ($T = -10^\circ\text{C}$, curve 4) as a function of temperature.

It is observed that even with the inclusion of up to 5% In, this characteristic is less prominent in the films produced at $T_p = -50^\circ\text{C}$ (curves. 2, 3). In the low-temperature modification of the C_3^+ state, it is possibly more stimulating to compensate for a significant increase in the concentration of intrinsic defects. The structures and their photo-induced alterations are still strongly affected by In. The selection solubility was observed to improve with a rise in the amount of supplied In. It was revealed by the discovery of a new organic solvent, P_4 (dimethylamine), that produces excellent performance on a layer within 5 wt.% the relation of the dissolution times of the irradiated and non-irradiated sections $\gamma=12$, the rest layer thickness β is above 75% at Fig. (2), and the non-irradiated section of the solubility time is $\alpha = 5$ s. (Table 1):

Table 1: Solubility time of the non-irradiated part

In (wt.%)	Solvent	α (s)	β / (%)	$\gamma = \alpha' / \alpha$
5	P_1	22	14	1.2
5	P_2	30	10	1.7
5	P_4	5	77	12
1	P_4	74	49	3.6
0	P_4	153	9	2.1

The irradiated parts dissolve slower in a solution of potassium dichromate than the non-irradiated areas do, while the opposite is true in a solution of sodium alkali.

To explore the effect of annealing, a 10-minute heating at various temperatures was performed, and two activation energies of the solubility time were measured after annealing the samples with 5 wt.% In. The energy associated in (Nissa *et al.*, 2020) with the As_2Se_3 annealing

process is the same as the high-temperature energy of 0.57 eV as shown in Fig. (3). As with layers without In, the resist is positive after annealing at temperatures over 180 °C.

The photo-current increases at low temperatures when Se is added when the temperature is -50 °C as shown in figure 1 curve 5. A rise exceeding 7% Se doesn't quite considerably affect the image. It is tough to describe the rise in photo-current except if we suppose that it is related to the creation of tight pairs (inaccurate bonds) with rising Se, which do not repair the Fermi level and open the door to the discovery of other charged states of defects, such as those connected with over coordinated As. Increases in Se have no positive effects on specific solubility, and at 20 wt.%, the solubility nearly completely vanishes.

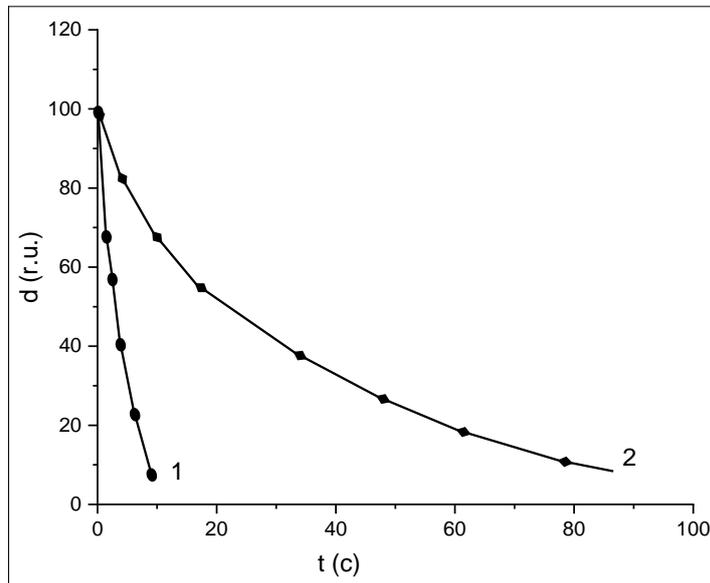


Fig. 2: Solubility kinetics of non-irradiated-1 and irradiated-2 layers of As_2Se_3 : In (~5 wt%) in P_4 solution.

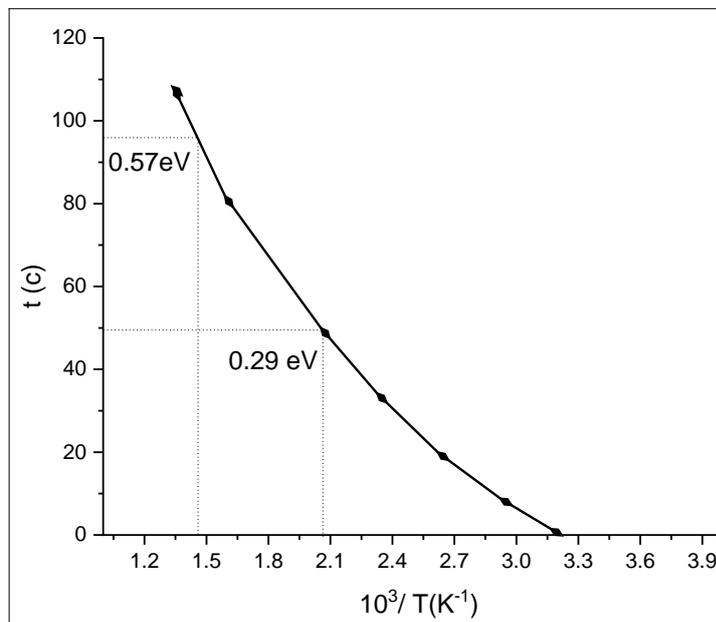


Fig. 3: The annealing temperature affects the solubility time of non-irradiated As_2Se_3 : (In) (5 wt%) layers.

CONCLUSION

The doping In and Se had a significant effect on the films' structural and photovoltaic properties when As_2Se_3 was deposited to simultaneous spray pyrolysis. Glassy As_2Se_3 was simultaneously deposited in a vacuum on cooled substrates and doped by In or Se in layers that varied in limiting thickness. Lithography can make use of the structural alterations and electrically active defects that result from films created on low-temperature substrates. According to the results, the annealing of As_2Se_3 requires 0.57 eV of high-temperature energy.

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الخصائص البصرية المعدلة للأغشية الرقيقة للزرنيخ سيلينيد عند درجات حرارة منخفضة

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الملخص

مع الرش الحراري المتزامن لسيلينيد الزرنيخ الزجاجي (As_2Se_3)، تم إنشاء تأثير كبير للإنديوم (In) والسيلينيوم (Se) على الخصائص الهيكلية والفولطية الضوئية للأغشية. تم ترسيب As_2Se_3 الزجاجي و In أو Se في وقت واحد عند 60 نانومتر/ ثانية على ركائز مبردة عند درجات حرارة مختلفة تتراوح من 70 إلى -50 درجة مئوية، طبقات بسماك 0.5 إلى 1 متر في الفراغ عند 3-10 باسكال. ينتج عن الأغشية الرقيقة التي يتم إنتاجها على ركائز منخفضة الحرارة تعديلات هيكلية يمكن استخدامها في الطباعة الحجرية والعيوب النشطة كهربائياً. الطاقة اللازمة لتقنية التلدين As_2Se_3 ، وفقاً للنتيجة، تساوي 0.57 eV من طاقة درجة الحرارة العالية. عندما يتم توفير Se عند درجة حرارة -50 درجة مئوية، رأينا أن التيار الضوئي يزيد في درجات الحرارة المنخفضة. تتأثر الصورة بالحد الأدنى من Se تزداد بنسبة تزيد عن 7%. وقت الذوبان للجزء غير المشع هو 5 ثوان، والطبقة المتبقية تذوب في 12 ثانية، وسماكة الطبقة الباقية أعلى من 75%.

الكلمات الدالة: غشاء رقيق، مضان للأشعة السينية، أنظمة الطاقة الفولتوضوئية.