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Enhanced photoresponse of PVP:GaSe nanocomposite thin film based photodetectors

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Abstract

Two-dimensional materials have become the focus of attention of researchers in recent years. The demand for two-dimensional materials is increasing day by day, especially with the inadequacy of graphene in optical applications. In this context, the optical and electrical characteristics of the PVP:GaSe thin film nanocomposites were investigated. The surface morphologies of the samples were characterized by SEM, the thin film thicknesses and refractive index parameters were measured by the Ellipsometer method, the structural characteristics were obtained by XRD, and Raman and PL spectroscopy was used to determine the optical characteristics. Critical parameters of Au/PVP:GaSe/n-Si photodetector were calculated under various illumination intensities. It is observed that photodetector with PVP:%5GaSe thin film has the best performance results. According to the experimental results, its responsivity, external quantum efficiency, and detectivity values are 0.485 A W⁻¹, %86, and 1.14 × 10⁷ cm Hz¹/² W⁻¹ respectively.

Keywords: 2D materials, metal chalcogenides, nanocomposite thin films, PVP:GaSe, photodetector

(Some figures may appear in colour only in the online journal)

Introduction

Since silicon technology does not challenge Moore’s law, increasing demand for performance and miniaturization in the microelectronic industry, discovering a new class of materials, and investigating their applications have become vital. Two-dimensional (2D) materials are greatly emerged interest due to their extraordinary physical and electronic properties after the discovery of graphene [1]. The success of graphene has made a revolution in view of researchers’ methodological approach owing to quantum confinement in one direction [2]. The early studies describe the performance imperfections of graphene-based devices, and the recent studies discuss its deficiency [3–5]. The researchers are alternatively focused on graphene beyond 2D materials especially having a sharp bandgap, which is very limited for graphene. The graphene beyond 2D materials is now an extended family, and the metal chalcogenides are the most willing member of this family [6, 7]. They have been widely used in many different areas, such as energy storage, catalysis, semiconductor, and high-performance protective composites [8].

The researchers have been reported diverse of study related to optoelectronic devices based on transition metal dichalcogenides (TMDCs) such as MoS₂, MoSe₂, WS₂, WSe₂, and metal chalcogenides (MCs) like GaSe, InSe, etc [9]. Despite the severe potential of GaSe and InSe materials in device applications, the device applications of these materials in comparison to TMDCs have not been adequately investigated in the literature [7]. Although these materials have oxidation problems, they have enormous potential for device applications [7, 10]. Accordingly, studies on encapsulation processes have also been reported in the literature [7]. Furthermore,
even though two-dimensional semiconductors are used to increase conductivity in the transistor, photodetector, and diode structures, there are very few structures in the literature in which two-dimensional semiconductors form composites with suitable polymers [8, 11].

The performances of monolayer or few-layer metal chalcogenides are strongly dependent on the production techniques including LPE, vdW epitaxy, PVD, PLD, CVD, and exfoliation [6, 9]. Among these techniques, mechanical or chemical exfoliation is preferred by researchers as it is an easy, inexpensive, and a reliable technique. GaSe is one of the materials which is extensively investigated among the layered III–VI semiconductors family because of the nonlinear optical properties it exhibits [12]. Moreover, Mounet et al classified 2D materials according to their van der Waals bond energies and interlayer distances [13]. They also noted that GaSe is in the group of easily exfoliated materials [13]. Another study emphasizes that GaSe can be exfoliated more easily in alcohols like ethanol [14]. Since PVP dissolves well in polar alcohols, ethanol was preferred to prepare PVP:GaSe nanocomposite thin films. This process will lead us to obtain nanocomposites embedded in the polymer matrix, which are expressed in the literature to have a high potential application for optoelectronic devices, gas sensors, etc [7, 15–19].

Due to its pseudodirect bandgap and thickness-dependent optoelectronic features, GaSe has become one of the promising candidate for the implementation of the photodetectors with fast response and high sensitivity [20]. As a result of its high resistivity, GaSe can be practicable for the photodetection applications owing to its low dark current. Also, the photocurrent measurement carried out by Lei et al shows that the indirect bandgap of monolayer GaSe is 3.3 eV, which makes it promising for the light detection at ultraviolet wavelengths [21]. Along with, GaSe combines the advantages of 2D structures for detection within the visible spectrum, with an easier route to integration with convensional silicon integrated circuits [22]. Moreover, the properties such as the absence of dangling bonds in GaSe and its thermal stability up to 600 °C make it draw attention in nanophotonic device applications [18].

In the presented study, PVP:GaSe thin films have been produced for enhanced photodetector applications. It was aimed to produce GaSe-based thin film nanocomposite due to its strong optical properties and promising potentials. Produced PVP:GaSe thin films were characterized by SEM, Ellipsometer, x-ray diffraction, Raman, and PL spectroscopy. We produced a novel Au/PVP:GaSe/Si photodetector and demonstrated the enhanced photoresponsivity with the increasing amount of GaSe in the composition. This research will pave the way for novel device designs and electronic applications for new nanocomposites decorated with different 2D materials.

**Experimental details**

Firstly, 20 grams of the gallium and selenium was sealed in a quartz ampoule, and gallium selenide (GaSe) was synthesized over the melting point with the help of a tube furnace. The GaSe was crystallized in the Bridgeman system with two independent temperature zones set to 980 °C and 850 °C. In this way, we successfully produced layered GaSe single crystals, which are ready for exfoliation. 2D structures of GaSe are shown in figure 1, taken from Materials Cloud Database [23].

After crystallization, the single crystal GaSe was mechanically exfoliated with the help of 3 M tape. The peeled GaSe pieces were weighed as 10 mg and ultrasonically sonicated for 2 h in glass tubes containing 100 ml ethanol to obtain few-layer GaSe flakes. After the GaSe flakes were formed in ethanol, three different rates of Polyvinylpyrrolidone (PVP) polymer (bought from Sigma Aldrich) were placed in and homogenized in glass tubes filled with 20 ml ethanol:GaSe solution. Each glass tube was mixed with dissolved PVP-ethanol and ethanol-GaSe solution. The concentrations of GaSe in PVP:GaSe solutions are set to be as 1%, 3%, and 5% in each glass tube. One tube was kept as the reference pure PVP solution. All tubes were mixed for 1 h with a magnetic stirrer operating at 600 rpm at 50 °C. Before coating, the n-type Si wafers were cleaned with acetone, isopropanol, and ethyl alcohol, respectively. Before thin-film coating, 100 nm of gold was evaporated on the backside of the Si wafer, and it annealed at 450 °C for a minute. Following, an equal volume of the solutions from each tube was dropped on the top surface of the n-type Si substrate. PVP:GaSe nanocomposite thin film was coated with a spincoater at 500 rpm for 60 s. The coated samples were annealed to evaporate the alcohol at 50 °C. The schematic description
of PVP:GaSe production was demonstrated in figures 2(a)–(h). As a final step, in order to fabricate the Schottky diode photodetector, a gold film with a thickness of 100 nm was coated on the surface of PVP:GaSe/Si/Au substrate by the evaporation method to obtain the top contacts.

The deposited thin film thicknesses were measured as about 300 nm with the help of a J. A. Wollam V-Vase Spectroscopic Ellipsometer. The surface images of thin films were captured by a Nanomagnetics Inst. AFM and a JEOL JEM-1400 SEM systems. The x-ray diffraction analysis of
PVP:GaSe was carried out with a Pan-Analytical X’Pert XRD system (Cu K-alpha/wavelength 1.540598 Å). WITEC Alpha 300R system is used for the Raman and Photoluminescence analysis of the samples. The I–V characteristics of the produced device are measured with the help of a FYTRONIX FY-5000 Solar simulator and a KEITHLEY 2400 Source meter.

Results and discussion

Before composing with the polymer, the AFM images of the exfoliated GaSe nano flakes on Si wafer are given in figure 3. The GaSe exfoliation process is carried out with the same procedures (please see the step in figure 2(d)) and coated on the Si wafer for the AFM measurement. The crosssection of the flakes in 2D images shows the thickness of the GaSe nano flakes. In figure 3(a), the measured thickness of the GaSe flakes corresponds to 8 layers (8 Å), which is almost 40 nm. Also, in figure 3(b), the layer number of the measured thickness of the corresponding flake is approximately 71, where the thickness is measured about 35 nm. Here, it is clearly observed that sonication of bulk GaSe yields to obtain GaSe nano flakes.

The surface morphology of the three samples was examined by SEM system. The SEM images show the distribution of the GaSe flakes encapsulated by PVP thin film on the surface of the Si substrate. According to the SEM results given in figure 4, it is seen that as the GaSe concentration in the PVP:GaSe composite thick film increases, the GaSe flakes appear denser on the Si surface. GaSe flakes with various dimensions on the substrate’s surface can be easily observed for all three samples. In the figure 4, the higher magnifications of the GaSe flakes are also shown, at 15 K, and the nano flakes are taken into circles with the dashed yellow lines for a better illustration.

The XRD results of the PVP thin film, PVP:GaSe nanocomposite thin film and bulk GaSe are shown in figure 5(a). According to the results, it is seen that the XRD peak values of grown GaSe bulk sample match with the peak values in the JCPDS card number of 37-931: (002), (004), (006), (008), (020), and (0010). These peaks are not observed on the purely PVP coated sample. As the XRD results of GaSe flakes at different percentages in the nanocomposite thin films are analyzed, the XRD peaks of the GaSe start to appear. Moreover, it is observed that the intensity values of the XRD peaks are increasing with the increase in the GaSe concentration in the PVP:GaSe composite. The FWHM values are calculated with the help of the XRD peaks at (002) direction given in the graph figure 5(a). The results are obtained as 0.047, 0.061, 0.063, 0.071 for the bulk GaSe, PVP:5%GaSe, PVP:3%GaSe, and PVP:1%GaSe, respectively. It is observed that the FWHM values decrease as the GaSe percentage concentration increases. The Debye–Scherer equation is used for grain size calculations where λ is the x-ray wavelength, θ is the FWHM value, and θ is the Bragg diffraction angle [25]

\[ d(\text{nm}) = \frac{0.94 \lambda}{B \cos \theta} \]

The grain size values according to the percentage of the GaSe concentration in the PVP solution are shown in figure 5(b). It is observed that as the GaSe concentration in the PVP solution increases, the grain sizes of the flakes increase.

In figure 6(a), the change of the refractive index regarding to the wavelength is graphically given with respect to the alterations of the GaSe concentration in PVP:GaSe nanocomposite thin films. From the graph, it is seen that as the wavelength increases, the refractive index of each sample exponentially decreases. Also, in the table given in figure 6(b), the change of the refractive index is numerically presented. According to the numerical results, as the wavelength is kept constant, it is observed that when the GaSe concentration in the PVP:GaSe composite increases, the refractive index of the corresponding nanocomposite thin film increases.

As seen in figure 7(a), the bulk GaSe flakes obtained by the exfoliation method, and used in the PVP solution, give the Raman shift at 283.96 cm⁻¹ and 343.04 cm⁻¹. Comparing with the Raman peaks in the literature, it is seen that there are some differences, which can be explained by the rapid oxidation of few-layer GaSe films. In the study of Chan et al it is seen that the GaSe nano-flakes give distinct Raman peaks than the bulk GaSe [24]. However, the peak at the ~284 cm⁻¹ indicates the oxidation of thin GaSe flakes and matches the SeO₂ peak given in the literature [26]. Moreover, when GaSe flakes in PVP:GaSe nanocomposite thin film are examined, it is observed that some new Raman peaks, different than the bulk GaSe, are appeared at the peaks of 186.44 cm⁻¹, 292.42 cm⁻¹, 318.95 cm⁻¹, 361.13 cm⁻¹. The peak around ~292 cm⁻¹ also matches the Raman peak of the Ga₂Se₃ given in the literature [10]. Additionally, PL results of the bulk GaSe is in compliance with the literature results [27, 28]. A dominated PL peak appears at 2.295 eV and a small peak at 2.287 eV for the bulk GaSe. Also, considering PL peaks, when PVP:GaSe nanocomposite thin films are formed, some new PL peaks start to appear at the points of 2.285 eV, 2.294 eV, 2.3 eV, and 2.31 eV. The measured PL results are given in figure 7(b) for both the bulk GaSe and PVP:GaSe composition. After composing GaSe, we obtained a remarkable PL signal from PVP which does not have any optoelectronic properties in its pure form. This PL result leads us to check the photodetectors of the PVP:GaSe nanocomposite thin films, including GaSe concentrations at different percentages. As it is seen from the insets in the figures 7(a) and (b), there is no PL and Raman spectra coming from pure PVP.

After completing optical characterizations of the samples, the electrical characterization is considered. The electrical characterization is made to observe the photo-responsivity of the samples with the help of the electrical measurement system. The illustration of the fabricated photodetector structure is given in figure 8. The reverse bias current–voltage characteristics of the fabricated devices are given in figure 9. As
Figure 4. The SEM images of (a) PVP:1%GaSe, (b) PVP:3%GaSe, (c) PVP:5%GaSe thin film surfaces for various magnifications.

Figure 5. The graph of the (a) XRD patterns of all samples and (b) grain size values.
Figure 6. (a) Refractive index of samples. (c) Refractive index values for some wavelength values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>400</th>
<th>800</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP</td>
<td>1.5676</td>
<td>1.5347</td>
<td>1.5286</td>
</tr>
<tr>
<td>PVP:1%GaSe</td>
<td>1.5767</td>
<td>1.5468</td>
<td>1.5413</td>
</tr>
<tr>
<td>PVP:3%GaSe</td>
<td>1.601</td>
<td>1.5664</td>
<td>1.56</td>
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<tr>
<td>PVP:5%GaSe</td>
<td>1.632</td>
<td>1.5934</td>
<td>1.5862</td>
</tr>
</tbody>
</table>

Figure 7. The graph of the (a) Raman spectrum and (b) PL spectrum of both the bulk GaSe and PVP:GaSe samples.

Figure 8. (a) The schematic illustration of fabricated photodiode, (b) the side and top view illustrations.
can be seen in figure 9., %1 GaSe composing with PVP thin film does not significantly affect the performance of the photodetector’s I–V characteristics. When composition rate increases the leakage current of the photodetectors tends to decrease. The values of leakage current are measured at −3 V as $1.07 \times 10^{-7}$ A and $8.26 \times 10^{-8}$ A for photodetectors including PVP:3%GaSe and PVP:5%GaSe thin film nanocomposites, respectively. Forward and reverse bias characteristics of photodetectors can be seen in inset of the figure 9. As the composition of GaSe increases, the series resistance of the device decreases, resulting in lower threshold voltage and higher current performance.

Photo-responsivity characteristics were analyzed by encapsulating layered GaSe flakes in PVP, whose optoelectronic properties are quite strong but less studied due to production and oxidation-related problems [18–23]. Thanks to the method we used, photodetectors with enhanced light absorption performance were demonstrated by obtaining low-dimensional 2D GaSe structures from the bulk structure. The electrical measurement results (current versus time) are graphically given for each corresponding sample in figures 10(a)–(d) under various illumination intensities. According to electrical measurement results, it is observed that when the same amount of solar power is applied to each sample, as the concentration of the GaSe percentages in the PVP:GaSe nanocomposite thin film increases, the current flowing through the Au-metal contacts taken on the sample starts to raise. The lowest current flow is obtained in pure PVP, $\sim 8.7 \times 10^{-5}$ A at 100 mW, and the highest current flow is obtained in the PVP:5%GaSe composition, $3.85 \times 10^{-4}$ A at 100 mW. The rising times are also calculated for each sample and obtained as 0.85 s, 0.83 s, 0.79 s, and 0.75 s for pure PVP, PVP:1%GaSe, PVP:3%GaSe, PVP:5%GaSe, respectively. Also, the falling times are calculated as 0.91 s, 0.86 s, 0.84 s, 0.82 s for each corresponding sample, respectively. Obtained results showed that both the rising and falling times also decrease in the Au/PVP:GaSe/n-Si photodetector when the concentration of the GaSe in PVP increases. These results lead us to conclude that the PVP:5%GaSe composition shows the highest performance at the photo-responsivity measurements.

The responsivity, quantum efficiency, and detectivity results of the photodetectors are calculated according to various GaSe percentages into PVP:GaSe nanocomposites. These crucial parameters help us to evaluate the performance of suggested photodetector structures. The equation for the calculation of the responsivity is given by [29]

$$\text{Responsivity} = \frac{I_{ph}}{P},$$

where $I_{ph}$ is photocurrent and $P$ is the light intensity. The external quantum efficiency (EQE) is obtained as follows,

$$\text{EQE} (%) = \frac{I_{ph} h c}{\lambda q 100},$$

where $h$ is Planck constant, $c$ is the velocity of light, $\lambda$ is the wavelength of the light, which is constant and taken as 700 nm,
and $q$ is the electron charge. The equations (3) and (4) are used to calculate detectivity values of photodetectors as follows [29].

$$\text{Detectivity} = \frac{\sqrt{A}}{\text{NEP}}$$  \hspace{1cm} (3)

$$\text{NEP} = \frac{1}{R} \sqrt{2q(I_d + I_{ph})},$$  \hspace{1cm} (4)

where $A$ is the photodetector area, $\text{NEP}$ is noise equivalent power, and $R$ is the responsivity of the photodetector. The calculation results are given in table 1.

It is observed that the responsivity, quantum efficiency, and detectivity values increase as the GaSe concentration in PVP:GaSe nanocomposite is increased. PVP:5%GaSe composition gives the highest performance results with the values of 0.485 A W$^{-1}$, 86, $1.14 \times 10^7$ cm Hz$^{1/2}$ W$^{-1}$ for the responsivity, quantum efficiency, and detectivity, respectively. The results are promising for novel nanocomposite thin film photodetectors when we compared atomically thin GaSe photodetectors [17–19, 30].

In the present study, there is no drastically change in the resistivity and mobility values of the film by decorating the GaSe flakes into the polymer. As it is graphically shown in figure 11, it can be seen that the quantum efficiency and photo-responsivity of the fabricated photodetector increases with increasing GaSe concentration in the film. When the light performance of the photodetectors produced from the obtained films is examined, it is seen that the amount of 5% GaSe in the PVP is a saturation point for photo-responsivity and quantum efficiency. Therefore, the processes are restricted with the 5% concentration of GaSe in PVP:GaSe composite. It is expected that slightly increase in photo-

<table>
<thead>
<tr>
<th>Samples</th>
<th>Responsivity (A W$^{-1}$)</th>
<th>Quantum efficiency (%)</th>
<th>Detectivity (cm Hz$^{1/2}$ W$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PVP</td>
<td>0.011</td>
<td>1.97</td>
<td>$7.89 \times 10^5$</td>
</tr>
<tr>
<td>PVP:1%GaSe</td>
<td>0.013</td>
<td>2.35</td>
<td>$9.40 \times 10^5$</td>
</tr>
<tr>
<td>PVP:3%GaSe</td>
<td>0.439</td>
<td>77.8</td>
<td>$9.87 \times 10^6$</td>
</tr>
<tr>
<td>PVP:5%GaSe</td>
<td>0.485</td>
<td>86</td>
<td>$1.14 \times 10^7$</td>
</tr>
</tbody>
</table>

Table 1. The numerical results of the electrical characteristics of the samples.

Figure 10. The short circuit current versus time graph of the (a) pure PVP, (b) PVP:1%GaSe, (c) PVP:3%GaSe, and (d) PVP:5%GaSe.
responsivity and quantum efficiency for devices containing the higher amount of GaSe concentration than 5% in the film. Another reason for achieving saturation at lower concentrations may be the presence of low-dimensional GaSe flakes in the structure.

Conclusion

In conclusion, we systematically investigated the morphological, structural, and optical properties of the PVP:GaSe nanocomposite thin films with the help of SEM, XRD, Ellipsometer, Raman, and PL techniques. By composing GaSe flakes into PVP solution, we successfully coated large area PVP:GaSe nanocomposite thin film. We fabricated nanocomposite thin film based photodetectors with different GaSe compositions. Here, it was observed that as the amount of GaSe in the nanocomposite film increases, the photocurrent increases. Rising and falling times decline with an increase of GaSe quantity in the nanocomposite. The photo-responsivity of the detector having PVP:5% GaSe thin film also raises approximately 43 times higher than the photodetector having pure PVP thin-film. The external quantum efficiency reaches 86%, and the detectivity gives the highest value of $1.14 \times 10^7$ cm Hz$^{1/2}$ W$^{-1}$ when the GaSe is 5% in the PVP:GaSe nanocomposite.

The solution based processing of the GaSe and other 2D materials can provide a low-cost production of the inks which allow the design and realization of the printed optoelectronic devices, along with enabling this technology to move from the laboratory to the industry in the future. This study will open the way for producing new two-dimensional metal chalcogenide-based nanocomposites for novel optoelectronic device applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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