Preparation and Study of Heterojunctions Based on Chalcogenide Glassy Semiconductors

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Four types of heterojunctions were prepared: $SnO_2-As_2(Se_{0.9}Te_{0.1})_3$, $SnO_2-(As_{0.67}Sb_{0.33})_2Se_3$, n-GaAs-As₂Se₃ and n-GaAs-As₂S₃. For all samples I-V characteristics and photosensitivity spectra were obtained. These heterostructures can be used for manufacturing rectifying devices and photoreceivers

Key words: Heterostructure; Chalcogenide Glassy Semiconductor; Spectra of Photosensitivity.

1. Introduction

Most semiconductor devices are based on crystalline semiconductors because of their perfect technology of manufacturing. Nevertheless heterostructures based on amorphous materials including chalcogenide glassy semiconductors have been the focus of active research for some time now [1,2]. They are of interest because their properties can be varied by their composition [3,4].

2. Experimental

Four types of heterojunctions, SnO_2 - $As_2(Se_{0.9}$ - $Te_{0.1})_3$, SnO_2 - $(As_{0.67}Sb_{0.33})_2Se_3$, n-GaAs- As_2Se_3 and n-GaAs- As_2S_3 , were prepared for the present study.

Heterojunctions based on SnO₂ were prepared on a glassy substrate by vacuum evaporation. The order of layer deposition was as follows: SnO2, thin film of chalcogenide glassy semiconductor, aluminium. The thickness d of the chalcogenide films was between 1 and 10 µm. The samples were illuminated through the SnO₂ layer, being transparent in the investigated spectral range. This layer was used as one electrode with the aluminium layer as the other one. For the preparation of n-GaAs-As₂Se₃ and n-GaAs-As₂S₃ heterojunctions Al-i-GaAs-n-GaAs-chalcogenide glassy semiconductor structures were made. Heterojunctions were prepared on the base of monocrystalline compensated GaAs, on the surface on which an epitaxial layer of n-type conductivity was grown. The carrier concentration in this epitaxial layer was about

 $1\cdot 10^{22}~\text{m}^{-3}$. The layer of chalcogenide semiconductor was deposited by vacuum evaporation on the epitaxial layer of GaAs. The thickness of the chalcogenide films was between 0.3 and 5 μ m. A semitransparent aluminium layer and a thick aluminium layer were deposited on the chalcogenide film by vacuum evaporation. Before deposition of the thick layer, the central part of the sample was covered by a mask. Under the mask the semitransparent aluminium layer was used as a "window" through which the heterostructure was illuminated. To make another contact, an aluminium layer was deposited on the GaAs backside of the sample.

The measurements were carried out using a special installation constructed in our laboratory. The bandwidth $\Delta\lambda$ can be varied from 0.002 to 0.008 μm in the range 0.4–1.2 μm . The minimum measured current was 10^{-12} A. For all samples I-V characteristics were obtained. These characteristics were measured under illumination of the sample in the range of maximum sensitivity and without illumination. The photosensitivity spectra were obtained at forward and reverse bias.

3. Results and Discussion

3.1. Heterojunctions Based on SnO₂

The I-V characteristics for all types of heterojunction are asymmetrical and nonlinear. A forward current flows when the SnO_2 electrode is positive with respect to the Al electrode. In the I-V characteristics

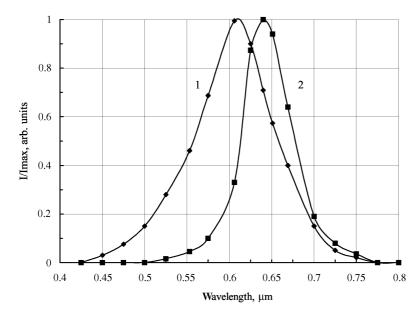


Fig. 1. Photosensitivity spectra of the SnO_2 - $(As_{0.67}Sb_{0.33})_2Se_3$ heterojunction at reverse bias for two chalcogenide film thicknesses: 1, $d=1~\mu m$; 2, $d=10~\mu m$.

obtained with and without illumination the forward current is higher than the reverse current. This difference can be explained by the following assumption. A hole barrier is formed in the contact region between metal and semiconductor. When the voltage sign is positive at SnO₂ the band bending is decreased in the chalcogenide film near the contact region between Al and the chalcogenide glassy semiconductor, and more holes can reach the aluminium. At reverse bias the barrier height for holes emitted from aluminium decreases when the voltage increases, and the current increases to a lesser extent since there is one more hole barrier in the contact region between chalcogenide glassy semiconductor and SnO₂. In the latter case the current flowing through the structure depends on the electronhole recombination velocity at the interface between the chalcogenide semiconductor and SnO₂. Therefore there is a low reverse current compared to a high current at forward bias.

The photosensitivity spectra of heterojunctions based on $As_2(Se_{0.9}Te_{0.1})_3$ and on $(As_{0.67}Sb_{0.33})_2Se_3$ at reverse bias were obtained for different thicknesses of the chalcogenide film. When the film thickness increases, the sensitive region shifts towards the long-wavelength region of the spectrum, and the width of the sensitivity curve decreases. The wavelength corresponding to the maximum of photosensitivity moves when the film width varies between $d=1~\mu m$ and $d=10~\mu m$. Figure 1 shows the photosensitivity spectra of the SnO_2 - $(As_{0.67}Sb_{0.33})_2Se_3$ heterojunction at

reverse bias for different chalcogenide film thicknesses.

At forward bias, the maximum of the sensitivity curve shifts to the short-wavelengths with respect to the maximum observed at reverse bias. As already noted, there is a hole barrier at the interface between Al and the chalcogenide film. The hole barrier height according to photoemission measurements [5] for the present compositions is about 0.6 eV. The shift of the maximum sensitivity curve at forward bias is an additional corroboration of the existence of this barrier. The more photon energy of absorbed light, the less depth of photon penetration and the closer to the barrier the main fraction of the photons is absorbed. Therefore it is necessary to expend more energy on the generation of holes. It leads to an up shift of the maximum.

3.2. Heterojunctions Based on GaAs

The I-V characteristics of these heterojunctions are also asymmetrical and nonlinear. In this case the semitransparent aluminium film deposited on a chalcogenide layer is a collector. A forward current flows when the collector is biased negatively with respect to a GaAs electrode.

The photosensitivity spectra were measured for samples with chalcogenide film thicknesses of 0.3 μ m, 1 μ m and 5 μ m. It was possible to change the range of the maximum sensitivity by variation of the film thickness.

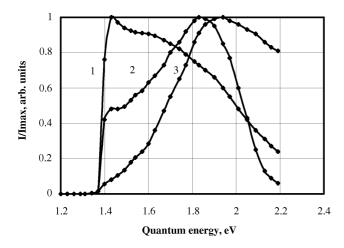


Fig. 2. Photosensitivity spectra of the GaAs-As₂Se₃ heterojunction at forward bias for three chalcogenide film thicknesses: 1, $d=0.3~\mu m$; 2, $d=1~\mu m$; 3, $d=5~\mu m$.

The photosensitivity spectra of heterojunctions at forward bias (1 V) for different thicknesses of chalcogenide As₂Se₃ films are shown in Figure 2. The curves of photosensitivity are standardize on the magnitude of peak response. For heterojunctions with the chalcogenide film thickness 0.3 µm only one peak is observable at hv = 1.43 eV. The peak is concerned with photoconductivity of GaAs. The influence of the semiconductor film leads to an increasing width of the sensitivity curve. There are peaks at the energies hv = 1.43 eVand hv = 1.85 eV when the film thickness is 1 μ m. The peaks are due to the absorption in GaAs and As₂Se₃, respectively. When the thickness of the chalcogenide film is $5 \mu m$ (curve 3), the peak due to the absorption in GaAs is practically unobservable, and photoconductivity is primarily due to the photoconductivity of As ₂Se₃. In that case the maximum of the sensitivity curve is located at 1.9 eV.

The study of the n-GaAs-As₂S₃ heterojunction shows that, contrary to the n-GaAs-As₂Se₃ heterojunction at low voltages (< 1 V), in the investigated spectral range the form of the sensitivity curve slightly varies with change of the chalcogenide semiconductor film thickness. A small difference is observable only in the range between 2.0 and 2.4 eV (Fig. 3). For the heterojunction with the most thick film the sensitivity curve is located higher than the curve obtained for the heterojunction with thin film. This difference can be explained by the following hypothesis. When the thickness of the chalcogenide film is 5 µm the fraction of photons absorbed in the film in the mentioned spectral region is much greater than for the heterojunction with film thickness 1 µm. But, it should be noted that for the heterojunction with the thinner film the photocurrent is

bigger. At low voltages the main peak of the sensitivity curve is at 1.4 eV. In this case the photoresponse is defined by the photoconductivity of GaAs.

A characteristic property of the GaAs-chalcogenide glassy semiconductor heterojunction is the form of the sensitivity curve depending on the voltage across the heterostructure. From the curves obtained for the GaAs-As₂Se₃ heterojunction with chalcogenide film thickness 1 μ m at +1 V and -1 V one can see that the photocurrent abruptly increases in the range between 1.3 and 1.4 V. There is only a peak due to the absorption in As₂Se₃. Figure 4 shows that at voltages from -4 V to -20 V there are two peaks. The main peak, concerned with photoconductivity of As 2Se3, is observable at hv = 1.97 eV, and the added peak at hv = 1.43 eV is concerned with the conductivity of GaAs. In all cases, at forward bias the direction of the photocurrent conforms with the hole flow towards the collector. Therefore, the separation of the photocarriers is carried out by the external electric field. At zero bias and at reverse bias the photocurrent conforms to the electron travelling towards the collector. The photocurrent at zero bias is explained by the separation of photocarriers at the barriers formed at the interfaces. This fact is corroborated by the fact that at low positive voltage ($\sim 1 \text{ V}$) the photocurrent slightly differs from the magnitude at zero bias.

For $GaAs-As_2S_3$ heterostructures the sensitivity curves obtained at low voltages of both voltage signs are the same within the limits of error. In both cases the photocurrent flows from the collector to the thick aluminium layer on the backside of GaAs. The sensitivity curve measured at zero bias coincides with the noted curves. At low voltage bias for this heterostruc-

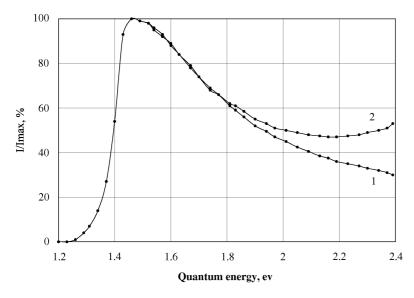


Fig. 3. Photosensitivity spectra of the GaAs-As₂S₃ heterojunction at forward bias for two chalcogenide film thicknesses: 1, $d = 5 \mu m$; 2, $d = 1 \mu m$.

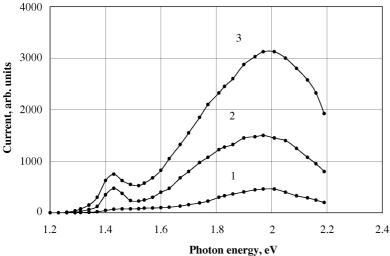


Fig. 4. Photosensitivity spectra of the $GaAs-As_2Se_3$ heterojunction at three voltages: 1, -20 V; 2, -10 V; 3, -4 V.

ture the separation of the photocarriers is carried out at the barriers existing in the heterostructure. The value of the photocurrent through the structure is practically independent of the external voltage bias.

At high voltages ($\sim 10 \text{ V}$) across the collector the form of the sensitivity curve substantially differs. For the samples with thick film there are two peaks at hv = 1.43 eV and hv = 2.3 eV. For the samples with thin film the second peak is less crisp, and if the film thickness increases the peak magnitude decreases. An analogous behavior is observable when the collector is biased negatively: there are two peaks of the sensitivity. The peaks are due to the absorption in GaAs (at hv = 1.43 eV) and in As₂S₃ (at hv = 2.3 eV).

The decrease of the second peak with decrease of the film thickness is defined by the reduction of the photon fraction absorbed in the chalcogenide glassy semiconductor.

Furthermore, at high voltages the direction of the photocurrent depends on the sign of the voltage applied to the collector. At reverse bias the photocurrent conformed to hole flow towards the collector, and at forward bias the carries travelled in the reverse direction. Thus, the direction and the value of the photocurrent are determined by the internal barriers, till the external electric field is small with respect to the fields existing near the interfaces. It should be noted that the increase of the photocurrent maximum with increase of

the voltage at forward bias is faster than at the reverse bias. The location of the photocurrent maximum in the region due to the absorption in the chalcogenide film is explained by the holes being the majority carriers in the glassy semiconductor. At forward bias, photogenerated holes drift from the chalcogenide glassy semiconductor to the collector. The mobility for the carriers in GaAs is much higher than in the semiconductor. Consequently, the recombination processes will not play an important role, and there will be a rapid increase of the photocurrent. At $hv \approx 1.43$ eV, where the photons are absorbed in GaAs, the values of the photocurrent at -4 V and +4 V are almost the same.

The photocurrent is observable at the forward bias over a range of energy between 1.0 and 1.3 eV, by contrast to the photocurrent at the reverse bias. The existence of the current can be explained by the hole photoemission from the thick aluminium layer on the backside of the sample. At the forward bias, photoemitted holes drift to the collector through GaAs and the semiconductor. This phenomenon was observable when studying the potential barrier at the Al-GaAs interface [5].

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4. Conclusions

Four types of heterojunctions: SnO₂-As₂(Se_{0.9}-Te_{0.1})₃, SnO₂-(As_{0.67}Sb_{0.33})₂Se₃, n-GaAs-As₂Se₃ and n-GaAs-As₂S₃ were prepared for experimental study. For all samples characteristics and photosensitivity spectra were obtained at forward and reverse bias. The I-V characteristics for the above heterojunctions are asymmetrical and nonlinear. All heterostructures have rectifying properties. For heterostructures based on SnO₂, the form of the sensitivity curve differs at forward and at reverse bias. At forward bias the peak of the sensitivity curve shifts to the short-wavelength region with respect to the peak observed at reverse bias. However, the latter peak shifts to the long-wavelength region with increase of chalcogenide film thickness. For heterostructures based on GaAs there is a shift of the maximum of the sensitivity curve and a variation of the form of the curve with a change of chalcogenide film thickness. The form of the sensitivity curve also depends on the applied voltage bias. All heterostructures can be used for manufacturing of rectifying devices and photoreceivers.

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