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Charge transition phenomena in the heterostructure crystalline Si–Bi–amorphous film $Ge_{33}As_{12}Se_{55}$

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Abstract. $Ge_{33}As_{12}Se_{55}$-Si(n) heterostructures with modified by bismuth atoms transition layer were obtained by the discrete thermal evaporation method. Described are formation and investigation methods for these heterostructures. The mechanism of charge transmission in this heterostructures was ascertained. It is illustrated that the barrier for holes at the boundary is absent. The energy diagram of the heterostructure was built. Analyzed is the absence of a soft breakdown, which is caused by the electrons transfer through interstices when the negative voltage is applied. The dependence of heterostructure electrophysical properties on $Ge_{33}As_{12}Se_{55}$ film thickness was investigated. It is shown that in heterostructures with a modified transition layer ther is a necessity to use $Ge_{33}As_{12}Se_{55}$ film with the thickness more than 0.4 μm. It is ascertained that at the modification of the transition layer the conversion from the sharp to smooth transition takes place, which is caused by diffusion of bismuth atoms to surface layers.

Keywords: heterostructure, modified transition layer, current-voltage characteristics, capacity-voltage characteristics, energy diagram.

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1. Introduction

$Ge_{33}As_{12}Se_{55}$ films are used as optical coatings in IR technique due to their transparence over the wavelength range from 1 to 12 μm and stability to aggressive media effect. Such films are also used for decreasing feedback currents in silicon diode structures [1].

One of the differences between homo- and heterojunctions is the formation of transition layers at the interface of two different semiconductors in the latter. Transition layers substantially influence the characteristics of heterojunctions worsening them, as a rule. The formation of transition regions depends on process conditions and methods of preparing the structures. One of the ways to improve the heterostructure properties is modifying a transition layer, which lies in introducing a small amount of impurity to the interface of semiconductors. The problem of choosing the substance for modification is of great importance. Our attention has been paid to the use of bismuth Bi as a modificator. It is known that bismuth has the largest diffusivity among metals and may result in the sign inversion of main charge carriers of chalcogenide vitreous semiconductors [2]. Modifying the transition region of Si(p)-$Ge_{33}As_{12}Se_{55}$ heterostructure by metals Cu, Pb, Sb, In, Bi was studied earlier [3]. Modifying the transition region of such structures by Bi atoms gives the best values of the rectification factor but in this case the formation of a soft breakdown at reverse bias is an essential drawback.

Up to date the influence of a transition layer on electrophysical properties of Si(n)-$Ge_{33}As_{12}Se_{55}$ heterojunction has not been studied properly. Therefore, the purpose of the present work was to study the influence of modifying the transition region on electrophysical properties of heterostructures Si(n)-$Ge_{33}As_{12}Se_{55}$ amorphous film.

2. Methods of investigation

To study current-voltage characteristics of experimental samples, the alternating voltage (in the form of a triangular pulses) was applied to the structure under investigation from a signal generator and was recorded by a recorder. The current flowing via the sample was amplified and supplied to the recorder. Single points of current-voltage characteristics were taken using a direct-voltage

supply, voltmeter and amplifier. The voltage was measured within the range of 0.001–5 V with the accuracy of 2 %, and the current - in the interval of 10^{-13}–10^{-4} A with the error of 3%.

To study capacity-voltage characteristics of structures, the voltage $U_b + U_i$ that controls the capacity of heterostructure was applied to the samples. It was formed by two sources: a bias source (U_b) and generator (U_i). The voltage U_b was measured with the generator switched off by a voltmeter with the accuracy of 2%. The capacity was measured at the frequency of 1 kHz. The zero-indicator was used to compensate the bridge. The capacity-voltage characteristics and an active conductivity component of heterostructure as a function of bias voltage were measured by this method. The accuracy of capacity measurements did not exceed 2% according to this procedure.

3. Results

1. Current-voltage characteristics

In Fig. 1, current-voltage characteristics of Sb-Si(n)-$Ge_{33}As_{12}Se_{55}$-Sb structure (a) without modifying a transition layer and (b) with the transition layer modified by bismuth Bi (that is Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb) are given. The thickness of $Ge_{33}As_{12}Se_{55}$ film is equal to 0.2 μm. The choice of Sb as the material for electrodes is conditioned by the fact that it forms injecting contacts with $Ge_{33}As_{12}Se_{55}$ film [3–5] and Si(n) [6]. The choice of Bi as the modifier is conditioned by the fact that bismuth can change the conductivity of chalcogenide vitreous semiconductor from p- to n-type [3]. We see that a Bi nanolayer really acts as a modificating one.

As it is seen from Fig. 1, modifying a transition layer by Bi results in a sufficient increase in the current that flows via the structure. This is partially explained by the decrease in the effective thickness of a high-resistance $Ge_{33}As_{12}Se_{55}$ film and decrease in the thickness (or a full alignment) of SiO_2 layer on the silicon surface due to Bi diffusion. Introducing a modifying Bi layer also results in qualitative changes in the form of current-voltage characteristics that testifies to the change in the charge carriers transfer mechanism in the structure.

2. Capacity-voltage characteristics

The study of the capacity-voltage characteristics of heterostructures allows one to make conclusions about the homogeneity of an impurity distribution in semiconductors [7], to analyze surface states at the interface [8] and to estimate the effective height of transition region barrier [8, 9].

In Fig. 2, the capacity-voltage characteristics of Sb-Si(n)-$Ge_{33}As_{12}Se_{55}$-Sb structures (curve 1) and Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb structures with the transition layer modified by Bi (curves 2,3) are presented. Introducing a modifying Bi layer results in the decrease of the capacity of the structure and shift of the maximum to the region of positive voltage values and to its widening (Fig. 2).

The capacity-voltage characteristics of Sb-Si(n)-Sb and Sb-Si(n)-Bi structures have been investigated by us. It has been established that the availability of barrier at the interface of Si(n)-$Ge_{33}As_{12}Se_{55}$ makes an essential contribution in capacity-voltage characteristics and, respectively, changes the properties of Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb heterojunction.

4. Discussion

The difference in current-voltage characteristics of Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb structures with different thick-

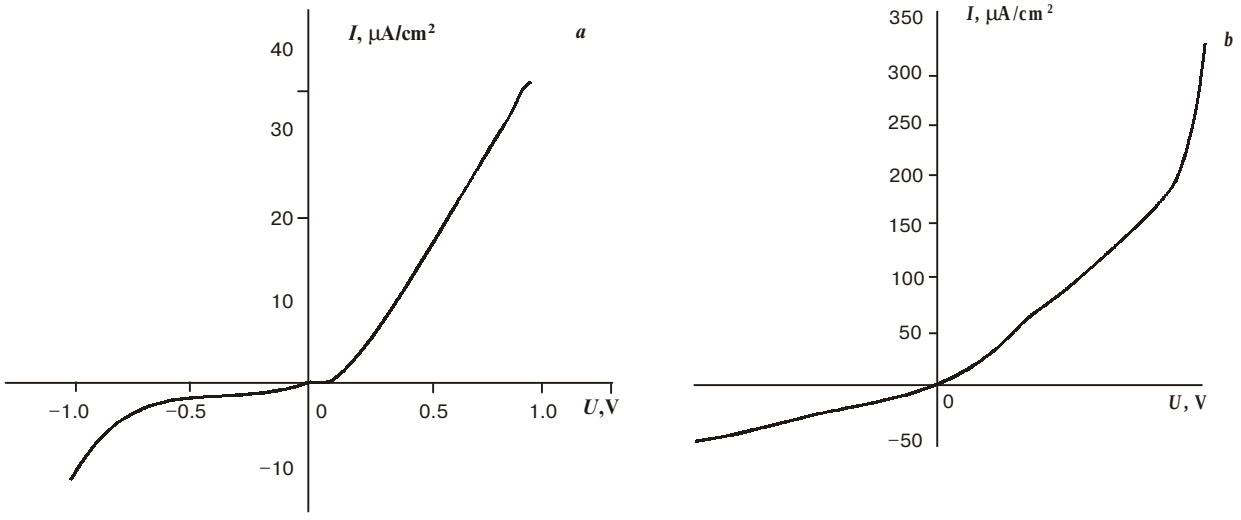

Fig. 1. Current-voltage characteristics of Sb-Si(n)-$Ge_{33}As_{12}Se_{55}$ Sb structure (the positive voltage is applied to Si, the thickness of $Ge_{33}As_{12}Se_{55}$ film is equal to 0.2 μm): a – without modifying the transition layer, b – with the transition layer of Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$ Sb structure modified by Bi.

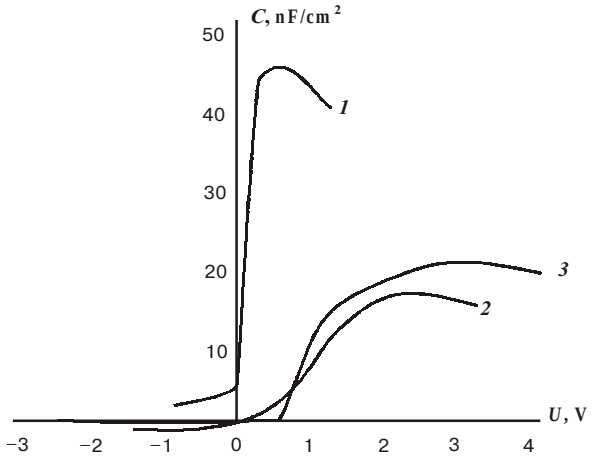

Fig. 2. Capacity-voltage characteristics of Sb-Si(n)-$Ge_{33}As_{12}Se_{55}$-Sb structures (curve 1) and Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb structures with the transition layer modified by Bi: curve 2 – the thickness of $Ge_{33}As_{12}Se_{55}$ film is 0.2 μm; curve 3 – the thickness of $Ge_{33}As_{12}Se_{55}$ film is 0.5μm (a positive voltage is applied to silicon).

ness of $Ge_{33}As_{12}Se_{55}$ film may be explained as follows. The rectification factor depends on the thickness of the film deposited [8]. This phenomenon is explained by the magnitude of the region of a bulk charge in the film. The rectification factor is maximal when the total bulk charge conditioned by a contact difference of potentials is put in the thickness of the film. At further increase of the film thickness, a sequential junction resistance increases that restricts a direct current, and this results in the decrease of the rectification factor. By analyzing current-voltage characteristics (Fig. 1,*b*) and values of rectification factors (Table 1), one can state that the bulk charge region and, respectively, the value of the contact field penetraton into *p*-region lies within the limits of 0.2 to 0.5 μm with Bi diffusion-error correction. As for $Ge_{33}As_{12}Se_{55}$ film with the thickness of 0.2 μm, the rectification factor is less than that of the thickness 0.5 μm. The film thickness is not sufficient to locate the whole bulk charge. For the film with the thickness of 0.5 μm the decrease in the value of a direct current in comparison with the heterostructures, $Ge_{33}As_{12}Se_5$ film thickness of which made up 0.2 μm is

Table 1. The rectification factors of structures under study at the voltage of 0.3 V.

Structure	Thickness of $Ge_{33}As_{12}Se_{55}$ film, μm	Rectification factor
Sb-Si(n)-$Ge_{33}As_{12}Se_{55}$-Sb	0.2	7
Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb	0.2*	2.7
Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb	0.5*	82.4

*– with Bi diffusion-error correctness.

observed. In this case, the film thickness is larger than the bulk charge region. So, we may take d = 0.4 μm as the magnitude of the contact penetration field in to *p*-region of the heterojunction.

The given fact does not agree with the theory that does not take into account the transition regions of heterojunctions. In accordance with the theory, the calculated thickness of the bulk charge layer in $Ge_{33}As_{12}Se_{55}$ film with the external field being not available makes up W_1=2.74 nm. Such inconsistency with the theory is explained by the availability of the transition region at the interface, in particular by the inhomogeneity in the thickness of $Ge_{33}As_{12}Se_{55}$ film equal to some tens of nanometer and SiO_2 layer with the thickness of ~5 to 10 nm on silicon surface. The study of capacity-voltage characteristics allows one to state that introducing Bi nanolayer results in the conversion from abrupt to gradual heterojunction.

In current-voltage characteristics in semilogarithmic scale, an exponential dependence of current on voltage is observed, which can be approximated by the following expression

$$I = I_{01} \cdot \exp(\beta_1 U) + I_{02} \cdot \exp(\beta_2 U), \quad (1)$$

the coefficient β_1 being equal for both curves and β_2 – different. It should be also mentioned that in current-voltage characteristics of such structures (Fig. 1,*a*) the ohmic area is absent at small values of applied positive voltage. This testifies to the absence of barrier at the interface of silicon- chalcogenide vitreous semiconductor. For Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb structure with $Ge_{33}As_{12}Se_{55}$ film having the thickness of 0.2 μm current-voltage characteristics are straightened in logarithmic coordinates, that is the power dependence of current on voltage is observed: $I \sim V^m$, and one can localize some areas with different m. To explain these results one can use the theory of currents restricted by the space charge for the case of monopolar injection [9, 10].

While modifying the transition region, a very interesting and useful peculiarity is the absence of a soft breakdown in the structures with a modified transition layer (Fig. 1) that improves characteristics of heterojunction. The absence of a soft breakdown may be explained by excluding electrons from the process of current-transfer when modifying the transition region by Bi nanolayer.

From capacity-voltage characteristics of Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb structure with $Ge_{33}As_{12}Se_{55}$ film having the thickness of 0.2 μm built in coordinates $1/c^2 = f(U)$ by extrapolating linear areas to $1/c^2 \rightarrow 0$ the inner difference of potentials is defined V_D = 0 eV. In the structure without a modified layer, the barrier value is also equal to zero. So, the absence of barrier at the interface is confirmed both by studies of current-voltage and capacity-voltage characteristics.

While studying capacity-voltage characteristics of Sb-Si(n)-Bi-$Ge_{33}As_{12}Se_{55}$-Sb heterostructure with $Ge_{33}As_{12}Se_{55}$ film having the thickness of 0.5 μm the following effect was observed. The capacity of the structure

Table 2. The parameters of semiconductors $Ge_{33}As_{12}Se_{55}$ and Si(*n*).

	E_g, eV	χ, eV	φ, eV	ε	N_{A1}, cm^{-3}	ND_2, cm^{-3}
$Ge_{33}As_{12}Se_{55}$	1.8	4.0	4.9	7.8	10^{17}	–
Si(*n*)	1.12	4.01	4.25	12.5	–	$5 \cdot 10^{15}$

does not depend on the applied bias voltage at all negative values of voltage within the interval under study and at positive voltages to 0.55 V. The capacity-voltage characteristics of such a heterostructure do not become straight in the Schottky coordinates that testifies to the transition to a gradual heterojunction. A more abrupt character of capacity-voltage characteristics of Sb-Si(*n*)-$Ge_{33}As_{12}Se_{55}$-Sb structure without modifying the transition region testifies to a localized distribution of impurities in a smaller near-surface region. With introducing Bi nanolayer, the widening of capacity-voltage characteristics is observed. The latter means a gradual distribution of impurities in the near-surface region, that is the transition from a gradual to abrupt heterojunction.

Such speculations explain the discordance of the thickness of bulk charge region calculated theoretically and that obtained from the study of current-voltage characteristics. So, introduction of Bi nanolayer results in the transition from abrupt to gradual heterojunction by diffusing Bi into a comparatively wide near-surface region.

The diagrams of energy bands for $Ge_{33}As_{12}Se_{55}$ and Si(*n*) semiconductors and the theoretical diagram [11] of an abrupt *p-n* heterojunction after bringing a semiconductor to a close contact under the condition of equilibrium were built. Semiconductors posess a different band gap E_g, different dielectric constant ε, different work function φ and different electron affinity χ. Their parameters [12,13] are given in Table 2.

Break in the conductivity zone is $E_c = \chi_1 - \chi_2 = 0.01$ eV.

Break in the valence zone is $E_v = (E_{g1} + \chi_1) - (E_{g2} + \chi_2) = 0.67$ eV.

Contact difference of potentials is $V_D = \varphi_1 - \varphi_2 = 0.65$ eV.

The barrier for holes makes up ~0.1 eV. As the barrier for electrons is much larger and makes up 0.65 eV, the current while applying a positive voltage will mainly be transferred by holes. When the polarity of voltage changes, the current does not practically flow. When the value of applied reverse voltage reaches the magnitude of 0.65 eV, the barrier for electrons will disappear. A soft breakdown that appears at the back bias is explained by this fact (Fig. 1,a). The value of voltage for cutting off a soft breakdown makes up 0.62 eV that approximately corresponds to the value of barrier for electrons.

At $V^I = \Delta E_V = 0.67$ eV the charge of surface states is equal to 0.115 C/cm^2.

5. Conclusions

1. The energy diagram of $Ge_{33}As_{12}Se_{55}$-Si(*n*) heterojunction has been built. For such a structure, the dependence of forward current bears an exponential character at all the values of the voltage applied. For holes, the barrier at the interface is absent.
2. In the structures with the modified transition layer, a soft breakdown conditioned by the transfer of electrons at back bias is not present. The barrier for electrons at the interface makes up 0.62 eV.
3. When modifying the transition region by Bi nanolayer the transition from abrupt to gradual one takes place that is conditioned by metal diffusion into near-surface layers and further increase in the space charge region.

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