ОПТИЧНІ, ОПТОЕЛЕКТРОННІ І РАДІАЦІЙНІ СЕНСОРИ

OPTICAL, OPTOELECTRONIC AND RADIATION SENSORS

PACS: 71.23.CQ; 73.61.JC; 78.20. — E

AMORPHOUS-CRYSTALLINE HETEROJUNCTIONS FOR OPTOELECTRONIC SENSORS: ELECTRONIC STRUCTURE AND PROPERTIES

N. D. Savchenko[1], A. B. Kondrat[2], T. N. Shchurova[1], I. I. Opachko[1], V. M. Rubish[3]

[1] Department of Electronic Systems, Faculty of Engineering, Uzhgorod National University, 13 Kapitulna St., 88000 Uzhgorod, Ukraine, tel. +380 3122 30656, e-mail: root@tv.uzhgorod.ua

[2] Department of Solid State Electronics, Faculty of Physics, Uzhgorod National University, 54 Voloshyn St., 88000 Uzhgorod, Ukraine, tel. +380 3122 32318, e-mail: akondrat@univ.uzhgorod.ua

[3] Uzhgorod Scientific-Technological Center of the Institute for Information Recording, NASU, 4 Zamkovi Skhody Str., Uzhgorod 88000, Ukraine, tel. +380 3122 37397, e-mail: vrubish@ustc.org.ua

Abstract

AMORPHOUS-CRYSTALLINE HETEROJUNCTIONS FOR OPTOELECTRONIC SENSORS: ELECTRONIC STRUCTURE AND PROPERTIES

N. D. Savchenko, A. B. Kondrat, T. N. Shchurova, I. I. Opachko, V. M. Rubish

We have performed calculation of the electronic structure in the range of the band gap for amorphous ($Ge_{33}As_{12}Se_{55}$) и and crystalline materials (Si) with the help of the technique based on the method of linear combination of atomic orbitals and psedopotential method. Theoretical energy band diagrams have been constructed for the amorphous-crystalline heterostructures and correlated with experimental data.

Keywords: amorphous-crystalline heterojunctions, chalcogenide semiconductors, LCAO, pseudopotential

Анотація

АМОРФНО-КРИСТАЛІЧНІ ГЕТЕРОПЕРЕХОДИ ДЛЯ ОПТОЕЛЕКТРОННИХ СЕНСОРІВ: ЕЛЕКТРОННА СТРУКТУРА ТА ВЛАСТИВОСТІ

М. Д. Савченко, О. Б. Кондрат, Т. М. Щурова, І. І. Опачко, В. М. Рубіш

Методом, який базується на методі лінійної комбінації атомних орбіталей та методі псевдопотенціалу, проведено розрахунок електронної структури в області забороненої зони аморфних ($Ge_{33}As_{12}Se_{55}$) і кристалічних (Si) матеріалів. Побудовані теоретичні енергетичні діаграми для гетероструктур і співставлені з експериментальними даними.

Ключові слова: аморфно-кристалічні гетеропереходи, халькогенідні напівпровідники, ЛКАО, псевдопотенціал

Аннотация

АМОРФНО-КРИСТАЛЛИЧЕСКИЕ ГЕТЕРОПЕРЕХОДЫ ДЛЯ ОПТОЭЛЕКТРОННЫХ СЕНСОРОВ: ЭЛЕКТРОННАЯ СТРУКТУРА И СВОЙСТВА

Н. Д. Савченко, А. Б. Кондрат, Т. Н. Щурова, И. И. Опачко, В. М. Рубиш

Методом, основанным на методе линейной комбинации атомных орбиталей и методе псевдопотенциала, проведен расчет электронной структуры в области запрещенной зоны аморфных ($Ge_{33}As_{12}Se_{55}$) и кристаллических (Si) материалов. Построены теоретические энергетические диаграммы для гетероструктур, и сопоставлены с экспериментальными данными.

Ключевые слова: аморфно-кристаллические гетеропереходы, халькогенидные полупроводники, ЛКАО, псевдопотенциал

1. Introduction

Amorphous-crystalline heterojunctions prepared from thin films deposited from multinary chalcogenide glassy semiconductors have found wide applications and are promising for the design of novel sensor components for opto- and nanoelectronics due to memory effects, non-linear and other properties observed in the films [1]. Because of a large variety of the compositions available in this group of materials prediction of material properties remains a top problem that partially can solved with the help of atomic and electronic structure modelling methods. One of theoretical approaches for electronic structure and physical properties modelling is the one developed by W. A. Harrison [2] based on the tight-binding theory and the pseudopotential. In this work we present theoretical and experimental results of the studies of heterojunctions composed from the epitaxial silicon (*n* and *p* type) and $Ge_{33}As_{12}Se_{55}$ amorphous film deposited by thermal evaporation in vacuum. We applied the above-mentioned approach to calculation of the electronic structure and construction of the energy band diagram for $Ge_{33}As_{12}Se_{55}$ - Si heterojunctions. The main purpose of the work is to define correlation between electronic structure and electrophysical properties found in earlier studies for the heterojunctions under investigation [3, 4].

2. Computational procedure

Modelling of the energy band diagram of $Ge_{33}As_{12}Se_{55}$ -Si heterojunctions was performed by the procedure based on linear combination of atomic orbitals method and pseudopotential [2] with atomic terms determined within Hartree-Fock approximation. We have accounted for the presence of oxide layers, especially, stoichiometric As_2O_3, and/or GeO_2, layers at the film surface and SiO_2 layer at the surface of silicon wafer. These oxides were confirmed by Auger electron spectroscopy and X-ray photoelectron spectroscopy measurements for $Ge_{33}As_{12}Se_{55}$ - *p*-Si heterojunctions [5]. We have performed calculations in the following steps.

At the first step, we calculated the energy positions for the conduction-band minimum, E_c and the valence-band maximum, E_v, for $GeSe_2$, As_2Se_3 and Si. We have used the universal tight-binding parameters including ε_s, ε_p, ε_h, V_1 Hartree-Fock terms [2, 6]; intratomic Coulomb repulsion energy, *U,* taken as weighted value for two components; energy of polar bond $V_3^{ph} = (\varepsilon_{h+} - \varepsilon_{p-})/2$, and covalent bond energy $V_2 = V_{ll'm} = \eta_{ll'm}\hbar^2/md^2$ (where $\eta_{ss\sigma} = -1.32$, $\eta_{sp\sigma} = 1.42$, $\eta_{pp\sigma} = 2.22$, $\eta_{pp\pi} = -0.63$; $\hbar$ is Planck's constant divided by 2π, m is the electronic mass, *d* is interatomic distance taken from literature [2, 7-9]).

The conduction-band minimum in the centre of the Brillouin zone was calculated following the equations:

$$E_c^{GeSe_2} = \varepsilon_h^{Ge} + \sqrt{V_{sp\sigma}^2 + V_{pp\sigma}^2 + 2V_{pp\pi}^2 + (V_3^{ph})^2} - V_1^{\sigma^*} + \frac{U}{2}, \quad (1)$$

$$E_c^{As_2Se_3} = \frac{\varepsilon_p^{As} + \varepsilon_p^{Se}}{2} + \sqrt{V_{pp\sigma}^2 + 2V_{pp\pi}^2 + (V_3^{ph})^2} - V_1^{\sigma^*} + \frac{U}{2}, \quad (2)$$

$$E_c^{Si} = \varepsilon_p^{Si} + \sqrt{V_{pp\sigma}^2 + V_{pp\pi}^2} - V_1^{Si} + \frac{U}{2}, \quad (3)$$

where $V_1^{\sigma^*} = [(1+\alpha_p)V_{1-} + (1-\alpha_p)V_{1+}]/2$ is the metallic bond energy calculated in terms of antibonding orbitals with account of polar bond $\alpha_p = V_3^{ph}/(V_2^2 + V_3^2)^{1/2}$.

The valence-band maximum in the centre of the Brillouin zone for $GeSe_2$ and As_2Se_3 compounds was determined as:

$$E_v = \varepsilon_p^{Se} + V_2^{LP} + \frac{U}{2}, \quad (4)$$

where $V_2^{LP} = 0.417\ \hbar^2/md^2$ is lone-pair (LP) electron band width.

The valence-band maximum for Si was computed as:

$$E_v^{Si} = \varepsilon_p^{Si} - V_{pp\sigma} - \Delta E_{s-o} + \frac{U}{2}, \quad (5)$$

where $\Delta E_{s\text{-}o} = 0.03$ eV is spin-orbit splitting [10].

Then, we have determined the energy position of the electronic states in $GeSe_2$ and As_2Se_3 band gaps formed by homopolar bonds in a form:

$$E^{Ge-Ge} = \varepsilon_h^{Ge} + \sqrt{V_{ss\sigma}^2 + 2V_{sp\sigma}^2 + V_{pp\sigma}^2 + 2V_{pp\pi}^2}, \quad (6)$$

$$E^{As-As} = \varepsilon_p^{As} + \sqrt{V_{ss\sigma}^2 + V_{sp\sigma}^2 + V_{pp\sigma}^2}, \quad (7)$$

The energy position of boron acceptor states in silicon was found from the equation [2]:

$$E_A^{Si} = E_v + \frac{m_h e^4}{2e_{stat}^2 \hbar^2}, \quad (8)$$

where $m_h = 0.16m$ is the effective hole mass, e is the electron charge, $\varepsilon_{stat} = 6.4$ is static dielectric constant calculated elsewhere [2].

The energy positions of electronic states at $GeSe_2$ and silicon surfaces, E_s, were determined shifting the positions of ε_h^{Ge} and ε_h^{Si} terms towards higher energies by the values $(U^{GeO2} + U^{GeSe2})/4$ and $(U^{Si} + U^{SiO2})/4$, respectively. To determine the E_s value for As_2Se_3 we have shifted the position of ε_p^{As} term by the quantity $U^{As2Se3}/2$.

At the second step, we have calculated the energy band diagram for $Ge_{33}As_{12}Se_{55}$ compound accounting for molar fraction of As-Se and Ge-Se chemical bonds in it. It is assumed that conduction band is formed by As-Se bonds, and the valence band is formed by LP states of Se atoms. The energy positions of the Ge-Ge and As-As homopolar bonds are consistent with the energy values calculated from Eq.(6) and Fermi level can be found as $E_{F1} = (E^{Ge\text{-}Ge} + E^{As\text{-}As})/2$. The Fermi level for silicon was obtained as $E_{F2} = (E_A^{Si} + E_v^{Si})/2$.

At the third step, we have calculated the energy band diagram for separate SiO_2, GeO_2, and As_2O_3 layers. Equations (1) and (4) with the respective changing of the chemical indices were used in calculation of E_c and E_v. The value of $V_1^{\sigma^*} = 7.74$ eV was taken for oxygen [2]. In E_c calculation for As_2O_3 the value $\eta_{ll'm} = 2.39$ was used in the expression for V_2. We took V_2^{LP} as zero in Eq. (4), because the E_v value for these materials is much lower in energy, so in our case we could neglect it. This step was omitted in our calculations for $Ge_{33}As_{12}Se_{55}$ - *n*-Si heterojunction.

At the forth step, equalizing the Fermi levels $E_{F1} = E_{F2}$, we constructed the energy band diagram for heterojunctions of both types. For $Ge_{33}As_{12}Se_{55}$ - *p*-Si heterojunction we accounted for the bendings at the interface and the presence of Si-Se and Si-Ge bonds in this region.

3. Results and Discussion

Table 1 presents interatomic distances and calculated matrix elements V_1, V_2, V_3, intra-atomic Coulomb repulsion energy, and parameters of energy structure E_c and E_v, for semiconductors ($GeSe_2$, As_2Se_3, Si) and oxides (GeO_2, As_2O_3, SiO_2,). Based on the calculated data for $GeSe_2$, As_2Se_3 we constructed the energy band diagram for $Ge_{33}As_{12}Se_{55}$. The ratio between the numbers of As-Se and Ge-Se bonds per atom was determined for this compound to be 2/3, and thus, we have found for E_c and E_v the values -3.99 eV and -5.76 eV, respectively. Thus, the band gap for $Ge_{33}As_{12}Se_{55}$ ($E_g = E_c - E_v$) is 1.77 eV. The reported earlier experimental optical band gaps were 1.80 eV for as-deposited films and 1.96 eV for the annealed ones [11].

Similar data for the electronic states in the band gap corresponding to As-As, Ge-Ge, Se-Se homopolar bonds and Ge-Si, Ge-Se heteropolar bonds ($E^{As\text{-}As}$, $E^{Ge\text{-}Ge}$, E^{Si}) in the bulk (E_s^{Ge}, E^{As}, E_s^{Si}) and at the interfacial region ($E_s^{Si\text{-}Se}$, $E_s^{Si\text{-}Ge}$) are given in Table 2. From these data we have determined the energy position of the Fermi level in $Ge_{33}As_{12}Se_{55}$ (-4.86 eV) and in silicon (-5.05 eV), and energy positions of the Si-Se and Si-Ge electronic states in the intermediate region.

Figure 1 shows the calculated energy band diagram for the $Ge_{33}As_{12}Se_{55}$ - Si amorphous-crystalline heterostructures with *p*-Si (a) and *n*-Si (b). We see, that the barriers with heights of about $eV_{D1} = 0.44$ eV and $eV_{D2} + \Delta E_v = 1.28$ eV are formed on the side of $Ge_{33}As_{12}Se_{55}$ layer and on the side of *p*-Si wafer, respectively. For $Ge_{33}As_{12}Se_{55}$ - *n*-Si heterojunction (Fig.1, b) the barriers height of 0.40 eV was found at the $Ge_{33}As_{12}Se_{55}$ layer side, and of 0.60 eV at the side of *n*-Si wafer determined by the valence band discontinuity.

Table 1

Interatomic distance (d), metallic (V_1), covalent (V_2) and polar bond energy (V_3), intratomic Coulomb repulsion energy (U), energy positions of the valence-band maximum (E_v), conduction-band minimum (E_c) for semiconductors and oxides.

Parameters	As_2Se_3	$GeSe_2$	Si	SiO_2	As_2O_3	GeO_2
d, nm	0.241	0.237	0.235	0.161	0.184[c]	0.188[c]
V_1, eV	2.70	2.41	1.80	5.99	6.27	6.38
V_2, eV	3.14	3.77	3.07 3.30	8.17	3.38	5.99
V_3, eV	0.83	0.70	-	3.69	2.65	3.74
U/2, eV	4.27	4.24	3.82	6.10	6.00	6.09
$-E_c$, eV	3.99	3.52	4.07	0.32	3.65	2.50
$-E_v$, eV	5.71	5.82	5.07	10.67	10.77	10.68

Table 2

Interatomic distance (d), covalent (V_2) and polar bond energy (V_3), intra-atomic Coulomb repulsion energy (U), energy positions of bulk (E_b) and surface (E_s) defect states.

Parameters	As-As	Ge-Ge	Si-Si	Si-Se	Si-Ge	Se-Se
d, nm	0.249	0.244	0.235	0.231	0.239[c]	0.232
V_2, eV	4.22	4.34	-	3.97	4.52	3.38
V_3, eV	-	-	-	0.65	0.06	-
U/2, eV	4.24	4.87	4.68	-	-	-
$-E_b$, eV	4.22	4.95	5.05	-	-	-
$-E_s$, eV	4.74	4.42	4.72	5.37	4.82	-

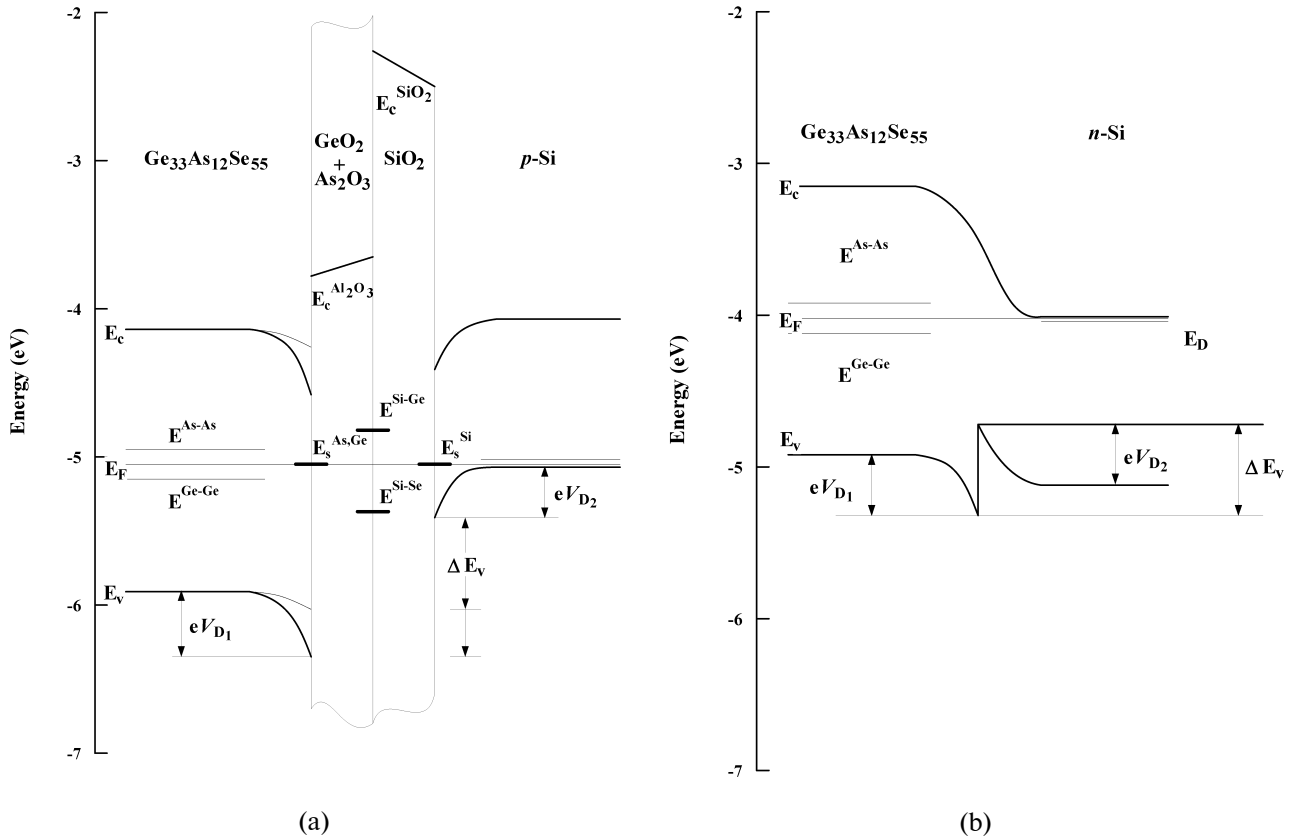

Figure 1. Energy band diagrams for $Ge_{33}As_{12}Se_{55}$-Si heterostructures: a — *p*-Si; b — *n*-Si.

The earlier studies of current-voltage and capacitance-voltage characteristics of $Ge_{33}As_{12}Se_{55}$ - *p*-Si heterostructures [3] have shown that these heterostructures can be considered as *p-p* heterojunction, comprising of two Schottky diodes with opposite polarity connected in series with a barrier height of about $eV_{D1} = 0.55$ eV at the $Ge_{33}As_{12}Se_{55}$ layer side and $eV_{D2} + \Delta E_v = (1.15 - 1.21)$ eV at the *p*-Si wafer side (ΔE_v is valence band discontinuity). For $Ge_{33}As_{12}Se_{55}$ - *n*-Si heterojunctions we have found that their properties are governed by the barrier height of 0.35 eV [4]. Thus the results of simulation energy level diagram of $Ge_{33}As_{12}Se_{55}$ film - Si amorphous-crystalline heterostructure based on linear combination of atomic orbitals and pseudopotential methods show agreement better than 20 % with experimental data.

4. Conclusions

The suggested theoretical approach is applicable to the computation of the energy band diagram of amorphous-crystalline heterojunctions. The heterostructures of $Ge_{33}As_{12}Se_{55}$ - *p*-Si type have been found to have better potentialities than $Ge_{33}As_{12}Se_{55}$ - *n*-Si ones for the design and production of optoelectronic sensors.

References

1. *Electronic phenomena in glassy semiconductors*. Ed. K.D. Tsendin. Nauka (Science), St. — Petersburg (1996).
2. W. A. Harrison. *Elementary Electronic Structure*. World Scientific Publishing Co., New Jersey, London, Singapore, Shanghai, Hong Kong, Taipei, Chennai (2004)
3. N. D. Savchenko. Energy band diagram for the $Ge_{33}As_{12}Se_{55}$ — Si heteroboundary // in *Inst. Phys. Conf. Ser.* No.152, pp. 723-726. IOP Publishing Ltd (1998).
4. N. D. Savchenko, A. B. Kondrat, N. I. Dovgoshey, Yu. I. Bertsik. Charge transfer phenomenon in $Ge_{33}As_{12}Se_{55}$ — X — Si structures with nanolayer X: Sb; Bi; In; Pb // *Functional Materials 6*(3), pp. 432-435 (1999).
5. T. N. Shchurova, N. D. Savchenko, A. B. Kondrat, I. I. Opachko. Auger analysis and simulation of electronic states for $Ge_{33}As_{12}Se_{55}$ - *p*-Si heterojunction // *Surface and Interface Analysis 38*, pp. 448-451 (2006).
6. J. B. Mann. *Atomic Structure Calculations, 1: Hartree-Fock Energy Results for Elements from Hydrogen to Lawrencium*. Clearinghouse, Springfield (1967).
7. O. Uemura, Y. Nagata, T. Usuki, Y. Kameda. Short-range Order in Amorphous $(Ge_{1-x}M_x)$ Se_2 (M = As, Sb and Bi) // *J Non-Cryst Sol 192&193*, pp. 74-78 (1995).
8. T. Shchurova, N. Savchenko, A. Spesivykh, N. Baran. Spectral Distribution of Photoemission Quantum Efficiency for $(As_2Se_3)_{1-x}Ge_x$ Glasses // *Jap J Appl Phys 39*(Suppl. 39-1), pp. 334-335 (2000).
9. A. Feltz *Amorphe und Glasartige Anorganische Festkorper*. Akademie-Verlag, Berlin (1983).
10. D. J. Chadi. Spin-orbit splitting in crystalline and compositionally disordered semiconductors // *Phys Rev B 16*, pp. 790-796 (1977).
11. N. I. Dovgoshey, L. G. Kesler, N. D. Savchenko. Relativistic electrons effect on the optical coatings of Ge-As-Se type // in *Kvantovaya Elektronika* (Quantum Electronics) Iss. 40, pp. 43-49, Naukova dumka, Kiev (1991).