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A.S. Saidov
Physicotechnical Institute NPO "Physics-Sun" them. S.A. Azimov AS RUz, amin@uzsci.net

Sh.N. Usmonov
Physicotechnical Institute NPO "Physics-Sun" them. S.A. Azimov AS RUz

U.P. Asatova
Urgench State University, umida72@rambler.ru

Sh.K. Ismailov
Urgench branch of Tashkent University of Information Technologies named after Muhammad Al-Khwarizmi, shavkat6819@mail.ru

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GROWING AND STUDYING THE PHOTOELECTRIC AND ELECTRICAL PROPERTIES OF EPITAXIAL FILMS OF GE$_{1-x}$SN$_x$ SOLID SOLUTIONS

A.S. Saidov$^1$, Sh.N. Usmonov$^1$, U.P. Asatova$^2$, Sh.K. Ismailov$^3$

$^1$Physicotechnical Institute NPO “Physics-Sun” them. S.A. Azimov AS RUz
$^2$Urgench State University
$^3$Urgench branch of Tashkent University of Information Technologies named after Muhammad Al-Khwarizmi

E-mail: amin@uzsci.net, umida72@rambler.ru, shavkat6819@mail.ru

Abstract
Monocrystal films of the Ge$_{1-x}$Sn$_x$ solid solution (0<x<0.3) were grown on Ge substrates by the method of liquid phase epitaxy from a limited volume of tin melt solution. The surface relief of the epitaxial film, as well as the spectral photosensitivity and current-voltage characteristics of the n-Ge-p-Ge$_{1-x}$Sn$_x$ heterostructures (0<x<0.3) are investigated. Hillocks of nanocrystals from the Ge$_{1-x}$Sn$_x$ solid solution with a base size of 150 to 400 nm and a height of 5 to 20 nm are formed on the film surface. The spectral photosensitivity of n-Ge-p-Ge$_{1-x}$Sn$_x$ heterostructures (0<x<0.3) covers the photon energy range from 0.4 to 1.4 eV.

Keywords: solid solution, liquid phase epitaxy, heterostructures, epitaxial film, band gap, nanocrystals.

Introduction
The technological features of growing and the study of the physical properties of two- and multi-component complex semiconductor solid solutions (TP) based on semiconductor and semi metallic elements of group IV is seemed as promising materials for electronics. The band gap of Ge$_{1-x}$Sn$_x$ TP semiconductor solid solutions varies in a wide range - from ~ 0.3 to ~ 2 eV which depends on the component composition therefore. They can be used as active elements of optoelectronic devices operating in the far and near infrared spectral regions.

The band gap of direct-gap diamond-like Ge$_1$-xSn$_x$ TPs depends on Sn concentration (Fig. 1.) [1]. The Ge$_{1-x}$Sn$_x$ and Ge$_{1-x-y}$Si$_x$Sny layers are attractive because they can be used as artificial substrates for further growing A$^3$B$^5$ and A$^2$B$^6$ semiconductor compounds on them. The Ge$_{1-x}$Sn$_x$ solid solutions are stable at high temperatures and their strain states can be regulated [2, 3, 4, 5]. The lattice parameter and thermal expansion coefficients of many semiconductor A$^3$B$^5$ compounds can be matched with the Ge$_{1-x}$Si$_y$Sny triple TP (Fig. 2).

Recently, along with double TP of group IV - Ge$_{1-x}$Sn$_x$ and Si$_{1-x}$Sn$_x$, much attention has been paid to the technological features of growing and studying the photoelectric and structural properties of triple TP - Si$_x$Sn$_y$Ge$_{1-x-y}$ [6, 7].

The electronic properties of Ge / Ge$_{1-x-y}$Si$_x$Sny structures are theoretically predicted.

It is shown that the crystal lattice with strained Ge layers and relaxed Ge$_1$-x-ySixSny epitaxial layers can have a straight band structure.

Fig. 1. Dependence of the band gap of the Ge$_{1-x}$Sn$_x$ solid solution on the Sn concentration: ■ - experimental points; solid line - linear-parabolic approximation of experimental points; Δ (dotted line) - according to the density functional theory for the solid solution GeSn of zinc blende [1].

The predicted value of the direct band gap reaches 0.6 eV [8]. The band gap widths of indirect-gap Ge-like TP films Ge$_{1-x-y}$Si$_x$Sn$_y$ grown on Si substrates through Ge buffer layers were determined in a wide range y>x [9]. It was found
that the band gap dependence on composition can be represented by a bilinear expression of the form: \( E = (0.668 \pm 0.008) + (0.67 \pm 0.15) \cdot x - (1.77 \pm 0.16) \cdot y \) (eV). In the Ge1-x-ySixSny ternary TPs, due to deformation and composition change, the fundamental absorption edge can be adjusted in the wide infrared range, which provides the basis for integrating microelectronics with optical components into a single chip [10, 11].

This paper presents the results of experimental studies of the liquid-phase growth, as well as the structural and some photoelectric and electrical properties of narrow-gap Ge1-xSnx TP.

The method of growing the epitaxial layer of the solid solution Ge1-xSnx.

Ge1-xSnx solid solutions were grown with using liquid-phase epitaxy from a limited volume of Sn solution-melt by forced cooling in an atmosphere purified by palladium hydrogen. To grow the layers, we used a vertical quartz reactor with horizontally arranged substrates. Ge plates with a resistivity of 1 \( \Omega \cdot \text{sm} \), crystallographic orientation (111), were used as substrates. The diameter and thickness of the substrate is 50 mm and ~ 400 m, respectively. First, a vacuum was created in the reactor to a residual pressure of 10–2 Pa, then purified hydrogen was passed through the reactor for 15 min, and then the heating process began. When the temperature reached the required value, the system switched to automatic mode. Within 40 min, the solution-melt was homogenized. Then the substrates on a graphite holder were brought into contact with the solution-melt and, after filling the gaps between the substrates with the solution-melt, they rose 1 cm above the level of the solution. The composition of the solution-melt was obtained on the basis of the results of preliminary studies of the Sn + Ge, Sn + Ge + Zn, Sn + Ge + ZnSe system and literature data [12].

At the initial moment of growth, Ge crystallizes from the solution-melt, since at the selected epitaxy temperature the solution is saturated with respect to Ge. At lower temperatures, conditions for growing the Ge1-xSnx solid solution are created. Samples were grown at various values of the parameters of liquid epitaxy. The composition of the solution-melt, the onset of the crystallization temperature, the cooling rate of the tin solution-melt, the distance between the upper and lower substrates is varied.

The Sn content, as well as the homogeneity of the distribution of the components, along the thickness of the epitaxial layer as well as in directions parallel to the crystallization front, depend on the composition of the solution-melt and the temperature of the onset of crystallization. With an increase in the Zn content, especially ZnSe in the solution-melt solution, the tin content in the solid solution sharply increased, which is probably due to the influence of the...
third component on the effective value of the distribution coefficient \[13\]. It was also established that with an increase the temperature of the onset of crystallization under identical conditions and the composition of the solution-melt, the Sn content in the Ge1-xSnx TP increases. In the grown TP epitaxial layers from the Ge + Sn + ZnSe solution – melt, at the crystallization start temperature of 740 °C, the Sn content was \( x = 0.1 \), and at 540 °C, \( x = 0.03 \).

Analysis of X-ray fluorescence spectra before and after successive deletions of part of the grown layers, which contain peaks with high intensities corresponding to germanium (\( \lambda = 1.244 \) Å) and tin (\( \lambda = 0.925 \) Å), showed that the content of Ge and Sn in the TP is the same for the area of films and along the growth direction of the layers. The thickness of the film layers varied in the range of 3–35 m depending on the growth mode and on the thickness of the gap between the substrates.

The quality of the Ge1-xSnx epitaxial layers also depends on the speed of forced cooling, the value of which varied in the range 0.5–7.5 grad / min, which corresponds to the actual crystallization rate of the layers 0.13–0.20 µm/min. The structural perfection of the grown layers also depends on the size of the gap between the horizontally positioned substrates, the value of which could be varied in the interval of 0.25-2.5 mm with the help of special graphite supports. At values of the gap smaller than 0.25 mm, the growth of epitaxial layers was not observed which, probably, due to the lack of wettability of the substrates with the solution-melt. The layers of solid solutions that are most perfect in structure, on the upper as well as in lower substrates, were grown at a gap of 0.65-1 mm. For values of the gap between the substrates greater than 0.85 mm, the quality of the layers grown on the lower substrates was always higher than the layers grown on the upper substrates.

This was also reflected in the surface dislocation density of the grown layers. This difference grew with the increase in the gap between the substrates. This is apparently due to the prevalence in the mechanism of mass transfer to the crystallization front of convection currents as compared with molecular diffusion with an increase in the gap \[14\].

Structural, photoelectric and electrical measurements of parameters of n-Ge – p – Ge1-xSnx heterostructures \( 0 \leq x \leq 0.03 \).

1. Study of the surface topography of the epitaxial film of the Ge1-xSnx solid solution \( 0 \leq x \leq 0.03 \).

The surface relief of an epitaxial film of a Ge1-xSnx solid solution \( 0 \leq x \leq 0.03 \) was studied using an atomic force microscope (AFM). A three-dimensional AFM image of an epitaxial film is shown in fig. 3. It can be seen that on the surface separate tubercles of various sizes are formed. The analysis showed that the diameter of the base of the hillocks varies in the range from 150 to 400 nm, and the height from 5 to 20 nm.

At heteroepitaxial growth the strain energy caused by the mismatch of the lattice parameters of the contacting semiconductors is the driving force for the formation of self-organizing three-dimensional islands. Since the mismatch of the lattice constants for Ge/\( \alpha \)-Sn systems is ~ 12%, it is possible to form nanocrystals from the Ge1-xSnx solid solution on the surface of the epitaxial film. The appearance of the selective reflection \( (222)_{\text{GeSn}} \) at \( 2\theta = 56.36^\circ \) in the diffraction pattern from the atomic planes of the solid solution indicates that the film contains coherently located nanocrystals from the Ge1-xSnx phase. Note that the lattice constant of Ge1-xSnx nanocrystals is 0.44% more than the lattice constant of the germanium substrate, which is possibly due to the deformation of the crystal lattice of the heteroepitaxial film. The dimensions of the hillocks obtained by AFM on the surface of the film and nanocrystalites, obtained by X-ray diffraction in the epitaxial film have similar values. Therefore, apparently, the solid solution Ge1-xSnx with a high Sn content forms nanocrystals in the epitaxial film of the solid solution. These quantum-sized objects in an epitaxial film can be used in mono-optical properties of heterostructures made on the basis of the studied solid solution.
Fig. 4. The linear dimensions of the average tubercle on the surface of the epitaxial film of the Ge$_{1-x}$Sn$_x$ solid solution (0≤x≤0.03).

2. Spectral photosensitivity of n-Ge – p-Ge$_{1-x}$Sn$_x$ heterostructures (0 ≤ x ≤ 0.03).

Non-isotype n-Ge – p-Ge$_{1-x}$Sn$_x$ heterojunctions (0 ≤ x ≤ 0.03) with a transition graded gap-gap buffer layer consisting of a Ge$_{1-x}$Sn$_x$ TR-replacement were obtained using liquid-phase epitaxy. The composition of the transition layer varies along the film thickness: Ge dominates closer to the substrate, and with grows the layer, the molar content of Sn increases. In the epitaxial film, the molar content of Sn is 3 at.%. The film is a TP of substitution Ge$_{0.97}$Sn$_{0.03}$. To clarify the role of the TR components, we experimentally investigated the spectral dependence of the photosensitivity of the fabricated structures using an IKS-21 infrared spectrometer. The measurement results are shown in Fig. 5. From fig. 5 it is seen that the photosensitivity of the structures studied covers the photon energy range from 0.4 to 1.4 eV.

It is known that the edge of the photosensitivity of germanium p-n junctions is 0.67 eV. The shift in the sensitivity of the studied structures to the long-wave side is due to the TP p-Ge$_{0.97}$Sn$_{0.03}$. However, the rise in spectral sensitivity is not sharp, which may be due to the thickness of the p-Ge$_{0.97}$Sn$_{0.03}$ TP layer which effectively absorbs low-energy quanta. Since p-Ge$_{0.97}$Sn$_{0.03}$ is an indirect-gap semiconductor material, to complete the absorption of long-wavelength photons, a layer of sufficient thickness is required, greater than 15 m. The decrease in photosensitivity at photon energies greater than 0.9 eV is due to the depth of the p-n-junction separating barrier, which in our case is determined by the thickness of the p-Ge$_{1-x}$Sn$_x$ layer and is ~ 15 m. The diffusion length of minority carriers in the p-Ge$_{1-x}$Sn$_x$ layer, as indicated above, is $L_n ≈ 3.16$ m, which is less than the depth of the separation barrier. Consequently, electron-hole pairs generated in the near-surface region of the structure by short-wave photons do not reach the separating barrier and do not participate in the creation of the photocurrent.

Fig. 5. Spectral photosensitivity of n-Ge–p-Ge$_{1-x}$Sn$_x$ heterostructures (0 ≤ x ≤ 0.03) at room temperature.

3. Current-voltage characteristics of n-Ge–p-Ge$_{1-x}$Sn$_x$ (0≤x≤0.03) heterostructures.

To measuring the current-voltage characteristics (I– V) the ohmic contacts of n-Ge–p-Ge$_{1-x}$Sn$_x$ heterostructures (0 ≤ x ≤ 0.03)were created by vacuum deposition of silver to the structure. A typical current-voltage characteristic and its straight branch, measured at room temperature, are presented in Fig. 6.

The reverse branch of the current-voltage characteristic is approximated by a power dependence, of the type $I = A \cdot V^n$, where A is a quantity that depends only on the parameters of the p-n-heterojunction. At low voltages $V<0.4$ V, the reverse current grows weakly with an increase in the bias voltage, with an indicator of $n<1$. With a further increase in voltage, a stronger dependence of the reverse current is observed with $n ≈ 1.5$. At higher voltages, impact ionization occurs in the region adjacent to the pn-heterojunction, resulting in soft electrical breakdown.

From the analysis of the direct branch of the I – V characteristic, its initial part ($V<0.5$ V) is well described by the exponential dependence, obtained in [15] for pn-diode structures with modulated resistance of high-resistance “long” ($d / L > 1$, where $d$ is the thickness of the base region, $L$ is the diffusion length of minority carriers) base, ideal injecting p-n junction and ohmic back by contact.
\[ I = I_0 \cdot \exp \left( \frac{qV}{ckT} \right) \]  

(1)

and refined in [16] for p-i-n-structures. The exponent \( c \) calculated in [15] has the value \( c = 20.8 \) and is described by the expression:

\[ c = \frac{2b + ch\left( \frac{d}{L_n} \right) + 1}{b + 1} \]  

(2)

where is the ratio of the mobilities of electrons and holes, \( d \) is the thickness of the base region from the solid solution p-Ge1-xSnx, \( L_n \) is the diffusion length of minority carriers in the base region. Electronic processes due to charge modulation when a current passes through the n-Ge–p-Ge1-xSnx \((0 \leq x \leq 0.03)\) structure are mainly determined by the transition layer and the p-Ge1-xSnx solid solution. Therefore, the thickness of the epitaxial layer, which was \( d \approx 15 \text{ µm} \), was taken as the base thickness. Considering that usually for semiconductors of the group \( C_4 \), \( \mu_n/\mu_p \approx 2 \), from (2) we find the value of the ratio \( d/L_n \approx 4.74 \), which actually turns out to be \( d/L_n > 1 \), and \( L_n = 3.16 \text{ µm} \). The mobility of the main carriers found by Hall method was at room temperature \( \mu_p = 80 \text{ cm}^2/(V \cdot \text{s}) \), which allows us to determine the mobility of minority carriers \( \mu_n = \mu_p \cdot b \), which turned out to be equal to 160 \text{ cm}^2/(V \cdot \text{s}) \). This, in turn, made it possible to determine the lifetime of minority carriers from the ratio, which turned out to be \( 2.4 \cdot 10^{-8} \text{ s} \).

![Fig. 6. Volt-ampere characteristic of n-Ge – p-Ge1-xSnx heterostructures (0 ≤ x ≤ 0.03) (a) and its straight branch on a logarithmic scale (b).](image)

The pre exponential factor \( I_0 \) in dependence (1) is described by the expression [15]:

\[ I_o = \frac{kT}{q} \cdot \frac{S \cdot b \cdot ch \left( \frac{d}{L_n} \right)}{2(b+1) \cdot L_n \cdot \rho \cdot tg \left( \frac{d}{2L_n} \right)} \]  

(3)

where \( S \) is the sample area, \( \rho \) - is the resistivity of the high resistance layer of the structure. Determining the value of \( I_0 = 8.82 \cdot 10^{-3} \text{ A} \), from the VAC data, the ratio of (3) found the calculated value of the specific resistance of the high-resistance transition layer from the solid solution, which was \( \rho = 2.2 \cdot 10^{3} \Omega \cdot \text{cm} \). The resistivity of the epitaxial layer, measured by the Hall method, was \( 5.3 \cdot 10^{-3} \Omega \cdot \text{cm} \). Apparently, a high-resistance p layer forms between the n-Ge substrate and the p-Ge1-xSnx epitaxial film \((0 \leq x \leq 0.03)\), hence the structure studied can be viewed as an n-p-p+ junction.

The exponential section is followed by areas with power dependencies of the current on voltage, for example, in the voltage range from 0.5 to 0.9 V, a quadratic dependence is observed - \( I = 133 \cdot V^2 \), and then a weaker current dependence is observed to 1.4 V - \( I = 123 \cdot V^{1.3} \), which at \( V > 1.4 \text{ V} \) is replaced by the second quadratic segment - \( I = 87 \cdot V^2 \). Such a dependence of the IVC can be qualitatively explained in the framework of the double injection model for n-p-p+ - structures with ohmic contacts to n- and p+ - layers (Fig. 7) using...
the drift mechanism of current transfer in ohmic relaxation mode taking into account the inertia of electron exchange between recombination complexes. The ohmic relaxation mode of the space charge is realized in the case when the injected space charge is less than the charge of uncompensated acceptors Na (i.e., the current through the OH-n-Ge-p-Ω-n-Ge-p-Ge1-xSnx base containing “negatively charged” recombination complexes of free electrons and holes, respectively, n, p are the statistical factors of Shockley-Reed, \( \tau_{RS} \) - time recombination-stimulated adjustment of \( N_e \). The ratio between the first two members and the last term in the denominator of expression (5) varies depending on the level of excitation of the high-impedance base of the studied structure. The last member of \( c_c c_p \tau_{RS} n p \) grows with arousal level. When the conditions \( c_c (n+n_1) c_p (p+p_1) >> c_c c_p \tau_{RS} n p \) are met, the expression for the recombination rate transformed to the expression of the Shockley-Reed statistic and the so-called Lambert double injection mode takes place. In this case, the solution of equation (4) taking into account the boundary conditions — the nonideality of the injecting contacts: \( n(0) \sim \sqrt{J}, \quad n(d) \sim \sqrt{J} \) (i.e., the current through the np-transition is determined not only by the pure electronic component, but also by the hole one; just the current through the p-p+ transition is not only purely hole component, but also electronic) gives the following form of IVC [18]:

\[
J = \frac{9}{8} \cdot \frac{q \mu_n \tau_n \mu_p N_a}{d^3} \cdot V^2
\]

Expression (6) well describes the quadratic section of the IVC of the investigated structure - \( I = 133 \cdot V^2 \) in the voltage range from 0.5 to 0.9 V. Using (6), the value of \( N_a = 7 \cdot 10^{16} \text{ cm}^3 \) was calculated from the first quadratic section of the IVC.

With an increase in the level of arousal, a moment comes when \( c_c (n+n_1) c_p (p+p_1) \sim c_c c_p \tau_{RS} n p \). In this case, at a sufficiently high level of excitation, when \( c_c \approx c_p \approx n, \) the recombination rate has an next approximate form - \( U = p/(2\tau_n) - c_c \tau_{RS} p/(4\tau_n) \), and solving equation (4) gives the following expression for IVC [18]:

\[
V = \sqrt{\frac{8d^3}{9q \mu_p \mu_n \tau_n N_a}} \cdot M(J) \cdot \sqrt{J}
\]

where \( M(J) = 1 + 3m(2 + C \tau_{RS} \sqrt{J})^2 \), \( m \) and \( C \) are quantities depending on the parameters of the pn-junction and the base. The dependence (7) close to the Lambert mode expresses a weaker dependence of the current on voltage than the quadratic one, which corresponds to the dependence \( I = 123 \cdot V^{1.5} \) in the experimental \( I - V \) plot from 1 to 1.4 V.
At higher excitation levels, when \( c_{n}(n+p) + c_{p}(p+n) \ll c_{n}E_{Rs}E_{np} \), the recombination rate reaches saturation \( U = \frac{N}{\tau RS} \), and the IVC has a quadratic dependence \[ J = B_0 \cdot (V - V_0)^2 \]  
where \[ B_0 = \left( q\mu_n (b + 1)C/d \right)^2 \], \[ V_0 = (b+1)d^2N_R / \left( 2N \mu_n \tau RS \right) \]. Dependence (8) corresponds to the second quadratic plot of the I–V characteristic \( I = 87 \cdot V^2 \) in plot \( V > 1.4 \) V.

**Conclusion**

Thus, it is shown that it is possible in principle to grow perfect single-crystal films of the Ge\(_{1-x}\)Sn\(_x\) substitution solid solution with (111) crystallographic orientation on single-crystal Ge substrates by the method of liquid phase epitaxy from a tin melt solution. Hillocks of nanocrystallites from the Ge\(_{1-x}\)Sn\(_x\) solid solution with a base size of 150 to 400 nm and a height of 5 to 20 nm are formed on the film surface.

The photosensitivity of n-Ge – p-Ge\(_{1-x}\)Sn\(_x\) heterostructures (0 ≤ x ≤ 0.03) covers the spectral photon energy range from 0.4 to 1.4 eV. Grown thin epitaxial layers can be used as photovoltaic material for designing optoelectronic devices operating in the infrared region of the emission spectrum, or as a substrate material for further growth of solid solutions on them.

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**References**


