On the Possibilities for Improving the Efficiency of Radiation in Heterostructures Based on IV-VI Semiconductors

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Abstract. It is shown that, even in isoperiodic heterostructures, significant mismatch arises during the process of epitaxial growth because of interdiffusion of the components at the heteroboundary. As a result, nonradiative recombination at the formed defects increases, which significantly decreases the quantum yield of radiation. The heterostructures with active layers of prex and postxinverse compositions are discussed. For overcoming the adverse effect of diffusion mismatch, it is proposed to bring the composition of the emitter closer to that of the active layer or to dope this layer with the impurities increasing the elastic limit.

1. Introduction
The search for new ways of increasing the operating temperatures of IR semiconductor lasers based on the IV-VI compounds continues [1]. It was noticed that, during the process of epitaxial growth of heterostructure layers, because of interdiffusion of the components and in the case of initially isoperiodic layers, a transition region of a variable composition was formed. The halfwidth of this region is larger than the critical thickness, while the maximum epitaxial deformation in it approximates the limiting value of the elastic state [2, 3]. If we consider the heterostructure as a radiative one, i.e. as an emitter-active layer pair, the approximation of elastic deformations to their critical values (formation of a network of dislocations) can cause decreases in the current carrier lifetime and in the quantum yield of radiation in the active layer.

This work deals with modeling of diffusion mismatch in the IV-VI heterostructures and the investigation of the ways of overcoming its adverse effect on the properties, in particular, of radiating devices (lasers).

2. Diffusion Mismatch Model and its Topicality
Behind the diffusion mismatch model are the experimental and theoretical investigations where the heteroboundary smearing mainly in isoperiodic structures was revealed and assessed [4]. The structures with active layers of pre- and post-inverse compositions were considered. As is well known, in solid solutions of chalcogens with lead and tin, with the increasing tin concentration the forbidden gap width decreases to zero at a certain tin concentration and then increases again in post-inverse compositions. In this case, the derivatives of the forbidden gap width, for instance, by composition and temperature reverse the sign. Table 1 gives the maximum relative mismatch (deformation) \( \frac{\Delta a}{a_0} \) and the values of critical deformations calculated by the interpolation formula. Because of the
difference in the tabular values of components in heterostructure layers at typical epitaxy temperature 500–600 °C, counterflows emerge at the heteroboundary. Owing to high concentration of nonstoichiometric defects >10^{18} \text{cm}^{-3}, the diffusion coefficients of tin and tellurium are taken equal to \(10^{-14}\) and \(10^{-12}\) \text{cm}^2/\text{s}, respectively. The diffusion distribution by composition \((x, y)\) at corresponding values of \(d\), and through them – function \(a(d)\) were determined by the relation:

\[ a = 6.126 - (0.01y + 0.123)x + 0.334y \]

**Table 1.** Maximum relative and critical deformations for active layers of pre-inverse compositions \(\text{Pb}_{1-x}\text{Sn}_x\text{Se}_{1-y}\text{Te}_y\).

| No. | Emitter composition | Active layer composition | \(\Delta y = y_a - y_c\) | \((\Delta a/a_0)_{\text{max}} \times 10^3\) | \(\varepsilon_{\text{cr}} \times 10^3\) |
|-----|---------------------|-------------------------|------------------------|--------------------------------|-------------------------|
| 1   | 0                   | 0.734 0.231 0.825       | 0.091                  | 1.87                          | 1.7                     |
| 2   | 0                   | 0.213 0.178 0.280       | 0.067                  | 1.42                          | 2.11                    |

Taking the plane with the maximum value \(\Delta a/a_0\) as a new heteroboundary, it makes sense to compare the obtained values with critical deformations \(\varepsilon_{\text{cr}}\) obtained when measuring the internal friction [5]. The following \(\varepsilon_{\text{cr}}\) values were obtained for binary compounds \(\varepsilon_{\text{cr}} \times 10^3 : 2.1 \text{(PbSe)}, 3.7 \text{(SnSe)}, 1.8 \text{(PbTe)}, 3.5 \text{(SnTe)}\). In the first and second cases (Table 1), the \(\varepsilon_{\text{cr}}\) values were calculated by the interpolation formula:

\[ \varepsilon_{\text{cr}} = (x, y) = \varepsilon_{\text{PbSe}}(1-x)(1-y) + \varepsilon_{\text{SnSe}}x(1-y) + \varepsilon_{\text{PbTe}}(1-x)y + \varepsilon_{\text{SnTe}}xy \]

The \(\varepsilon_{\text{cr}}\) values given in Table 1 correspond to the elastic limit deformations under torsional vibrations of block monocrystals. Though, for the layers, \(\varepsilon_{\text{cr}}\) values should have been smaller, the maximum relative deformations had some spread of values even without consideration for additional defects by the dislocation density in individual cases and approximated the calculated \(\varepsilon_{\text{cr}}\) values. A similar analysis could be performed by comparing the critical thickness \(h_{\text{cr}}\) with the halfwidth of mismatched regions \(\Delta\). However, because the mismatched region halfwidth appreciably depends on the growth time, while \(h_{\text{cr}}\) changes less in time, such a comparison would be time-dependent as well as in the first case. Although, just at the first consideration by the maximum relative deformations, the elastic state was revealed at the thickness less than \(h_{\text{cr}}\). Thus, relation between \((\Delta a/a_0)_{\text{max}}\) and \(\varepsilon_{\text{cr}}\) and position \((\Delta a/a_0)_{\text{max}}\) near the heteroboundary depend from the growth time and thickness of the layers. Table 2 gives the values of maximum relative and critical deformations for active layers of post-inverse compositions. As is obvious from table 2, in this case the maximum deformations exceeded the elastic limit and plastic deformation occurred, which caused dislocation multiplication, a decrease in the current carrier lifetime and, accordingly, in the quantum yield of radiation. In this case, because of the growing rate of nonradiative recombination, threshold current in lasers increases.

\[ I_{th} \sim \left(\frac{\tau_{\text{ef}}}{\tau}\right)^{-1} = \frac{d + 2S\tau}{d} \]

where \(\tau_{\text{ef}}\) is the current carrier lifetime in the active layer with account for recombination centers at mismatch, \(\tau\) is the initial current carrier lifetime in the active region (corresponding to the current carrier concentration), \(d\) is the active region thickness, \(S\) is the surface recombination rate. In turn, \(S = \sigma \cdot v \cdot N\), where \(\sigma = a^2\) is the recombination cross-section; \(v\) is the thermal velocity of current carriers; \(N = 1/a^2 \cdot \Delta a/a_0\) is the density of recombination centers (two-dimensional density of dislocations).
Table 2. Maximum relative and critical deformations for active layers of post-inverse compositions Pb$_{1-x}$Sn$_x$Se$_{1-x}$Te$_y$

| No. | Emitter composition $y$ | Active layer composition $y$ | $\Delta y = y_a - y_e$ | $(\Delta a/a_0)_{\text{max}} \cdot 10^3$ | $\varepsilon_{\text{cr}} \cdot 10^3$ |
|-----|-------------------------|-------------------------------|-------------------------|------------------------------------------|------------------------------|
| 1   | 0.052                   | 0.720                         | 0.506                   | 0.900                                    | 0.18                        |
|     |                         |                               |                         |                                          | 3.68                        |
|     |                         |                               |                         |                                          | 2.67                        |
| 2   | 0.020                   | 0.177                         | 0.427                   | 0.375                                    | 0.20                        |
|     |                         |                               |                         |                                          | 3.26                        |
|     |                         |                               |                         |                                          | 2.68                        |

Taking into consideration that $\Delta a/a_0$ are maximum values equal to $3 \cdot 10^{-3}$ in the mismatched layer, $v = 3 \cdot 10^7$ cm/s, $\tau = 5 \cdot 10^9$ s and $d = 0.6$ µm, because of diffusion mismatch, the threshold current in lasers increases $\sim 8$ times. Thus, it is important to find the ways of neutralization of the adverse effect of diffusion mismatch.

3. The Ways of Elimination of the Adverse Effect of Diffusion Mismatch on the Characteristics of Radiating Devices (Lasers)

From the above data, it is obvious that, if we decrease the concentration of Te between the active layer and the emitter by 0.024, the maximum mismatch will decrease by almost a fourth. It is possible to decrease significantly the maximum mismatch $(\Delta a/a_0)_{\text{max}}$ by bringing the composition of the emitter closer to that of the active layer with simultaneous doping of the emitter with calcium or strontium. Calcium and strontium have low diffusion coefficients, but their introduction allows avoiding the decrease in the forbidden gap width of the emitter (heterobarrier) when its composition is changed. Table 3 gives the values of maximum relative and critical deformations for post-inverse compositions of active layers.

Table 3. Maximum relative and critical deformations for active layers of post-inverse compositions Pb$_{1-x}$Sn$_x$Se$_{1-x}$Te$_y$ (with bringing of the composition of the emitter closer to that of the active layer)

| No. | Emitter composition $y$ | Active layer composition $y$ | $\Delta y = y_a - y_e$ | $(\Delta a/a_0)_{\text{max}} \cdot 10^3$ | $\varepsilon_{\text{cr}} \cdot 10^3$ |
|-----|-------------------------|-------------------------------|-------------------------|------------------------------------------|------------------------------|
| 1   | 0.205                   | 0.780                         | 0.506                   | 0.900                                    | 0.12                        |
|     |                         |                               |                         |                                          | 2.03                        |
|     |                         |                               |                         |                                          | 3.68                        |
| 2   | 0.205                   | 0.390                         | 0.427                   | 0.375                                    | 0.08                        |
|     |                         |                               |                         |                                          | 1.80                        |
|     |                         |                               |                         |                                          | 3.26                        |

As is seen from table 3, in the result of bringing of the composition of the emitter closer to that of the active layer, the maximum mismatch $(\Delta a/a_0)_{\text{max}}$ in the heterostructure significantly decreases. In the general case the elastic limit was assessed by critical strain $\sigma = E/1 - \nu \cdot \varepsilon_{\text{cr}}$, where E is the modulus of elasticity; $\nu$ is the Poisson ratio; $\varepsilon_{\text{cr}}$ is the critical deformation. In the above cases, the modulus of elasticity was constant. However, as the investigation of internal friction showed [5], the modulus of elasticity increased 1.8–2 times at doping with such impurities as manganese or chrome (decreasing the lattice constant of the layers of IV-VI semiconductors). Then, with account for the 3-fold increase in the critical deformation at doping, the critical strain increased $\sim 6$ times. The possibility of doping of the active layer, especially of doping without decreasing the quantum yield of radiation, could be universal for expanding the elastic deformation range. This opens up possibilities for avoiding the dislocation multiplication, the decrease in the current carrier lifetime and, accordingly, the decrease in
the radiation yield. As a result, actually measurable threshold current decreases by a factor of 5 to 10 and, accordingly, the operating temperature of lasers can be increased. As the lattice constants of considered binary compounds and triple solid solutions of IV-VI semiconductors are higher than those of fourfold ones, in these cases efficient “negative” pressure is realized which maybe used both in lasers and photodetectors [6, 7].

It is noteworthy that of interest are the heterostructures with “temperature-self-regulating” heterojunctions. In the structures of that kind, the emitter is designed on the base of fourfold solid solutions of the pre-inverse composition and active layers of the post-inverse composition and doped by manganese. At the same time, the compositions of the layers are selected so that, at liquid–nitrogen temperature, the forbidden gaps have similar width equal to 0.18 eV. However, because of sign-inverse temperature coefficients \( \frac{dE_g}{dT} \) in these layers, at room temperature \( E_g \) of the active layer decreases, while that of the emitter increases. With consideration for \( \frac{dE_g}{dT} \approx 4 \cdot 10^{-4} \) eV/K , the energy barrier \( \Delta E_g = 0.18 \) eV at room temperature is provided.

4. Conclusions
It is obvious that, according to the model considered, complete matching of the lattice constants of conjugated lattices at the heteroboundary of the layers at technologically conditioned temperature of epitaxial growth yet does not provide the desired matching even with account for corrections made during heterostructure cooling to room temperature. The interdiffusion of components between the layers at the heteroboundary causes disturbances in isoperiodicity, appearance of a mismatched layer and emergence of strain. In most cases, the emerged deformations and, accordingly, strain exceed the elastic limit - the strain relaxes with formation of mismatch dislocations.

In the work, it is shown that bringing of the composition of the emitter closer to that of the active region and doping of this region with manganese impurity on the one hand decreases the maximum relative deformations and on the other hand increases the modulus of elasticity, critical deformations and the elastic limit at large. This allows preventing the strain relaxation, spread of nonradiative recombination centers, and, accordingly, suppressing the threshold current in lasers.

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