Photo-, cathodic- and electroluminescence-band models in solid (SiC)$_{1-x}$(AlN)$_x$ luminescence centers and SiC/SiC-AlN LEDs

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Abstract. The paper presents models of bands (levels) in solid (SiC)$_{1-x}$(AlN)$_x$ luminescence centers and n- SiC/p-(SiC)$_{1-x}$(AlN)$_x$ heterostructures (light-emitting diodes). The diagram of (SiC)$_{1-x}$(AlN)$_x$ energy gaps shows the positions of luminescence levels, subject to x. A SiC/SiC–AlN series of electroluminescence bands, for the first time, is found to have a continuous relationship between the positions of short-wave and long-wave band maxima in a K-minimum conduction band, respectively, as continuous functions of contact current density.

1. Introduction
Wide-band semiconductors and, in particular, solid (SiC)$_{1-x}$(AlN)$_x$ solutions with the energy gap ($E_g$) from 3.3 to 6.0 (eV) are of considerable interest for creating high-temperature, stable, high-voltage instruments, optoelectronic devices in a short-wave region of electro-optic emission. With the advent of new technology, it became possible to obtain heterostructures and almost ideal Schottky barriers, thereby enabling to design power electronic components and devices with extreme characteristics. This is related to an enormous interest from researchers in the physics and wide-band heterostructures. These materials are currently used to develop LEDs, sensors, microwave signal mixers, low-inertia modulated photodetectors and field-effect transistors [1-3]. Their characteristics are attributed to the height of a potential barrier and to surface states and mechanisms of thermionic, thermo-field and field emissions [4-6].

SiC solid solutions are currently being massively studied. In particular, in [7-10], the regions of stabilization of a number of polytypes (3C, 2H, 4H, 6H, 15R) of (SiC)$_{1-x}$(AlN)$_x$ solid solutions at $T = 2370-2190$ °C for compositions $0.04 \leq x \leq 0.95$. The data on photo-, cathodic- and electroluminescence of (SiC)$_{1-x}$(AlN)$_x$ solid solutions and resulting structures are presented. The technology is implemented enabling variband heterostructures of SiC/(SiC)$_{1-x}$(AlN)$_x$ LEDs for ultraviolet (UV) radiation sources.
The authors, based on experimental data available [7], proposed models enabling to determine the positions of levels of a series of photo- and cathodoluminescence (PL/CL) bands as continuous functions of the composition $0.05 \leq x \leq 0.95$ of the target $(\text{SiC})_{1-x} (\text{AlN})_x$ radiation spectrum from 1.8 to 3.8 (eV). It is shown that, subject to a slight variance ($K_x = 1$), a similar model is also suitable for the position of the maxima of a series of electroluminescence emission bands of n-SiC/p-(SiC)$_{1-x}$ (AlN)$_x$ LEDs (heterostructures). A continuous relationship is obtained between the positions of the maxima of a series of long-wave and short-wave transitions in K-, M-minima of the band structure, respectively, and the contact current density. It is shown that as the composition $x$ increases, the energy levels of the luminescence centers shift towards the corresponding energy gaps of $(\text{SiC})_{1-x} (\text{AlN})_x$ LEDs towards a conduction band. This is due to the relocation of luminescence centers in SiC, which are even likely to emerge on the surface of an AlN crystal at $x \approx 1$.

2. Results

**Photo- and cathodoluminescence (PL/CL)** (Figure 1). Based on the experimental data [7] for intense maxima positions of long-wave transitions to the K-minimum conduction band in the case of SiC-AlN luminescence, the following semiempirical formula can be proposed:

$$E_0^\delta = E_g^x - (1 - K_x x) \Delta E_x$$  \hspace{1cm} (1)

Here $E_0^\delta$ is the position of a transition band maximum with a Gaussian distribution:

$$I(E) = A G_0 / [(E - E_0)^2 + G_0^2]$$  \hspace{1cm} (2)

where $A$ is a relative normal distribution at the luminescence band maximum. In case [7] $A = 65G_0$ and max $I(E_0^\delta) = 65$ RU; $G_0$ is the width of the distribution of 0.2 eV order or the width of a possible effective impurity band formed by the levels of luminescence centers with different local nearest neighbours and different depths of their levels.

It is known [7] that the energy gap $E_g^x$ in $(\text{SiC})_{1-x} (\text{AlN})_x$ solid solutions can be represented as:

$$E_g^x = E_g^0 - ax + bx^2$$ \hspace{1cm} (3)

where $E_g^0$ is the position of the luminescence band maximum, $E_g = 3.3$ eV; $a = 0.56$ and $b = 3.86$ (eV).

Thus, for the compositions used in the experiment $x_1 = 0.12; x_2 = 0.24$ and $x_3 = 0.54$ (Figure 1), as well as $x_1 = 0.05; x_2 = 0.24$ (Fig. 2.) we get:

1. $1'$ $x = 0.05; 1, 2 - J = 3 \mu$A; $1', 2' - J = 20 \mu$A (direct current). $2, 2', 3 - x = 0.24; 3 - J = 30 \mu$A (reverse current); $E_1^1, E_1^2$ are transitions to the K-minimum and $E_1^0, E_1^2$ to the M-minimum; $E_3^1, E_3^2 - J = 20$ and $E_3^3 - J = 30$ (\mu$A), respectively. $E_3^3 = 3.28 (x_1 = 0.05); E_3^3 = 3.29 (x_1 = 0.12); E_3^3 = 3.39 (x_1 = 0.24)$ and $E_3^3 = 4.115$ (eV). The parameters $K_1 = K_3 = 0.25; K^2 = 0.02$ in expression $(1 - K_x x)$ are related to the degree of approximation of the $E_0^\delta$ level to the corresponding energy gap (Figure 3).

The energy $\Delta E_x$ is an average depth of impurity luminescence centers: donors (for example, V is vanadium and O is oxygen) and acceptors (Al-aluminum, N-nitrogen). The depth of donor levels refers to the $E_c$ conduction band, and of the acceptor levels to the $E_v$ valence band, respectively. According to [11, 12, 13], for the depths of impurity centers (V, O and Al, N) we have:

$$V, E_c = 0.97 \div 0.70; \quad G_0' = 0.27; \quad Al, E_c = 0.27 \div 0.10; G_0' = 0.17;$$
$$O, E_c = 0.90 \div 0.95; G_0' = 0.05; \quad N, E_v = 0.142 \div 0.081; G_0' = 0.061$$ (eV).
Figure 1. Spectra and level diagram of photoluminescence 1,2 and cathodoluminescence 3, at x: (1) – 0.12, (2) – 0.24, (3) – 0.54; T=77 °K for (SiC)\(_{1-x}\)(AlN)\(_x\) LEDs [7]

Figure 2. Spectra and diagram of electroluminescence levels of SiC/(SiC)\(_{1-x}\)(AlN)\(_x\) LEDs at 300 °K [7]

The average value of \(G_0\) in the experiment is 0.2 eV.

Certainly, other luminescence centers, defects and impurities found to be present in SiC can also contribute to the emission. In this case, as can be seen from the data presented in (4) for probable emission centers (V, O and Al, N), the distribution of depths or widths of arising impurity zones is generally quite significant. Therefore, assessing the positions of emission band maxima, subject to the experimental data, is based on the following average values:

For V and O: \(\Delta E_1=\Delta E_3=1.24; (K_1=K_3=0.25)\),

Whereas, for Al and N: \(\Delta E_2=1.05, (K_2=0.02=K)\). \(\text{(5)}\)

Then, for the positions of SiC-AlN luminescence maxima in the K-minimum conduction band for intense long-wave transitions, according to (1), we find:

\[
2.29 - (1 - 0.25 \cdot 0.12)1.24=2.09= E_{01},
\]

\[
E_0(x_1,x_2,x_3) = 2.39 - (1 - 0.2 \cdot 0.24)1.05=2.41= E_{02},
\]

\[
4.115 - (1 - 0.25 \cdot 0.54)1.24=3.24= E_{03}\text{ (eV)}.
\]

The output values of energy maxima for the corresponding emission bands are in line with the experimental data and are given in Table 1.
Table 1. Calculated (C) and experimental (E) positions of PL/CL emission band maxima of SiC/AlN at 77 ºK

| Uel | PL (eV) | CL (eV) |
|-----|---------|---------|
|     | $E_0$   | $E_0^{1}$ | $E_0^{2}$ | $E_0^{1i}$ | $E_0^{2i}$ | $E_0^{3}$ | $E_0^{3i}$ |
| $\xi$ | 0.12   | 0.24   | 0.12   | 0.24   | 0.54   | 0.54   |
| $E_0^{E}$ | 2.10 | 2.44 | 2.61 | 3.08 | 3.25 | 3.82 |
| $E_0^{C}$ | 2.09 | 2.41 | 2.62 | 3.10 | 3.24 | 3.81 |

For less dense short-wave emission bands, which are most likely due to transitions to the K-minimum conduction band, based on the relevant parameters of the occurrence of levels (states) $\xi_i$ and experimental outputs, we obtain:

$$E_0^{x}=E_g^{x} (\xi_i+\xi).$$  \hspace{1cm} (7)

Where $\xi_i=0.68=0.7=\xi_2=\xi_3$ parameters are meant to indicate that the bands corresponding to this emission are likely to correspond to impurity centers located near the heterointerface, the surface of the (SiC)$_{1-x}$(AlN)$_x$ epitaxial layer or surface states [11]. In this case, for $E_0^{x1}$ and $E_0^{x2}$ emission maxima, we find:

$$E_0^{x1}=E_g^{x1}-\Delta E=4.11-1.05=3.06(eV).$$ \hspace{1cm} (8)

$$E_0^{x2}=E_g^{x2}-\Delta E=3.39-1.05=2.34(eV).$$ \hspace{1cm} (9)

The output values by (7) and (9) agree with the experimental data and are shown in Table 1. As a result, formulas (1), (7), and (9) ensure good agreement with the data on the (SiC)$_{1-x}$(AlN)$_x$ EL luminescence in a wide energy range $1.80 \leq h\nu \leq 3.90$ (eV).

Electroluminescence of SiC/(SiC)$_{1-x}$(AlN)$_x$ LEDs (Figure 2). For a series of n-SiC/p-(SiC)$_{1-x}$(AlN)$_x$ LEDs bands, similarly to (1) at $K=x=1$, in accordance with the experimental data, we find:

$$E_0^{x}=E_g^{x}-(1-x)\Delta E.$$ \hspace{1cm} (10)

Here, $\Delta E \equiv \Delta E_2 \equiv 1.05$, and the factor $(1-x)$ determines the degree of approximation of the levels (bands) $E_0^{x}$ to the corresponding gap $E_g^{x}$ as the composition $x$ enhances (see Fig. 3). In this case, for the maxima of $E_0^{x1}$ and $E_0^{x2}$ long-wave luminescence bands at $x_1=0.05$; $E_g^{x1}=3.28$ and $x_2=0.24$; $E_g^{x2}=3.39$, according to (10), we obtain:

$$E_0^{x1}=3.28-(1-0.05)1.05 =2.62=E_0^{x1},$$
$$E_0^{x2}=3.39-(1-0.24)1.05 =2.63=E_0^{x2}(eV).$$ \hspace{1cm} (11)

For the maxima of less intense short-wave emission bands of $E_0^{x1}$ and $E_0^{x2}$ LEDs at the corresponding values $x_1=0.05$; $x_2=0.24$ and $\xi_2=0.73$; $\xi_2=0.65$, according to (7) we find:

$$E_0^{x1}=3.28(0.73+0.05) =2.56=E_0^{x1},$$
$$E_0^{x2}=3.39 (0.65+0.24) =3.01=E_0^{x2}(eV).$$ \hspace{1cm} (12)
The presence of $J_i$ current density through the LED contact results in a deviation of emission bands to a short-wave region of the spectrum. In this case, if the derivative $dE_0^i/dJ_i=tg\alpha$ is denoted by $\beta$, then, similarly to (10), with an increment of the current $\Delta J_i$ for the maxima of emission bands, we obtain:

$$E_i^s = E_0^s + \beta (1-x) \Delta J_i.$$

(13)

Whereas the experimental data, $\beta = 0.010-0.012$. If we assume that at $x=0.05$ the maximum of the luminescence band is $E_0^{s, i}=2.53$ and $\Delta J_i=3$, then for the initial $E_0^{i, 1}$ band (i.e., for the maximum of the first electroluminescence band $E_0^{i, 1}$) according to formula (13) we find:

$$E_i^s = 2.53+0.01(1-0.05)3 = 2.56 \text{ (eV)}.$$

(14)

This corresponds to an experimental value of 2.55 eV (Table 2).

| $E_0$ = $E_0^{i, 0}(\text{eV})$ | $E_0^{i, 1}$ | $E_0^{i, 2}$ | $E_0^{i, 3}$ | $E_0^{i, 4}$ | $E_0^{i, 5}$ |
|-----------------|---------------|---------------|---------------|---------------|---------------|
| $J$, $\mu A$    |               |               |               |               |               |
| 0.05            | 2.25          | 2.51          | 2.62          | 3.00          | 2.69          |
| 0.24            | 3.00          | 2.69          | 3.10          | 2.70          | 3.12          |
| 0.24            | 3.00          | 2.69          | 3.10          | 2.70          | 3.12          |

For the maxima of electroluminescence bands in the presence of contact currents, similarly to (13), we obtain:

$$E_{0j}^i = E_{0j}^s + \beta (1-x) \Delta J_i,$$

(15)

Then for the values $x_1=0.05; x_2=x_3=0.24$ and contact currents $J_1=3, J_2=20$ and $J_3=30$ ($\mu A$), given that $\Delta J_1=17, \Delta J_2=17$ and $\Delta J_3=27$, according to formula (15), we find:

$$E_{0j}^i = E_{0j}^s + \beta (1-x) \Delta J_i, \Delta J_i = Jx - Jx(i-1)$$

(16)

The output values of the maxima of the emission bands in the presence of contact currents agree with the experimental data [7] for SiC/(SiC)$_{1-x}$(AlN)$_x$ and are given in Table 2.

**Table 2. Calculated vs experimental positions of SiC/AlN emission maxima**

| $E_0^i$ (eV) | $E_0^{i, 1}$ | $E_0^{i, 2}$ | $E_0^{i, 3}$ | $E_0^{i, 4}$ | $E_0^{i, 5}$ |
|--------------|--------------|--------------|--------------|--------------|--------------|
| 2.25         | 2.51         | 2.62         | 3.00         | 2.69         | 3.10         |
| 2.56         | 3.01         | 2.70         | 3.12         | 3.27         |

Level positions of luminescence centers as continuous functions of composition $x$.

Let us estimate the relationship between the composition $x$ and the level deviations of the (SiC)$_{1-x}$(AlN)$_x$ luminescence centers for the maxima of the long-wave $\nu^1$, and short-wave $\nu^5$ transitions, respectively. These deviations of the levels of the luminescence centers with increasing $x$ are estimated with respect to the energy gaps of the band structure and appear when $x$ deviate from 0 to 1 (Figure 3).

The calculated values of maxima positions of $E_0^i$ and $E_0^{i, 5}$ photo- and cathodoluminescence bands can be plotted on the diagram of the main energy gaps ((SiC)$_{1-x}$(AlN)$_x$) [7] Figure 4). The positions of these maxima enable to determine the corresponding variance of the luminescence centers for the compositions $x_1, x_2, x_3$, as well as for arbitrary $x$ using formulas (1), (7), (10), (15). The corresponding variance of the luminescence centers are shown in Fig. 3. It can be seen that along lines 5, 5’ and 6, 6’, (dashed line), the emission maxima approximate the corresponding gaps of (SiC)$_{1-x}$(AlN)$_x$ band as the composition enhances from $x=0.05$ to $x=0.65$. Such deviations of luminescence levels are apparently caused by the relevant relocation of luminescence centers, defects and variance in their immediate environment. It is possible that at $x \to 1$ some defects could appear on the surface of AlN crystal. It would be interesting to try to verify the latter assumption in the course of special experiments.
Assumption is associated with both the displacement of the corresponding luminescence centers and
the rearrangement of the band structure. With a variance in x from 0 to 1, the energy gap increases
according to (6) from 3.3 to 6.6 eV during the transition from SiC to AlN. The depths of impurity
levels and $\nabla x L$ reduce, which can be seen from Table 3. The values $\nabla x L = 0.90$ and $\nabla x S = 0.31$ (eV),
(Table 3, line 3), within the limits 0.05±0.10 eV, escape the general scheme of band gaps ([7] Figure
4), since the corresponding cathodoluminescence transitions occur in deeper levels of luminescence
centers.

Table 3. Parameters of luminescence depths from $x_1$, $x_2$, $x_3$ compositions

| x   | $\nabla x L$ (eV) | $\nabla x S$ (eV) |
|-----|----------------|-----------------|
| 0.12| 1.20           | 0.69            |
| 0.24| 1.01           | 0.31 0.34       |
| 0.54| 0.90           | 0.31            |

The derived curves are shown in Figure 3.

Figure 3. Composition x vs (SiC)$_{1-x}$(AlN)$_x$, energy gaps ([7] Figure 4) and luminescence depths for $\nabla x S$ and $\nabla x L$ transitions

Curves 5, 5' and 6, 6' constructed according to formulas (1), (7), (9); points (Δ – 5, 5') and (Ο –
6, 6') were calculated for a series of compositions $x_i$, (SiC)$_{1-x}$(AlN)$_x$, respectively.

3. Conclusion

For the first time, models were proposed, enabling to determine the positions of emission band
maxima in the region $1.80 \leq h\nu \leq 3.90$ (eV) as continuous functions of the composition x in the region
of stable polytype structures (SiC)$_{1-x}$(AlN)$_x$ at $x \geq 0.05$ and $T \geq 2100$ K. On the energy diagram of the
SiC – AlN gaps, the positions of the luminescence levels are determined as continuous functions of the
composition. It is shown that as the composition x ($0.05 \leq x \leq 1.0$) increases, the luminescence depths
deviate towards the conduction band. This is apparently due to the fact that the photoluminescence
centers are relocated or possibly even emerge on the surface of the AlN crystal at $x \to 1$. The authors
defined the relationship between the position of the maxima of the bands of direct and indirect
transitions of photo-, cathode -, electroluminescence (SiC)$_{1-x}$(AlN)$_x$ and SiC/SiC – AlN LEDs, the
composition x and the value of the contact current density of the LED transition.

Long-wavel luminescence bands characteristic of SiC appear to arise due to the transition of
electrons from the (SiC)$_{1-x}$(AlN)$_x$ epitaxial layers to a narrower-gap SiC substrate. Short-wave bands
are attributed to the emission of impurities from epitaxial layers located near heterointerfaces or
surface states in the contact region. Formulas (1), (7), (10), (15) make it possible to continuously trace
the rearrangement of emission bands and predict the position of the maxima of the emission spectra bands of (SiC)$_{1-x}$,(AlN)$_x$ luminescence centers and SiC/(SiC)$_{1-x}$,(AlN)$_x$ LEDs over the entire region of the visible spectrum when the composition of x changes from 0 to 1.

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