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Research Article

Electron and hole injection barriers between silicon substrate and RF magnetron sputtered In_2O_3 : Er films

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Abstract

 In_2O_3 : Er films have been synthesized on silicon substrates by RF magnetron sputter deposition. The currents through the synthesized metal/oxide/semiconductor (MOS) structures (Si/In₂O₃: Er/In-contact) have been measured for *n* and *p* type conductivity silicon substrates and described within the model of majority carrier thermoemission through the barrier, with bias voltage correction to the silicon potential drop. The electron and hole injection barriers between the silicon substrate and the film have been found to be 0.14 and 0.3 eV, respectively, by measuring the temperature dependence of the forward current at a low sub-barrier bias. The resulting low hole injection barrier is accounted for by the presence of defect state density spreading from the valence band edge into the In₂O₃: Er band gap to form a hole conduction channel. The presence of defect state density in the In₂O₃ : Er band gap is confirmed by photoluminescence data in the respective energy range 1.55–3.0 eV. The band structure of the Si/In₂O₃ : Er heterojunction has been analyzed. The energy gap between the In₂O₃ : Er conduction band electrons and the band gap conduction channel holes has been estimated to be 1.56 eV.

Keywords

silicon, indium oxide, erbium, thin films, heterojunction, band structure, band discontinuity, barrier, injection, thermoemission, electrons, holes

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1. Introduction

The integration of fiber-optic data communication systems directly in processors will seemingly be the next development step of computing systems. In 2015 a CPU was demonstrated featuring core-memory data exchange via a single fiber-optic line by means of an external laser [1, 2]. Industrial implementation of this system requires integration of light-emitting diodes (LED) with a wavelength within the transparency window of fiber-optic lines (1.5 μ m) inside the CPU, i.e., on silicon [3, 4].

The common approach to this task world over is to employ a complex technological process of transferring a proven A3-B5 LED material (InGaAs) to a silicon substrate, by either transferring and bonding to the substrate [3, 4], or direct growth on the substrate by molecular beam epitaxy (MBE) [3, 5, 6]. This process is complex and expensive but reliable and promising. Currently research in this domain is focused on avoiding degradation, i.e., aging of the material [6-8]. A prominent result was achieved: a LED remaining stable over continuous operation at 80 °C for 1200 h, from which the LED time to failure was extrapolated to be 22 years [9]. Despite the encouraging success in this endeavor, the above cited time to failure estimate still has to be confirmed, especially for up to 90 °C CPU operation conditions. However the complexity and high cost of A3-B5 technology transfer to silicon still delays the industrial application of this process in CPUs and gives impetus for the research community to explore alternative solutions that may be less efficient than $A^{\text{III}}B^{\text{V}}$ technologies but cheaper.

One technologically simple and cheap alternative is the use of erbium ions Er^{3+} having the 1.54 µm wavelength ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ intracenter transition [10, 11] in the transparency window of fiber-optic lines.

Starting from the earliest works by H. Ennen [12], a direct approach has been developed, i.e., direct erbium atom incorporation in silicon (Si: Er) [13–16]. This approach has the advantage of simplicity and compatibility with silicon technologies. However, despite the appreciable effort of the international research community, LEDs synthesized employing this approach had too low guantum efficiency [15, 16] for practical implementation. One origin of this drawback was the technological complexity of heavy silicon doping with erbium atoms in an optically active state [13, 17, 18]. Another unresolved issue is thermal quenching of photoluminescence (PL) at room temperature as a result of reverse de-excitation of erbium ions generating electron-hole pairs in silicon lattice without photon emission (the so-called back transfer) [13, 19, 20].

It is well-known from literature that erbium de-excitation processes observed in silicon are suppressed in dielectrics since erbium PL occurs at room temperature in a wide range of dielectrics [13]. This is the fundamental operation principle of fiber-optic lasers and amplifiers with Er atoms in SiO₂ based dielectric optic fiber [21]. The difference is that Er is excited in the optic fiber by external A3-B5 LEDs. However, Er should be electrically excited by passing current. Electroluminescence **(EL)** was demonstrated earlier for erbium and a range of other rare-earth elements in silicon oxide [22, 23] and other dielectrics such as Si_3N_4 [24], TiO_2 [25] etc. upon hot-electron impact excitation in strong electric fields. The high-energy electron impact excitation cross-section for erbium was found to be $6 \cdot 10^{-15}$ cm⁻² [22]. However, the high electron injection barrier between silicon and these dielectrics (~3.2 eV for Si/SiO₂) leads to low injection currents and high working electric fields [22–24]. Furthermore, hot electron impact excitation of erbium has a very low efficiency as compared with electron-hole pair recombination excitation.

There were a number of works demonstrating the possibility of generating room temperature EL of Er ions in optically transparent oxides, e.g. ZnO [26] and TiO₂ [27], where Er is excited by the electron-hole pair recombination mechanism. However, the lattice defect ZnO band gap levels proved to be optically active in the visible range [26]. In TiO₂, the lattice defect band gap levels excite the visible range Er³⁺ levels [27]. This makes the fundamental infrared (IR) 1.54 µm emission in these oxides inefficient. The above-cited works state the problem of choosing a more suitable oxide for erbium atom excitation by the efficient electron-hole pair recombination mechanism. The test oxide was erbium doped indium oxide $(In_2O_3: Er)$. This choice was based on the fact that room-temperature PL of Er in indium oxide was observed earlier [28, 29], e.g. by us [30]. Its related material ITO $(In_2O_3:SnO_2)$ is well-known and was tested in the synthesis of optically transparent conducting layers [31, 32].

The first problem to be solved is to develop conditions for the injection of both carrier types (electrons and holes) from silicon to In_2O_3 : Er films. This requires finding the height of the carrier injection barriers at the Si/In₂O₃: Er heterointerface. Literary data on band discontinuity at the Si/In₂O₃ heterointerface are scarce and very inconsistent. Theoretical calculation yielded a negative electron injection barrier between silicon and indium oxide [33]. Open circuit voltage and short circuit current measurements for a Si/In₂O₃ heterointerface solar cell showed the electron affinity of In₂O₃ to be 4.45 eV [34]. Comparison with the electron affinity of Si (4.05 eV) also yields a negative electron injection barrier. However, the same work [33] contains a reference to unpublished Si/In₂O₃ electron injection barrier data of +0.61 eV. For the related material on the p-Si/In₂O₃: Mo heterostructure, I–V measurements showed the conduction band discontinuity to be +0.86 eV [35]. Despite the noticeable scatter of literary data, one can expect the electron injection barrier to Si/In₂O₃ to be low, taking into account the intrinsic *n* type of conductivity of undoped In_2O_3 [36, 37] originating from its intrinsic defects, i.e., oxygen vacancies, as well as the well-known application of *n* type conductivity doped In_2O_3 : SnO₂ (ITO) in optically transparent conducting layers and contacts [31, 32].

In the previous work [30] the Authors found the electron injection barrier between n type conductivity silicon substrates and In_2O_3 : Er films to be $\Phi_{ef} = 0.14 \text{ eV}$ (Fig. 1). This barrier is low and electrons can easily be injected through it. However, the magnitude of this barrier questions the possibility of hole injection from silicon. Proceeding from the well-known literary data on the silicon band gap $E_{gSi} = 1.12$ eV and the indium oxide fundamental band gap $E_{gIn2O3} = 2.69 \div 2.93$ eV [38, 39], the hole injection barrier between silicon and In2O3: Er film should be equal to the valence band (E_V) discontinuity between these materials, i.e., approximately 1.64 eV (see Fig. 1 b). That high hole injection barrier makes it seemingly impossible at a first glance to achieve simultaneous opposite injection and transport of electrons and holes in In_2O_3 : Er films.

The aim of this work is to find, using direct electrical methods, the hole injection barrier between the *p* type conductivity silicon substrate and the films (Φ_{hf} for *p*-Si/In₂O₃ : Er) and correct the band structure of the Si/ In₂O₃ : Er heterointerface taking into account the estimated electron and hole injection barriers.

2. Experimental

In₂O₃: Er were sputtered onto *n* and *p* type conductivity (100) silicon substrates (KEF 7.5 and KDB 7.5, respectively). For back contact doping the back sides of the *n* and *p* type conductivity substrates were implanted with 10^{15} cm⁻² 100 keV As⁺ ions and 10^{15} cm⁻² 30 keV B⁺ ions, respectively, and heat-treated at 1000 °C for 1 h in an inert argon (Ar) gas atmosphere. Before film deposition the silicon substrates were RCA chemically treated [40].



Figure 1. Schematic band diagrams of n-Si/In₂O₃: Er heterostructure for (*a*) forward and (*b*) reverse bias showing earlier estimated [30] electron injection barrier 1 between silicon and In₂O₃: Er film (0.14 eV) and barrier 2 between surface indium contact and film (0.21 eV)

- Ar flow 8 sccm, O_2 flow 2 sccm (1 sccm = standard cm³/min);

- chamber working pressure $P = 6 \cdot 10^{-3}$ mbar;

- magnetron power $W_{\rm RF} = 120$ W;
- power unit frequency 13.56 MHz;
- substrate temperature 100 °C;
- deposition time t = 50 min.

This deposition mode produced 200 nm In_2O_3 : Er films on *n* type conductivity substrates. 60 nm In_2O_3 : Er films were deposited on *p* type conductivity substrates under different conditions, i.e., Ar flow 20 sccm, O_2 flow 20 sccm, $W_{RF} = 100$ W, but the final film structure proved to be the same.

The microstructure of the films [30] represents an array of ~ 10 nm diam. nanowires densely grouped in bunches (discrete 50–100 nm diam. nanorods) spreading from the substrate to the film surface. All the nanowires have a body-centered cubic (bcc) In₂O₃ lattice (PDF No. 01-071-2194) but each nanowire has an individual orientation [30].

Top metallic indium contacts were applied through a $0.7 \times 0.7 \text{ mm}^2$ mask. The back-side contacts were produced by In sputtering without masks on the whole back surface area.

The I–V curves and their temperature functions for the Si/In_2O_3 : Er/In-contact structures were recorded on Keithley 4200-SCS and Keithley 2400 equipment fitted with Linkam LTS420E PB4 temperature control modules.

Steady-state PL was excited with a 325 nm He–Cd laser, power density 1 W/cm². The emission spectrum was recorded with an SDL-1 double monochromator spectrometer fitted with a photomultiplier at room temperature.

3. Results and discussion

3.1. I-V curves of *n*-Si/In₂O₃ : Er structure

Figure 2 *a* shows the I–V curve of structures on *n* type conductivity silicon substrates (*n*-Si/In₂O₃ : Er) for room temperature and 300, 350 and 360 K. At a low positive (forward) top contact bias (0 to +0.5 V) the current through the structure is controlled by electron injection from *n* type conductivity silicon over a forward barrier (Φ_{ef}) at the Si/In₂O₃ : Er interface to the film (the so-called sub-barrier mode, Fig. 1 *a*). Since the barrier height decreases due to the applied bias ($\Phi_{ef} - V_{Si}$, where V_{Si} is the silicon potential drop, Fig. 1 *a*), the current through the barrier exhibits an exponential growth depending on the bias. Furthermore, the sub-barrier current through the barrier increases with temperature (Fig. 2 *a*) in the 0 < V < 0.5 rang. This growth is controlled by the high-en-



Figure 2. Analysis of Si/In₂O₃ : Er/In-contact structure I–V curves for *n* type conductivity silicon substrates: (*a*) I–V curves for different temperatures for forward (+*V*) and reverse (–*V*) bias; (*b*) approximation of forward (+*V*) currents (J_f) through the barrier as per Eq. (1b); (*c*) corrected approximation of forward (+ V_{si}) currents J_f through the barrier as per Eq. (3)

ergy tail of Boltzmann's electron distribution curve for silicon: the higher the temperature, the more electrons capable of overcoming the barrier and the higher the current, pursuant to the electron thermoemission model [41]. For a sufficiently high forward bias 0.5 < V < 2 V (Fig. 2 *a*) the band bending in silicon becomes greater than the barrier height (Fig. 3 *a*) and all the carriers, i.e., substrate electrons, can easily overcome the barrier (over-barrier mode). In over-barrier mode the current through the structure is controlled by the resistance of the space charge region (**SCR**) in silicon and the In₂O₃: Er film resistance. The current *vs* temperature dependence in over-barrier mode is inverse to that for sub-barrier mode, i.e., the current declines with an increase in temperature. This behavior is controlled by the temperature function of

the conductivity, more specifically, the carrier mobility: the higher the temperature, the lower the mobility since high-temperature carrier mobility is mainly controlled by carrier scattering at lattice phonons [36].

At a negative (reverse) bias applied to the top In contact, electrons are injected from the metal to the film through the backward barrier (Φ_{eb}) at the In/In₂O₃ : Er interface (Fig. 1 *b*). At sufficiently high temperatures (room and above) the backward currents have a saturated pattern (Fig. 2 *a*) in accordance with the barrier thermoemission model [41]:

$$J = J_{\rm s} \left[\exp\left(\frac{V}{nkT}\right) - 1 \right]. \tag{1a}$$

For the forward branch V > 3kT the simplified expression (Eq. (1a)) has an exponential growth pattern:

$$J = J_{\rm s} \exp\left(\frac{V}{nkT}\right),\tag{1b}$$

where V is the bias, n is the nonideality factor, k is Boltzmann's constant, T is the absolute temperature and J_s is the saturation backward current determined as follows:

$$J_{\rm s} = A^R T^2 \exp\left(-\frac{\Phi}{kT}\right),\tag{2}$$

where Φ is the barrier height and A^R is Richardson's constant ($A^R = 120 \text{ A/(cm}^2 \cdot \text{K}^2)$) for electrons in silicon and $A^R = 30 \text{ A/(cm}^2 \cdot \text{K}^2)$ for holes in silicon [41]).

Figure 2 *b* shows an exponential approximation of the forward I–V curve branches for low bias (at the sub-barrier section) as per Eq. (1b). It can be seen from Fig. 2 *b* that the initial I–V curve sections can be described with exponents but the nonideality coefficients prove to be excessively large ($n = 3 \div 5$). Correct analysis requires taking into account that the *n*-Si/In₂O₃ : Er/In-contact structure in question is a metal/dielectric/semiconductor (**MDS**) or a metal/oxide/semiconductor (**MOS**) structure where the In₂O₃ : Er is the intermediate dielectric layer between the silicon substrate and the metallic contact. Although In₂O₃ is not a classic dielectric but rather a wide-band semiconductor ($E_{gIn_2O_3} = 2.69 \div 2.93$ eV [38, 39]) and has a low electron injection barrier as will be shown below, its barrier current expression (Eq. (1b)) should be corrected.

To correct Eq. (1b) one should take into account that bias applied to an MDS structure drops not only in the silicon SCR but also in the dielectric, with the barrier height

$$J = J_{\rm s} \exp\left(-\frac{V_{\rm Si}}{nkT}\right). \tag{3}$$

The silicon potential drop V_{Si} as a function of the bias V was calculated by numerically solving Poisson's equation in Boltzmann's carrier statistics approximation [41] and is shown in Fig. 3 b for different temperatures by solid curves for the KEF 7.5 n type conductivity Si substrate. The respective calculated curves for the Si/SiO₂ system were reported in the cited work [41]. Those curves can be used with a dielectric permeability correction for In₂O₃ ($\varepsilon_{\text{In}_2\text{O}_3} = 8.9$ [31, 32]) instead of SiO₂. Reconstructing the I–V curves in the silicon potential drop coordinates (V_{Si}) instead of the applied bias ones (Fig. 2 c) provides a good fit between the resultant I–V curves and the exponent described by Eq. (3). The nonideality coefficient is close to unity in this case (Fig. 2 c).

Thus the initial (sub-barrier) sections of the forward I-V curves for the *n*-Si/In₂O₃: Er structures can be described within the barrier thermoemission model with a silicon potential drop correction of the bias.

3.2. I–V curves of *p*-Si/In₂O₃ : Er structure

Figure 4 *a* shows the I–V curve of structures on *p* type conductivity silicon substrates (p-Si/In₂O₃: Er) for room temperature and 280, 300 and 400 K. These curves also demonstrate a rectifying pattern, by analogy with those



Figure 3. Barrier thermoemission model correction (Eq. (1b)) for silicon potential drop (Eq. (3)): (*a*) band structure calculation in electrostatic approximation (Poisson's equation and Boltzmann's carrier distribution [41]) for T = 360 K; (*b*) $V_{Si}(V)$ calculation for different temperatures *T* (solid curves are for KEF 7.5 *n* type conductivity Si substrate and 200 nm In₂O₃: Er film, dashed curves are for KDB 7.5 *p* type conductivity Si substrate and 60 nm In₂O₃: Er film)

for the *n* type conductivity silicon substrate (Fig. 2 *a*) but with an inverse polarity: the forward branch (negative bias) corresponds to hole injection from the *p* type conductivity substrate to the film through the forward barrier Φ_{hf} (Fig. 1 *b*) while the backward branch (positive bias), to hole injection from the surface metal contact to the film through the backward barrier Φ_{hb} (Fig. 1 *a*). The forward I–V curve branch also has a sub-barrier current section from 0 to –1 V and a over-barrier current section from –1 to –3 V (Fig. 4 *a*). By analogy with electron injection, the sub-barrier current for hole injection grows with an increase in temperature following the increase in the concentration of over-barrier energy holes in Boltzmann's distribution. Whereas for electron injection the sub-barrier mode is at 0 to +0.5 V, for hole injection the sub-barrier mode covers a wider range, from 0 to -1 V which may indicate a higher hole injection barrier which is nevertheless lower than it follows from the valence band discontinuity (1.64 eV, see Fig. 1 *b*). The forward over-barrier current in the -1 to -3 V range (Fig. 4 *a*) drops with an increase in temperature by analogy with the case of the *n* type conductivity substrate since it is controlled by the same carrier scattering mechanism, i.e., at lattice phonons [36]. For a reverse bias (0 – +5 V) the currents have a saturating pattern in accordance with the barrier thermoemission model as per Eq. (1a) [41].

By analogy with the electron injection case discussed above (Figs. 2 and 3), hole injection from the *p* type conductivity substrate through the barrier to the In_2O_3 : Er film was also analyzed within the barrier thermoemission



Figure 4. Analysis of Si/In₂O₃: Er/In contact structure I–V curves for *p* type conductivity silicon substrates: (*a*) I–V curves for different temperatures for forward (–*V*) and reverse (+*V*) bias; (*b*) approximation of forward (–*V*) currents (J_f) through the barrier as per Eq. (1b); (*c*) corrected approximation of forward (– V_{Si}) currents J_f through the barrier as per Eq. (3)



Figure 5. Forward current *vs* temperature functions in Schottky coordinates at low sub-barrier bias (color dashed lines) and backward currents at saturation (gray dashed lines) for Si/In₂O₃: Er structures on (*a*) n and (*b*) *p* type conductivity silicon substrates. Slope and barrier height analysis for electron and hole injection

model. Figure 4 b shows I-V curve exponential approximation in accordance with uncorrected Eq. (1b). The nonideality coefficients prove to be large $(n = 5 \div 7)$. Then, by analogy with the solution of Poisson's equation in Boltzmann's carrier statistics approximation, the KDB 7.5 p type conductivity Si substrate / 60 nm thick In₂O₃ dielectric MOS structure ($\varepsilon_{In_2O_3} = 8.9 [31, 32]$) was simulated for different bias ($V = 0 \div -3$ V) and 228, 300 and 400 K. For each bias the silicon potential drop $V_{\rm Si}$ was found. The calculated V_{Si} vs V curves are shown in Fig. 3 b by dashes. Figure 4 c shows the I–V curves for forward currents $J_{\rm f}$ as a function of silicon potential drop. Then the initial (sub-barrier) sections of the I–V curves can be approximated with exponents in accordance with corrected Eq. (3) and the nonideality coefficients will be close to unity (n = 1).

Thus the initial I–V curve sections for the Si/In_2O_3 : Er structures on silicon substrates, whether *n* or *p* type conductivity, can be described within the majority carrier barrier thermoemission model with a silicon potential drop correction of the bias.

3.3. Determination of electron injection barrier height between n type conductivity silicon substrate and In₂O₃: Er film

To determine the forward electron injection barrier Φ_{ef} between *n* type conductivity silicon and the In₂O₃ : Er film (Fig. 1 *a*), we measured the forward current *vs* temperature functions at low bias in sub-barrier mode V = +0.2 and +0.4 V (Fig. 2 *a*). To determine the backward electron injection barrier Φ_{eb} between the metallic In contact and

the In₂O₃: Er film (Fig. 1 *b*), we measured the backward current *vs* temperature functions at saturation V = -2 V (Fig. 2 *a*). The resultant temperature functions were plotted in Schottky coordinates in accordance with Eqs. (2) and (3) (Fig. 5 *a*).

For reverse bias at saturation V = -2 V (Fig. 2 *a*), the backward current *vs* temperature function in Schottky coordinates (Fig. 5 *a*, grey dashes) fits a line the slope of which corresponds to the backward electron injection barrier height between the metallic In contact and the In₂O₃: Er film: $\Phi_{eb} = 0.21$ eV (Fig. 1 *b*). At low temperatures (T < 150 K, see Fig. 5 *a*) the backward current no longer depends on temperature, probably due to a change of the current mechanism from thermoemision to barrier tunneling.

For low forward sub-barrier bias V = +0.2 and +0.4 V (Fig. 2 a) the current vs temperature functions in Schottky coordinates have 82 and 14 meV slopes, respectively (Fig. 5 a, red and green dashed lines) corresponding to the forward barrier height less the silicon potential drop, i.e., $\Phi_{ef} - V_{Si}$ (Fig. 1 *a*). Addition of $V_{Si} = 61$ and 94 mV (Fig. 3 b, blue solid line) yields the forward electron injection barrier height between silicon and the films $(n-\text{Si/In}_2\text{O}_3:\text{Er})$ $\Phi_{\text{ef}} = 0.143$ and 0.108 eV, respectively. However, since V = +0.4 is already close to the over-barrier mode (Fig. 3 a), barrier thermoemission is coupled with barrier tunneling and the thermoemission barrier height $\Phi_{ef} = 0.108 \text{ eV}$ appears to be underestimated. Thus, a more correct barrier height estimate can be obtained in purely sub-barrier mode at low bias V = +0.2 V. Thus, the forward electron injection barrier between the silicon substrate and the film (*n*-Si/In₂O₃ : Er) is $\Phi_{ef} = 0.14$ eV.

3.4. Barrier height determination for hole injection to In_2O_3 : Er film from *p* type conductivity silicon substrate

To determine the forward hole injection barrier between p type conductivity silicon and the In₂O₃: Er film (e.g. Φ_{hf} in Fig. 1 *b*), we measured the forward current *vs* temperature functions at low bias in sub-barrier mode $-0.5 \text{ V} \le V \le 0$ (Fig. 4 *a*). To calculate the backward hole injection barrier between the metallic In contact and the In₂O₃: Er film (e.g. Φ_{hb} in Fig. 1 *a*), we measured the backward current *vs* temperature functions at saturation for V = 2 V (Fig. 4 *a*). The resultant temperature functions were plotted in Schottky coordinates in accordance with Eqs. (2) and (3) (Fig. 5 *b*).

For reverse bias at saturation V = +2 V (Fig. 4 *a*), the backward current *vs* temperature function in Schottky coordinates (Fig. 5 *b*, grey dashed line) fits a line with a slope corresponding to the backward hole injection barrier height between the metallic In contact and the In₂O₃ : Er film: $\Phi_{hb} = 0.5$ eV (Fig. 6 *b*).

For low forward sub-barrier bias V = -0.2, -0.3, -0.4and -0.5 V (Fig. 4 *a*) the current *vs* temperature functions in Schottky coordinates have slopes of 0.22, 0.21, 0.206 and 0.203 meV, respectively (Fig. 5 *b*, color dashed lines) corresponding to the forward barrier height less the silicon potential drop, i.e., $\Phi_{hf} - V_{Si}$ (Fig. 6 *a*). Correction by the calculated $V_{Si} = 0.08, 0.1, 0.12$ and 0.13 V, respectively (Fig. 3 *b*, blue dashed line) yields the forward hole injection barrier height between silicon and the films in the *p*-Si/In₂O₃ : Er structures: $\Phi_{hf} = 0.3$ eV (Fig. 6 *a*).

Thus, the temperature functions of the backward saturation currents and the forward sub-barrier currents for the In₂O₃ : Er film structures on *n* and *p* type conductivity silicon substrates (Si/In₂O₃ : Er) suggest that the forward electron injection barrier between *n* type conductivity silicon and the films (*n*-Si/In₂O₃ : Er) is $\Phi_{ef} = 0.14$ eV, the backward electron injection barrier between the metallic In contact and the film (In/In₂O₃ : Er) is $\Phi_{eb} = 0.21$ eV, the forward hole injection barrier between *p* type conductivity silicon and the films (*p*-Si/In₂O₃ : Er) is $\Phi_{hf} = 0.3$ eV and the backward hole injection barrier between the metallic In contact and the films (In/In₂O₃ : Er) is $\Phi_{hf} = 0.5$ eV.

3.5. Analysis of Si/In_2O_3 : Er heterojunction band structure

The data on carrier injection barriers are shown in the schematic band diagrams of the Si/In₂O₃. Er heterostructure in Fig. 6 for *p* type conductivity silicon substrate. The conduction band discontinuity between silicon $E_{\rm C}$ and the film $E_{\rm CIn_2O_3\rm Er} - E_{\rm CSi}$ is shown in Fig. 6 to be equal to the calculated electron injection barrier $\Phi_{\rm ef} = 0.14$ eV. This assumption was made on the basis of indirect literary data on low electron injection barriers both for Si/In₂O₃ (e.g., there are data on a negative barrier [33, 34]) and for related materials Si/In₂O₃: Mo [35] and

Si/In₂O₃: Sn [31,32]. Judging from the calculated electron injection barrier $\Phi_{ef} = 0.14$ eV, the literary data on the silicon band gap $E_{gSi} = 1.12$ eV [41] and the film band gap $E_{gln_2O_3} = 2.69 \div 2.93$ eV [38, 39] (we accept it to be 2.9 eV for clarity), the valence band discontinuity between silicon E_V and indium oxide $E_{Vln_2O_3Er} - E_{VSi}$ appears to be excessively large, i.e., 1.64 eV (Fig. 1 *b*).

Despite the large calculated valence band discontinuity ($\Delta E_V \sim 1.64 \text{ eV}$), the hole injection barrier between silicon and the film proved to be but moderate: $\Phi_{hf} = 0.3 \text{ eV}$ (Fig. 6 *a*). This indicates that the band gap of the synthesized films has a hole conduction channel. It is shown by the dotted line E_{ds} in Fig. 6.



Figure 6. Schematic band diagrams of p-Si/In₂O₃: Er heterostructure for (*a*) forward and (*b*) reverse bias with electron and hole injection barriers shown

It seems that the hole conduction channel in the band gap is associated with the defect states caused by an imperfect structure of the RF magnetron sputtered In_2O_3 : Er films. Possibly, high defect concentrations introduced by magnetron deposition form multiple defect levels in the band gap. These multiple defect levels merge to form a defect state density spreading from the valence band edge E_V to the hole conduction channel in the band gap E_{ds} . In Fig. 6 the defect state density in the band gap of the In_2O_3 : Er films is schematically shown by the green curve D_{ds} .

Thus, electron transport in the film occurs via the conduction band $E_{\rm C}$ (Fig. 1 *a*) and hole transport occurs inside the band gap via the conduction channel $E_{\rm ds}$ (Fig. 6 *a*) generated by the tails of the defect state density $D_{\rm ds}$ in the band gap. Taking into account the literary data on the silicon band gap ($E_{\rm gSi} = 1.12 \text{ eV}$ [41]) and the calculated electron and hole injection barriers between silicon and the In₂O₃: Er film, i.e., $\Phi_{\rm ef} = 0.14 \text{ eV}$ and $\Phi_{\rm hf} = 0.3 \text{ eV}$, respectively (Fig. 6 *a*), the energy gap between the conduction band electrons and the band gap conduction channel holes is $E_{\rm C} - E_{\rm ds} = 1.56 \text{ eV}$ (Fig. 6 *b*).

3.6. Defect state density in In₂O₃ : Er band gap

The 400–800 nm PL spectra (Fig. 7) confirm the existence of defect levels in the In₂O₃ band gap [42–48]. These levels fall in the 1.55–3.1 eV energy range, i.e., inside the In₂O₃ band gap $E_{gln2O3} = 2.69 \div 2.93$ eV [38, 39].

 In_2O_3 films synthesized using different methods were studied earlier [42–48]:

metallic In sputtering followed by thermal oxidation [42];

 growth and oxidation in an argon + oxygen gas atmosphere on an InP substrate with gold as surfactant by vapor-liquid-crystal mechanism (VLS) [43];

oxidation of 1–3 mm metallic In grains in an argon
+ oxygen gas atmosphere [44];

 In evaporation and transport in an argon + oxygen gas atmosphere and deposition on substrate [45];

 In evaporation and redeposition in an argon flow atmosphere in a furnace [46];

- In₂O₃ vapor phase deposition in an argon + oxygen gas atmosphere on a silicon substrate with gold surfactant [47];

- metallic indium deposition on differently oriented silicon substrates ((100), (110), (111)) and 850 °C oxidation in a wet argon flow atmosphere [48].

These methods produce completely different film structures: 400–600 nm nanocrystals consisting of agglomerated finer 40–60 nm nanocrystals [42]; square cross-section 15–150 nm thick nanowires reaching decades of microns in length [43]; 40–120 nm diam. nanowires 15–25 μ m in length [44]; 20–100 nm diam. nanowires (30 nm on average) up to 100 μ m in length [45]; octahedral faced crystals several microns in



Figure 7. In_2O_3 : Er PL spectra compared against literary data on PL of In_2O_3 films synthesized using different methods [42–48]

size [46]; 20–40 nm diam. nanowires 1 μ m in length with gold drops at ends [47]; 0.1–1.0 μ m sized polycrystals [48].

The 400–800 nm PL falling into the In_2O_3 band gap was attributed to the following defects in the band gap [42–48]: oxygen deficiency related defects [42]; oxygen vacancies [43]; single-ionized oxygen vacancies $[V_0^+]$ [44]. One of the peaks at 420 nm was attributed [45] to oxygen deficiency related defects [V₀], and the other 630 nm one, to excess oxygen atom related defects, e.g. interstitial oxygen atoms [O_I], In vacancies [V_{In}] or In atoms substituted for O [O_{In}] [45]. In another work [46] PL was attributed to interstitial In atoms $[In_i^{3+}]$ rather than oxygen vacancies, while in [47, 48], again to oxygen vacancies. Thus the defect origin is most often reported to be oxygen atom deficiency, but exceptions occur [45]. However, the specific defect type is most often reported to be oxygen vacancy, the authors not having a general consensus though.

Similar 400–800 nm PL is observed in our magnetron sputtered films (Fig. 7, blue curve). The PL absorption edge 1.55 eV (Fig. 7) is in a good agreement with the energy gap between the electrons and the holes $E_{\rm C} - E_{\rm ds} = 1.56$ eV (Fig. 6 b). The electrons are in the conduction band $E_{\rm C}$ In₂O₃: Er, and the holes are in the conduction channel $E_{\rm ds}$ caused by the defect state density $D_{\rm ds}$ spreading from the valence band edge $E_{\rm V}$ to inside the In₂O₃: Er band gap (Fig. 6 b). Thus, the defect state density $D_{\rm ds}$ (Fig. 6) in the band gap is confirmed by PL and accounts for the low hole injection barrier obtained for our structures.

4. Conclusion

 In_2O_3 : Er films were RF magnetron sputtered on silicon substrates.

The I–V curves for the structures $(Si/In_2O_3 : Er)$ on *n* and *p* type conductivity silicon substrates have rectifying patterns and at low bias can be described within the majority carrier barrier thermoemission model with a silicon potential drop V_{Si} correction of the bias *V*.

The electron injection barrier between *n* type conductivity silicon and films $(n-\text{Si}/\text{In}_2\text{O}_3 : \text{Er})$ was found to be $\Phi_{\text{ef}} = 0.14$ eV and the hole injection barrier between *p* type conductivity silicon and films $(p-\text{Si}/\text{In}_2\text{O}_3 : \text{Er})$, $\Phi_{\text{hf}} = 0.3$ eV.

The band structure of the Si/ In_2O_3 : Er heterojunction has a small conduction band discontinuity, $\Delta E_{\rm C} = 0.14 \text{ eV}$ and a large valence band discontinuity, $\Delta E_{\rm V} = 1.64 \text{ eV}$. However, the presence of the hole conduction channel $E_{\rm ds}$ in the In_2O_3 : Er band gap caused by the defect state density tail $D_{\rm ds}$, spreading from the valence band to the band gap provides for a low hole injection barrier, $\Phi_{\rm hf} = E_{\rm ds} - E_{\rm VSi} = 0.3 \text{ eV}$. The energy gap between the conduction band electrons and the band gap conduction channel holes is $E_{\rm C} - E_{\rm ds} = 1.56 \text{ eV}$. The presence of the defect state density D_{ds} in the In₂O₃: Er band gap is confirmed by the PL data for the respective 1.55–3.0 eV energy range.

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