# CdF$_2$:Er$^{3+}$/Si(111) Heterostructure For EL Displays

**Abstract**

This report results from a contract tasking Institut of Applied Physics as follows: The contractor will investigate state of the art, experimental facilities and growth methods for CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) as well as (Ca, Sr, Ba)F$_2$/Si(Ge) heterostructures for potential applications in the design and development of electroluminescent display technology. Samples of the prepared materials (2-4) will be presented to the customer as well as all of the related procedures of pretreatment, growth, and characterization. The entirety of the described work will be documented in a final report as well as interim joint papers.

**Subject Terms**

Physics, Opto-electronic Materials
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“CdF₂:Er³⁺/CaF₂/Si(111) HETEROSTRUCTURE FOR EL DISPLAYS”

by

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Abstract

Growth and characterization of films of the group II-a and II-b fluorides on Si or InP substrates starting from 1991 have been fulfilled to the date of this report compilation. Both reduced and high temperature cleaning and passivation procedures were elaborated that to get before a fluoride film growth atomically clean and flat surface of Si(111) or InP(100) substrates. Cleaning and passivation procedures, an ultrahigh vacuum (10⁻⁶ Pa) MBE chamber with in situ diagnostics as well as ex situ characterization facilities have been prepared especially for the CdF₂:Er³⁺/CaF₂/Si(111) heterostructure growth and characterization.

A noticeable property of CdF₂ is the efficient electroluminescence which is observed in the crystals doped with Mn or rare earth impurities. It is possible to change the emission wavelength from infrared to ultraviolet. So, epitaxial CdF₂, in particular, grown on CaF₂ / Si(111) is an attractive structure for monolithic multicoloured EL displays. Note that CaF₂ film with +0.6% lattice mismatch to Si(111) is an important element of a perfect CdF₂ /CaF₂ /Si(111) heterostructure due to the facts that the lattice constant of CdF₂ is smaller than that of Si(111) (-0.8% at room temperature), so only a combination of both fluorides gives a coherent heterostructure.

In the growth experiments we use an MBE system equipped with cryoshrouds, RHEED, Knudsen-cell type ovens with CaF₂ , CdF₂ and ErF₃ crystals, computer monitored shutters, substrate holder and heater with manipulator and a sample load lock. After standard chemical cleaning, Si(111) substrate is loaded into the MBE system. Then the passivating silicon oxide layer is evaporated in situ to obtain a distinct 7x7 Si(111) superstructure. CaF₂ , CdF₂ and ErF₃ molecular beams to grow fluoride layers are obtained by sublimation of the respective single crystals at fixed temperatures sustained with high accuracy by a computer system. Rate of a fluoride deposition is calibrated by measuring of RHEED intensity oscillations. Quality of the fluoride films is controlled by RHEED patterns.

A set of CdF₂:Er³⁺/CaF₂/Si(111) heterostructures that to find an optimal for EL concentration of Er³⁺ has been grown in a course of preliminary investigation. Fluorescent characteristics of CdF₂:Er³⁺ films grown on CdF₂/Si(111) coherent surface are studied by photo- and cathodoluminescent methods. Distinct broad band fluorescent spectra covering at room temperature visible region centered at 450 nM and slightly shifting with the level of doping have been measured using standard equipment.

Keywords: group II-b fluoride CdF₂, Molecular Beam Epitaxy (MBE), growth, in situ characterization, photoluminescence (PL), cathodoluminescence (CL) and electroluminescence (EL) of CdF₂:Er³⁺/CaF₂/Si(111) heterostructure.
Preface

The presented report deals with MBE growth of CdF₂ doped by Er³⁺ onto Si(111) as well as with \textit{ex situ} and \textit{in situ} characterization of substrate surface, interface and this fluoride overlayer. Due to the fact that CdF₂:Er⁺³/Si(111) structure is rather perspective for multi-coloured solid state electro-luminescent screens we describe also photoluminescent, cathodoluminescent as well as electroluminescent properties of the structure. Growth of an fluoride layer onto a semiconductor substrate in optoelectronic integrated circuitries (OEIC) structure fabrication for some important cases is only an intermediate stage for the next crystalline overlayer growth, so, some methods of crystalline semiconductor film growth are also reported, mainly, those of which were realized by the author and his colleagues from the Laser Research Laboratory (LRL) or in collaboration with outer organizations and could be useful for nondestructive temperature reduced epitaxy onto pre-made device structures.

In principle, II-a and II-b group fluoride film growth on a semiconductor substrate (mainly, on Si or any III-V compound) and even the next crystalline overgrowth for a few scientific and industrial centers are routine operations, but not all of those centers willingly publish their high technological know-how’s in this promising sphere of opto- and microelectronics. Besides, concrete technological contrivances are dispersed in a lot of papers as well as open publications on closed technological cycles of semiconductor-crystalline dielectric-semiconductor (SCDS) for OEIC’s are very scant. Concerning compounds of II-b group, note, that only growth technology for CdF₂ can be described on literature sources originated from our collaborators on the current work [1-7], meanwhile CdF₂ doped by Er³⁺ or any rare earth element, can be found up to now only in the graduate work of one of participant of this work [8] as well as in the current report.

At the present report to the United States Air Force European Office of Aerospace Research and Development (EOARD) the author tried to collect the all of known data on CdF₂:Er⁺³/ Si (111) as well as some useful results on fluoride film grown onto semiconductor, SCDS growth technologies and structure \textit{ex situ} and \textit{in situ} characterization methods, including the original results, obtained by the author and his colleagues in course of previous [9-10] and current contract work.

1. Short Review: Main Results on Growth of II-a and II-b Fluorides on Semiconductor Substrates

Recently, group II-a cubic fluorides, CaF₂, SrF₂ and BaF₂, have received considerable attention as epitaxial dielectric films on semiconductor substrates because they have a cubic crystal structure similar to the diamond structure of Si and the zinc-blende structure of the III-V compound semiconductors [11-34]. Their large electronic bandgaps make them interesting for the development of new metal-insulator, and metal-insulator-semiconductor field effect transistor (MISFET) structures and for achieving the long range goal of building three-dimensional devices. In addition, II-a and II-b group fluoride molecules can be sublimed from a Knudsen-cell type oven congruently due to their high energy of dissociation, automatically solving the problem of film stoichiometry. Because the lattice parameters of the fluorides bracket those of
semiconductors as Si and III-V, it is possible to grow a mixture of the fluorides which is lattice matched to the substrates [11]. If such single-crystalline lattice-matched dielectric films can be grown on a semiconductor substrate, the interface trap densities, in principle, can be reduced and the electrical properties of the insulator-semiconductor interface improved [19]. The possibility is specially interesting for III-V compound semiconductors because of the lack of good insulating films on the III-V materials. Lattice-matched single-crystalline insulators are also important for epitaxial semiconductor-crystalline dielectric-semiconductor structures (SCDS) in allowing the growth of a better quality top epitaxial semiconductor layer. Ishiwara and Asano [12] have grown Ge / Ca\textsubscript{x}Sr\textsubscript{1-x}F\textsubscript{2} / Si(111) by vacuum evaporation, where Ca\textsubscript{x}Sr\textsubscript{1-x}F\textsubscript{2} is lattice matched to Ge. Tu et al. [17] have grown by molecular-beam epitaxy (MBE) the first epitaxial III-V SCDS double heterostructures with InP/ fluoride/ InP(100), which may be potential for novel devices in three-dimensional integrated circuits (3-d IC's) and in monolithic integrated optics. The surface morphology of the insulating overlayers is important, e.g., for the preparation of SCDS structures by growing a second semiconductor onto the insulator overlayer.

Since epitaxial growth of CaF\textsubscript{2} onto Si was reported in 1981 for the first time [11], much work was done to characterize the geometric and electronic structure of epitaxial group II-a fluoride layers and of the semiconductor-insulator interfaces. This was done on different orientation of Si [17,18, 26, 35, 36], GaAs [28, 29, 31] and on InP substrates [15, 26-28, 31-34]. In particular, in the report to EOARD on previous contract work SPQ-94-4098 [9] we have described the methods of preparation and characterization of (CaSrBa)F\textsubscript{2} / InP(100) heterostructures. Taking into account known literature data and long experience of the Laser Research Laboratory in epitaxial growth of semiconductor and dielectric films by the methods of Laser Vacuum Epitaxy (LVE) and Molecular Beam Epitaxy (MBE) the procedures of optimal cleaning and substrate passivation as well as temperature-reduced growth process of the above mentioned fluorides onto InP(100) were newly developed. It was shown that the passivation is necessary that to keep InP substrates in conventional atmospheric conditions and can be used for epitaxial growth at the temperatures above 500°C. The developed by us cleaning procedures were effective for MBE epitaxial fluoride growth onto InP(100) in ultra-high vacuum chamber at 350°C. 0.05 - 0.4 μ single crystal fluoride films were also MBE grown under ultra-high vacuum conditions and at 350°C without or with very simple temperature-reduced pretreatment onto substrates from specially prepared and individually packed InP(100) wafers. Experimental facilities of the Laser Research Laboratory were considerably improved in the course of this work that to be able to grow by MBE and/or LVE in common cycle semiconductor-semiconductor (SS), semiconductor-crystalline dielectric (SCD) or semiconductor-crystalline dielectric-semiconductor (SCDS) heterostructures for optoelectronic integral circuitries (OEIC). In particular, it gave an opportunity to grow in common cycle more complicate heterostructures such as InP/ SrF\textsubscript{2} / InP double heterostructure [10] and CdF\textsubscript{2}:Er\textsuperscript{3+} / CaF\textsubscript{2} / Si(111) for electroluminescent (EL) displays (current contract work).

Very interesting compound of group II-b fluorides is CdF\textsubscript{2} which was recently grown on Si (111) by MBE method [1-8]. It has the same fluorite structure as group II-a fluorides. However, its electronic properties are different. Undoped CdF\textsubscript{2} crystals are good insulators (the band gap is equal to 8 eV). Being doped with trivalent impurities and annealed they convert into a semiconductor state with binding energy of shallow donor levels about 0.1 eV and free electron concentration up to 4\times10\textsuperscript{18} cm\textsuperscript{-3} [37]. Another remarkable property of CdF\textsubscript{2} is the efficient multicoloured electroluminescence which is observed in the crystals doped with Mn or rare earth
impurities [38]. It is favorable for growth of pseudomorphic layers and coherent CdF₂ - CaF₂ superlattices on Si substrates (the lattice mismatch between CdF₂ and Si is only -0.8%)

Taking into account the above mentioned information, let us consider the requirements to candidates for insulator / Si and III-V compound epitaxy. Obviously, dielectrics selected for epitaxial growth onto semiconductor surfaces must meet the following requirements.

1. It is necessary to have strong chemical bonds at the semiconductor-insulator interface, so an insulating material must have similar to semiconductor crystal structure and react with it that the chemical bonds were arranged perpendicular to the interface.

2. That to decrease the misfit dislocation density the lattice parameter of the insulator must be close to the lattice parameter of the semiconductor.

3. That to avoid strong mechanical tensions during thermal treatment of the grown heterostructure thermal expansion coefficients of the chosen semiconductor substrate, dielectric layer and, if necessary, next semiconductor overlayer must be close to each other.

4. The next obvious requirement - exsistence of a method of epitaxial growth of the chosen insulator onto semiconductor surface. This method must supply high pressure of the insulator constituents at reasonable temperatures. MBE is suitable for this purpose.

5. The grown insulator layer must be stable at high temperatures that to meet all the next thermal tretments.

6. At last, the grown crystalline fluoride must be a good insulator that usually correlate with broad band gap, excluding the special case of CdF₂ when its high electric conductivity can be reached, if it is necessary at EL structure formation, by thermal treatment.

Table 1. Properties of candidates for insulator/Si and III-V compound epitaxy

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>Lattice constant</th>
<th>( \alpha \times 10^6 \text{K}^{-1} ) (b)</th>
<th>( \varepsilon ) (b)</th>
<th>Melting point (°C)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF</td>
<td>NaCl</td>
<td>5.34</td>
<td>31</td>
<td>5.8</td>
<td>858</td>
<td>~ 11</td>
</tr>
<tr>
<td>RbF</td>
<td>NaCl</td>
<td>5.64</td>
<td>27</td>
<td>6.2</td>
<td>795</td>
<td>~ 10</td>
</tr>
<tr>
<td>LiCl</td>
<td>NaCl</td>
<td>5.13</td>
<td>44</td>
<td>11.3</td>
<td>605</td>
<td>~ 10</td>
</tr>
<tr>
<td>LiBr</td>
<td>NaCl</td>
<td>5.49</td>
<td>49</td>
<td>12.1</td>
<td>801</td>
<td>~ 8</td>
</tr>
<tr>
<td>NaCl</td>
<td>NaCl</td>
<td>5.628</td>
<td>40</td>
<td>5.9</td>
<td>550</td>
<td>~ 8</td>
</tr>
<tr>
<td>CdF₂</td>
<td>Cubic fluorite</td>
<td>5.3880</td>
<td>19</td>
<td>8.3</td>
<td>1100</td>
<td>8</td>
</tr>
<tr>
<td>CaF₂</td>
<td>Cubic fluorite</td>
<td>5.4640</td>
<td>19</td>
<td>6.8</td>
<td>1423</td>
<td>12.1</td>
</tr>
<tr>
<td>SrF₂</td>
<td>Cubic fluorite</td>
<td>5.7996</td>
<td>18</td>
<td>6.5</td>
<td>1473</td>
<td>11.25</td>
</tr>
<tr>
<td>BaF₂</td>
<td>Cubic fluorite</td>
<td>6.2001</td>
<td>18</td>
<td>7.4</td>
<td>1355</td>
<td>11.0</td>
</tr>
<tr>
<td>LaF₃</td>
<td>Hexagonal</td>
<td>a=4.148</td>
<td>17</td>
<td>-</td>
<td>1493</td>
<td>-</td>
</tr>
<tr>
<td>NdF₃</td>
<td>Hexagonal</td>
<td>a=4.060</td>
<td>17</td>
<td>-</td>
<td>1374</td>
<td>-</td>
</tr>
<tr>
<td>CeF₃</td>
<td>Hexagonal</td>
<td>a=4.107</td>
<td>13 (c)</td>
<td>-</td>
<td>1430</td>
<td>-</td>
</tr>
</tbody>
</table>

a) linear thermal expansion coefficient; b) relative permittivity; c) basal plane thermal mismatch
Table 2. Lattice constants for II-a group fluorides and advanced semiconductors

<table>
<thead>
<tr>
<th>Semiconductor Films</th>
<th>NaCl Type</th>
<th>PbS</th>
<th>PbSe</th>
<th>SnTe</th>
<th>PbTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal ZnS Type</td>
<td>ZnS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS Type</td>
<td>ZnS</td>
<td>ZnSe</td>
<td>CdS</td>
<td>CdSe</td>
<td></td>
</tr>
<tr>
<td>Cubic ZnS Type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond Type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoride Films</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF₂ Type</td>
<td>CaF₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SrF₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BaF₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equivalent Lattice Constant in Hexagon. Structure</td>
<td>3.8</td>
<td>4.0</td>
<td>4.2</td>
<td>4.4</td>
<td>4.6</td>
</tr>
<tr>
<td>Lattice Constant in Cub. str. [Å]</td>
<td>5.4</td>
<td>5.6</td>
<td>5.8</td>
<td>6.0</td>
<td>6.2</td>
</tr>
</tbody>
</table>

One can see that group II-a fluorides are good materials for all of group III-V materials, CaF₂ as well as CdF₂ (absent in the Table 2, ) suit for Si, but fluorides on the base of Rare Earth elements are interesting only for epitaxial growth onto (111) surface. The essential advantage of all the fluorides is their high molecular chemical bond energies (appr. 200 kCal/mol) that leads to molecular sublimation of the fluorides and gives an opportunity to prepare their stoichiometric compositions. On the other hand, relatively high thermal expansion coefficients of some of them compared to semiconductors lead to definite troubles at thermal treatments of the obtained heterostructures.


To form an interface between two crystalline materials with different lattice parameters and/or crystal structures methods of active modifications of the substrate surface are widely used. These methods are aimed to conjugate smoothly mechanical as well thermal properties of a
To form an interface between two crystalline materials with different lattice parameters and/or crystal structures methods of active modifications of the substrate surface are widely used. These methods are aimed to conjugate smoothly mechanical as well thermal properties of a heteropair constituents that to overcome creation of numerous misfit dislocations near their interface and/or degradation of the whole device heterostructure.

That to form perfect interface between heteropairs having a strong differences in the type of crystal structure, in lattice periods as well as in thermal expansion coefficients, at our laboratory since 70-th is developed the method of Laser Vacuum Epitaxy (LVE) which gives an opportunity to smoothly conjugate various materials (see, for instance, [39-44]). LVE is a very important method for this purpose because atoms and ions in a laser produced plasma effective re-evaporate matter of the substrate and penetrate into it due to their relatively high density and kinetic energy. In [44] LVE was used for the first stage of a film growth in order to modify the substrate surface and to obtain a smooth conjugation of lattice parameters, as well as thermal and mechanical characteristics of both III-V film and Si substrate; the second stage of film growth up to the thickness which are typical for microelectronic applications (1-2 μ) was fulfilled with the help of classic methods such as Gas Transport Epitaxy (GTE) or Molecular Organic Vapour Phase Epitaxy (MOVPE). We have shown the importance of LVE for the formation of perfect interfaces between the materials with a considerable mismatch of lattice periods, thermal and mechanical characteristics such as Si/GaAs, Si/InP and Si/InAs. Besides, we have selected the composition of LVE produced intermediate layers which would give the best results at minimum thickness of the intermediate layer as well as tested compatibility of LVE with other growth methods, especially, with GTE and MOVPE.

The experimental set-up for LVE is shown in Fig. 1. In the chamber (1) with residual atmosphere of 10^8 Pa one can see the pulse laser (1) which evaporates the target (3) (2mm thick GaAs, InP or InAs plates), the substrate (4) heated by a thermal (5) or by a laser (2) heaters (the latter heats the substrate just a few microseconds before a new portion of the condensate (6) from the laser produced plasma (7) of the target material enters the substrate). Depending on the type of the laser (2) its characteristics are: the pulse energy 0.1 - 1.0 J; the pulse duration 10^-8 - 10^-11 s; the repetition frequency 10 - 100 Hz and the wavelength 0.337 - 1.06 μ.

The plasma cluster (7) and the condensate (6) differ in composition: the first consists of only atoms and ions of the target materials in a ratio of appr. 9:1 at the laser power density of 10^8 W/cm^2 while the latter contains both the target material particles and re-evaporated substrate material particles which are thermalized in the counter flow. The ratio between the target and the substrate particles depends on the laser power density. This ratio changes its composition increasing the target particle concentration from pulse to pulse (see Fig.2). Monitoring composition, density and energy of the condensate (6) and the cluster (7) was made with the help an optical system (8), a monochromator (9), photomultiplier (10), boxcar-integrator (11), computer (12) and display system (13). A standard set of diagnostic equipment inside the ultrahigh vacuum chamber (1) includes an Auger spectrometer (14) with an argon gun (15), a mass-sectrometer (16) and low (LEED) and fast (RHEED) energy electron diffractometers (17). With help of the effusion cells (18) it was possible to change the ratio of group III and group V elements in the condensate (6) or to prepare by MBE fluoride or semiconductor overlayer. Thus, the described apparatus developed at our laboratory can be used not only for semiconductor - semiconductor (SS) preparation but also for growth of SCDS structures in a common cycle, consisting of LVE and MBE methods (see, for instance [10]).
GTE and MOVPE were also used by us for growth of some III-V films, such as InP or GaAs (see, for instance, [44]) on substrates or intermediate layers grown by LVE. The thickness of the layers grown by these one or two step methods was 1-2μ and the growth temperatures were
Fig. 1. LVE experimental set-up.
4. Substrate. 5. Thermal heater. 6. Thermolized condensate consisting of target and substrate particles.
16. Mass-spectrometer. 17. LEED and RHEED.

Fig. 2. 589.0 nm Na(I) spectral line intensity vs number of laser pulses evaporating GaAs target. LVE growth of GaAs on NaCl substrate.

Fig. 3. Distribution of Ga, As and Si concentration inside LVE produced intermediate layer according to Auger spectroscopy measurements.
450 and 650°C for GTE and 450 or 700°C for MOVPE. Due to the fact that these growth temperatures were considerably more than it is necessary for non-destructive temperature reduced epitaxy now we use mainly LVE and MBE in a common cycle with help of the apparatus presented in Fig.1.

The ion component of the target flow caused sputtering of the substrate and of the growing film [39,44]. This sputtering effect in LVE method was directly observed during condensation of a semiconductor target material onto substrate. For instance, Fig.2 demonstrates this phenomenon for GaAs condensation onto NaCl substrate. NaCl is the most convenient for this kind of experiment on observing of the sputtering phenomenon due to intense fluorescence of Na atoms at 589.0 nm. Fig.2 shows the dependence of fluorescence intensity of the 589.0 nm spectral line of Na registered a few mm apart from NaCl substrate on number of laser pulses evaporating GaAs target. The decrease in fluorescence intensity shows that each portion of the material re-evaporated from the substrate surface contains a lower quantity of the original substrate material than the previous one. It has been also shown with the help of the secondary ion mass-spectroscopy (SIMS) and Auger spectroscopy of layer by layer etched surfaces that in LVE grown heterostructure there is a clearly determined buffer layer, the composition of which is smoothly changed from the substrate to the target material (see, for instance, Fig.3 for the case of LVE grown GaAs onto Si. Depending on the growth conditions the thickness of the intermediate layer between substrate and evaporated materials is 0.02-0.1μ. It was also shown [39,44] that the intermediate layer is a metastable solid solution having the composition of the type of T_{1-x}S_x (where T - the target, S - the substrate; GaAs_{1-x} - Si_{2x} in the case presented in Fig.3). This intermediate layer (primer) obtained by LVE method has been used for the next growth of a semiconductor overlayers in the formation interfaces between semiconductors having big lattice mismatch and considerable differences in thermal and mechanical characteristics of chosen heteropairs. Therefore, the LVE method developde at our laboratory seems to be very perspective for various p-n junction growth. Besides, the method is compatible with MBE due to similar (practically, the same - see Fig.1) technological and diagnostical equipment that gives an opportunity to organize a common cycle of SS, SCD or SCDS structure growth inside the same apparatus.

A special pure ultra-high vacuum system was elaborated for MBE growth of CdF₂ doped by Er³⁺ (see Fig.4). The main parts of the system are growth chamber, block of effusion (Knudsen) cells and free-of oil pumping facilities providing up to 10⁻⁸ Pa of residual atmosphere. Heater of the samples is surrounded by cryoshrouds which improve the work vacuum and protect samples from contaminations. Residual atmosphere and in situ quality of substrate surface, interface and grown layer are monitored respectively by a mass-spectrometer and a RHEED systems. Patterns of electron diffraction are registered by high-sensitive television receiver and through special interace introduced into computer’s processor. Growth rate and thickness of fluoride layers have been measured with the help of 5 MHz calibrated piezo-electric quartz resonator mounted beside the sample at the growth chamber. Thickness can be also measured outside the growth chamber with the help of a computirized ellipsometer. Note, that the same equipment was used in the course of previous contract work for EOARD on MBE growth of SrF₂/InP heterostructure for optoelectronics [9].
Fig. 4. Experimental set-up for MBE growth of II-a and II-b fluorides on semiconductors.
3. MBE growth and characterization of CdF₂ grown on CaF₂/Si(111)

The MBE system shown in Fig 4 was used for growth of CdF₂ and CaF₂ layers on Si(111). Quality of the layers could be controlled with a 15 keV electron gun and a screen for observation of RHEED patterns. After standard chemical cleaning [45] and evaporation of silicon oxide layer \textit{in situ} at 1250°C a distinct 7x7 Si(111) superstructure was observed in the RHEED patterns (see Fig. 5). Then the fluoride layers were deposited from CaF₂ or CdF₂ molecular beams obtained by sublimation of CaF₂ crystals at 1200°C and CdF₂ crystals at 800°C.

Fig.5. RHEED pattern from 7x7 superstructure of atomically clean Si surface at 770°C

Fig.6. RHEED pattern from Si substrate covered at 770°C by the first 3 monolayers of CaF₂ destroying the 7x7 superstructure of the atomically clean surface of Si.
To form a well ordered interface with silicon substrate we started CaF$_2$ deposition at high temperature (770°C). The observed RHEED pattern was typical for flat (111) fluorite face with 1x1 surface structure. The coherent CaF$_2$ layers were obtained by a two-step growth technique: the first several monolayers were deposited at high temperature, then the substrate was cooled to 100°C, and the growth was resumed until the thickness reached 5-10 nm. Figs. 5, 6, 7 show evolution of the surface from 7x7 Si(111) (Fig. 5) through an intermediate structure after deposition of the first 3 monolayers of CaF$_2$ (Fig 6) to 1x1 structure of CaF$_2$ after deposition of 15 monolayers (5 nm) of this buffer layer (Fig 7). One can see that the diffraction pattern for 7x7 structure consists of a few bright spots along the Laue arc and 7 weak superreflexes between them (Fig 5). The deposition even a part of monolayer of CaF$_2$ destroys the 7x7 superstructure, one can see only 3 bright spots which correspond to the lattice of CaF$_2$ (Fig 6). When the growth temperature takes lower the mobility of atoms also decreases and the relative pattern with horizontal streaks demonstrates non-ideal smooth surface (Fig 7).

Fig. 7. RHEED pattern of the CaF$_2$/Si(111) surface after MBE growth of 15 monolayers of CaF$_2$ (5 nm) at 200°C demonstrates the appearance of Kikuchi lines (horizontal streaks).

Fig. 8. RHEED pattern of the CdF$_2$ : Er$^{3+}$/ CaF$_2$/Si(111) after MBE growth of 300 monolayers of CdF$_2$ : Er$^{3+}$. 
The buffer layer of CaF$_2$ gives an opportunity to improve crystalline quality of CdF$_2$ Er$^{3+}$ grown onto Si(111) substrate. According to [46], the most favorable temperature for preparation of perfect interface CaF$_2$ / Si(111) is 770°C, but the lattice mismatch at this temperature is 2.6%, so the breakdown of the pseudomorphism takes place already after deposition of a few monolayers. These difficulties can be overcome with the noted above two-step growth technique described for the first time in [47].

After the preparation of the CaF$_2$ buffer layer we started the growth of CdF$_2$ doped with Er$^{3+}$ from an ErF$_3$ source to a concentration up to a few mol %. For that purpose the cells with CdF$_2$ and ErF$_3$ were preheated up to the temperatures providing necessary thickness and doping level of the film at a few nanometer per minute growth rate, then the shutters was open and the layers CdF$_2$ Er$^{3+}$ with the thickness 0.1-0.4μ were grown. Fig. 8 demonstrates a RHEED pattern.

Fig. 9. A view of the surface of 155 nm thick CdF$_2$ Er$^{3+}$ layer grown onto CaF$_2$ / Si(111)
for 300 monolayer thick CdF$_2$:Er$^{3+}$ grown at the substrate temperature 100°C. One can see bright thin streaks (Kikuchi lines) that confirms layer by layer 2-dimensional growth and high quality of the whole structure CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) of 0.1 μ thickness. However, distinct Kikuchi lines can be seen only on RHEED patterns from rather thin (until 0.1 μ thick CdF$_2$:Er$^{3+}$) layers, patterns for thick layers show appearance of point reflexes, broadening of the lines as well as narrowings along them that can be characterized as roughening of atomically flat surface when the thickness of the layer increases. The same trends demonstrates images of the surfaces obtained with the computerized Scanning Probe Microscope, model P4-SPM-MDT (Russia), working in scanning tunneling or scanning force modes with high resolution and software X-Y linearity correction of images. Figs. 9-12 show the changes in flatness and roughness of the CdF$_2$:Er$^{3+}$ surface with the increase in thickness of the layer. One can see appearance of a slightly rougher surface for 155nm layer (Fig 9), a rather rough surface for 310 and 350 nm layers (Figs.10, 

Fig.10. A view of the surface of 310 nm thick CdF$_2$:Er$^{3+}$ layer grown onto CaF$_2$/Si(111)
11) as well as a considerable roughness and cracks for 390 nm layer (Fig 12). Note that the thickness as well as the rate of the fluoride deposition of the layers were determined with high accuracy by measuring of the period of RHEED intensity oscillations. For instance, Fig 13 shows the specular beam intensity behaviour in RHEED pattern during growth of CdF$_2$ layer on coherent CaF$_2$ / Si (111). The period of observed oscillations corresponded to the growth of one triple F-Cd - F layer (0.312nm). Distinct oscillations was observed, which meant two-dimensional growth mode of the CdF$_2$ layer.

In conclusion, MBE growth of high quality epitaxial CdF$_2$:Er$^{3+}$ layers on CaF$_2$ / Si(111) surface have been demonstrated for the first time. The surface structure of the layers was studied by the RHEED and Scanning Probe Microscope techniques. RHEED intensity oscillations have been observed during CdF$_2$ growth. They indicated a 2D layer by layer growth mode. Taking into account the unusual features of cadmium fluoride single crystals the results obtained in MBE

![Fig.11. A view of the surface of 350 nm thick CdF$_2$:Er$^{3+}$ layer grown onto CaF$_2$ / Si(111)]](image-url)
growth of CdF$_2$:Er$^{3+}$ on CaF$_2$ / Si(111) reveal new heterostructure with potentially attractive electroluminescent properties.

Fig. 12. A view of the surface of 390 nm thick CdF$_2$:Er$^{3+}$ layer grown onto CaF$_2$ / Si(111).

Fig. 13. RHEED intensity oscillations during the growth of CdF$_2$ layer.
4. Cathode- and Photoluminescence of CdF₂:Er⁺⁺⁺/CaF₂/ Si(111) Heterostructure

The groups II-a and II-b fluorides doped by RE elements have been thoroughly investigated and widely used as advanced laser media, cathode-, photo- and electroluminescence materials during the last 30 years. Wide band gap fluorides doped by Er⁺⁺⁺, obviously, are the most interesting materials between them, because irradiative inner 4f³¹ transition of this RE at 1.55µ coincides with transparency window of standard quartz lightguides, its other irradiative transitions are also of a great interest due to a good opportunity to generate or transform light in visible and infrared regions (see Fig.14).

![Fig. 14. The structure of energy levels for Er³⁺. The irradiative transitions are denoted by the letter A, B, C, D and E respectively for blue, green (B and C), red and infrared regions of the electromagnetic spectrum.](image)

Excited by 15 kV, 30-100 nA electron beam or appr. 0.1 Wt, 488 and 514 nm Ar⁺ laser light MBE grown by us CdF₂:Er⁺⁺⁺/CaF₂/ Si(111) heterostructures develop effective cathode- and photoluminescence (CL and PL respectively). The relevant spectra measured by standard methods depending on Er³⁺⁺ concentration and temperature since 5°K until 300°K are shown in Figs.15-23. One can see a good correlation in spectral positions of irradiative lines between electronic structure of Er⁺⁺⁺ transitions, Er⁺⁺⁺ CL and PL spectra in bulk and epitaxial layers (see, for instance, Figs. 14-18, 22). According to our data between epitaxial layers the most intense spectra depending on the selected spectral region have those which are doped by 4 - 16 mol % of Er⁺⁺⁺ (see Figs.15 and 23).

Thus, the most effective fluorescent CdF₂:Er⁺⁺⁺/CaF₂/ Si(111) heterostructures have been grown by MBE and investigated by CL and PL methods.
Fig. 15: Photoluminescent spectra of CdF$_2$:Er$^{3+}$ films compared with the spectrum of bulk CdF$_2$:Er$^{3+}$. Samples 3240, 3150 and 3149 are doped with 0.9, 1.6 and 16 mole % of Er$^{3+}$ respectively. Bulk crystal contains 4 mole % of Er$^{3+}$. 5°K.
Fig. 16. Photoluminescent spectrum of CdF$_2$:Er$^{3+}$ film (16 mole % of Er$^{3+}$) compared with the spectrum of bulk CdF$_2$:Er$^{3+}$ (4 mole % of Er$^{3+}$) 80°K.
Fig. 17. Photoluminescence of Er$^{3+}$ (16 mole %) in CdF$_2$ epitaxial layer. 80°K, 500-1100 nm.

Fig. 18. Photoluminescence of Er$^{3+}$ (16 mole %) in CdF$_2$ epitaxial layer. 80°K, 800-1800 nm.
Fig. 19. Cathodoluminescence of Er$^{3+}$ (0.9 mole %) in CdF$_2$ epitaxial layer. Room temperature.

Fig. 20. Cathodoluminescence of Er$^{3+}$ (1.6 mole %) in CdF$_2$ epitaxial layer. Room temperature.
Fig. 21. Cathodoluminescence of Er$^{3+}$ (12.3 mole %) in CdF$_2$ epitaxial layer. 520-560 nm. Room temperature.

Fig. 22. Cathodoluminescence of Er$^{3+}$ (12.3 mole %) in CdF$_2$ epitaxial layer. 350-850 nm. Room temperature.
Fig.23. Cathodoluminescence of CdF$_2$ epitaxial layers depending on concentrations of Er$^{3+}$. 350-800 nm. Room temperature.

5. CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) Heterostructures for EL Displays

It is known that the only effective mechanism of electroluminescence in CdF$_2$ is the shock ionization of impurity centers. A strong electric field region which can be obtained near the Schottki barrier or in a metal-insulator-semiconductor (MIS) structure is necessary that to accelerate electrons for this ionization of impurities. An electric contact to Schottki barrier gives an opportunity to control an EL device with a direct current, but the results published in [48] show that some processes near the contact lead to nonstability and fast degradation of the devices. Compared to Schottki barrier a MIS structure of the EL device is considerably more stable and controlled by asymmetric alternative voltage. High negative voltage depletes electron traps and accelerates captured electrons which in their turn accomplish the shock excitation of the luminescent centers. The next positive voltage charging the empty traps again leads to depolarization of the structure and then the process of the shock excitation will be repeated. The scheme of the MIS EL element for the first time prepared on base of bulk CdF$_2$ RF [49] is shown in Fig.24.

MBE grown CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) heterostructure is perspective for EL displays because CdF$_2$:Er$^{3+}$ can be easily transform into conductive state [37, 50] that gives a good opportunity to realize shock ionization of Er$^{3+}$ luminescent centers with intense irradiation in visible and infrared regions controlled on spectral composition and intensity with Si logics. In framework of the current work test structures with 100 nm thick upper Au contact thermally
deposited onto CdF$_2$:Er$^{3+}$ layer and an ohmic contact to Si(111) substrate were prepared and investigated.

Fig. 24. The first EL cell on the base of bulk CdF$_2$ RE

Unfortunately, measurements of electroluminescence of CdF$_2$:Fr$^{3+}$/CaF$_2$ / Si(111) heterostructures could not be easily carried out due to the fact that the integral intensity of the light from a very thin CdF$_2$:Er$^{3+}$ layer is rather low and can not be measured through thick flat Au upper contact. So, our test structures gave an opportunity to measure EL with a rather low spectral resolution from back side of the test structure through Si substrate cutting the light with photon energies more than bandgap of Si.

Fig. 25. Experimental set-up for EL measurements.
Fig. 26. Electroluminescent spectra of CdF$_2$:$\text{Er}^{3+}$/CaF$_2$/Si(111) test structures measured through Si(111) window in comparison with EL spectrum of Si(111) substrate. Er$^{3+}$ concentration increases from sample 1507 to 1508.
The experimental set-up for EL measurements is shown in Fig.25. The EL test structure 1 was mounted on the cold finger 2 of a cryostat. Collected by the condenser 3 at about 90 Hz, 100V, 50 mA modulated and excited by the generator 4 fluorescence was focused on the slit of the monochromator 5, received by the sensitive p-i-n InGaAs detector 6, amplified with the Lock-in amplifier 7 and through the analog-to-digital transformer 8 was displayed on the computer 9.

Fig.26 shows the EL spectra from the test structures including only Si substrate and two CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) heterostructures with electric contacts. One can see no, but a weak signal near to Si bandgap electroluminescence for Si substrate as well as a broad EL band since the position of Si bandgap until the end of spectral sensitivity of the p-i-n InGaAs receiver (approx. 1700 nm) for CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) heterostructures. Thus, these structures for the first time demonstrate electroluminescence spectra arising, obviously, at shock ionization of Er$^{3+}$ center by free electrons. Of course, these test EL structures must be modified to increase the intensity and realize all the spectral region of the EL actual for Er$^{3+}$ in CdF$_2$.

6. Summary

We report on preparation and characterization of CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) heterostructures as well as on investigation of fluorescence of the relevant test structures. Using known literature data and experience of the Laser Research Laboratory and our counterparts in epitaxial growth of semiconductor and dielectric films and their investigations, optimal methods of cleaning and passivation procedures of Si(111) substrates, a temperature reduced MBE growth of doped by Er$^{3+}$ perfect CdF$_2$ layers onto coherent CaF$_2$ layer that to form a well ordered interface with silicon substrate were chosen and newly developed. The surface structure of the layers was studied by RHEED and Scanning Probe Microscope techniques. RHEED intensity oscillations have been observed during CdF$_2$ growth. They indicated a 2D layer by layer growth mode.

MBE grown CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) heterostructures develop effective cathode- and photoluminescence. A good correlation in spectral line positions between electronic structure of Er$^{3+}$ transitions, Er$^{3+}$ CL and PL spectra in bulk and epitaxial CdF$_2$:Er$^{3+}$ has been observed. The most intense spectra depending on the selected spectral region have those layers which are doped by 4 - 16 mol % of Er$^{3+}$. Thus, the most effective fluorescent CdF$_2$:Er$^{3+}$/CaF$_2$/Si(111) heterostructures have been grown by MBE and investigated by CL and PL methods.

In framework of the current work test structures with 100 nm thick upper Au contact thermally deposited onto CdF$_2$:Er$^{3+}$ layer and an ohmic contact to Si(111) substrate were prepared and investigated. These structures for the first time demonstrate electroluminescence arising, obviously, at shock ionization of Er$^{3+}$ center by free electrons.

Experimental facilities of the Laser Research Laboratory were improved in the course of present work that to be able to grow heterostructures of the type of semiconductor-semiconductor, semiconductor-crystalline dielectric as well as semiconductor-crystalline dielectric-semiconductor. Methods of doping by RE elements, in situ and ex situ characterization and investigation of the obtained structures have been elaborated or newly developed.
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