VĚDECKÉ SPISY VYSOKÉHO UČENÍ TECHNICKÉHO V BRNĚ

*Edice PhD Thesis, sv. 463*

*ISSN 1213-4198*

***Mustafa M. Abdalla Ahmed, MSc.***

# Alternating-Current Thin-Film Electroluminescent Device Characterization

BRNO UNIVERSITY OF TECHNOLOGY
Faculty of Electrical Engineering and Communication
Department of Physics

**Mustafa M. Abdalla AHMED, MSc.**

# ALTERNATING-CURRENT THIN-FILM ELECTROLUMINESCENT DEVICE CHARACTERIZATION

## Charakterizace tenkovrstvých elektroluminiscenčních součástek

Short version of Ph.D. Thesis

| | |
|---|---|
| Study field: | Microelectronics and Technology |
| Supervisor: | Prof. RNDr. Pavel Tománek, CSc. |
| Opponents: | Prof. RNDr. Miroslav Hrabovský, DrSc.<br>Ing. Ondřej Číp, Ph.D. |
| Presentation date: | 25. 4. 2008 |

**Keywords**

alternating-current thin-film electroluminescence (ACTFEL), electrolumi-nescent displays, phospors, ZnS:$Mn^{2+}$, evaporated ZnS:Mn, atomic layer epitaxy ZnS:Mn, green $Zn_2GeO_4$:Mn, ZnS:Mn doped with KCl, topography, electrical characteristics, subthreshold voltage-induced transferred charge, hole drift length, transport characteristics, optical characteristics, brightness and threshold voltage, photo-induced charge, photo-induced luminance, temperature and thickness effects, aging process, aging analysis, aging trends, Scanning Near-field Optical Microscopy (SNOM), measurement

**Klíčová slova**

elektroluminiscenční tenká vrstva řízená střídavým proudem (ACTFEL), elektroluminiscenční displej, luminofor, ZnS:Mn, napařený ZnS:Mn, epitaxe atomové vrstvy, Zn2GeO4:Mn, ZnS:Mn dotovaný KCl, topografie, elektrické charakteristiky, přenesený náboj, podprahové napětí, děrová driftová délka, transportní charakteristiky, optické charakteristiky, jas, prahové napětí, fotoindukovaný náboj, fotoindukovaná svítivost, teplotní jevy, vliv tloušťky, proces stárnutí, analyza stárnutí, trendy stárnutí, mikroskopie v optickém blízkém poli (SNOM), měření

The manuscript of this thesis is deposited and available
at the Department of Physics, Faculty of Electrical Engineering and Communication,
Brno University of Technology
Technická 8, 616 00 Brno, Czech Republic

ISBN 978-80-214-3651-0
ISSN 1213-4198

# CONTENTS

# 1 INTRODUCTION

An introduction to Alternating-current thin-film electroluminescent (ACTFEL) device technology begins with the discovery of the category of materials that luminesce, known as phosphors [1,2]. Luminescence is the non-thermal conversion of energy from some excitation source into light. The phenomenon of luminescence is observable in many forms, such as bioluminescence, triboluminescence, photoluminescence, cathodo-luminescence and electroluminescence [3].

Electroluminescence (EL) is the conversion of electric energy into light by subjecting a phosphor to an electric field. High-field EL was first discovered by Destriau [2], which observed light emission after applying a high AC voltage to a thin layer of fine Cu doped ZnS powder particles suspended in castor oil. Practical high-field ACFEL devices in the form of powder lamps were later developed by Sylvania after the emergence of the transparent conductor ITO in the early 1950's. The development of powder AC-EL gave way to thin-film EL technology after Vlasenko and Popkov showed brighter luminance from thin-film ZnS doped with Mn [3]. Thin-film electroluminescence suffered stability problems until 1974 when Inoguchi et al [4] reported a TFEL ZnS:Mn device sandwiched between two insulators which showed high luminance and a long operating life under an applied AC voltage. ACTFEL technology has since matured with the commercialization of monochrome at panel displays in the early 1980's and the development of multicolor displays in the 90's.

The primary application of ACTFEL technology is as a thin display in the flat-panel display (FPD) industry, which is driven by the demand for portable displays [5]. The leading FPD technology is the liquid-crystal display (LCD), found in a number of applications, such as watches, calculators, laptop computer monitors, and hand-held electronic devices. The LCD display is expanding into the desktop monitor market, replacing cathode-ray tube (CRT) technology. Other FPD technologies are the plasma display panel and the field-emission display (FED). The advantages of ACTFEL displays over LCDs are full-viewing angle, performance over a wider temperature range, sufficient ruggedness, and the ability to pattern smaller pixels.

An ACTFEL device has the structure of a metal-insulator-semiconductor-insulator-metal (MISIM) thin-film stack. The standard ACTFEL device structure, shown in Fig.1, employs a transparent substrate, typically glass, coated with a transparent conducting layer, which serves as the bottom electrode. The bottom insulator, phosphor, and top insulator layers reside between the bottom transparent conductor and a top conducting layer, which is opaque. The top conducting layer serves both as an electrical contact and as a reflector to direct light generated in the phosphor layer out through the glass substrate. The standard structure is the most prominently used structure by ACTFEL researchers. It is also used in manufacturing.

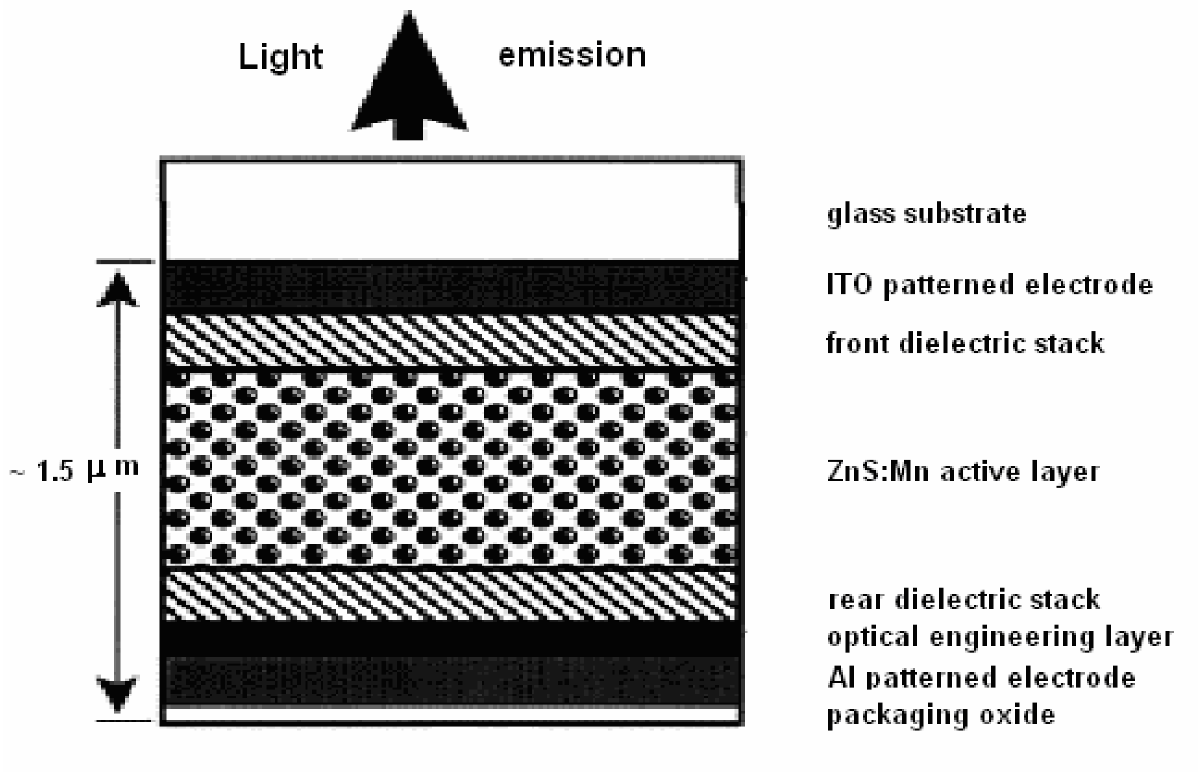


**Fig.1:** ACTFEL thin-film stack

ACTFEL displays are inferior to LCDs in that they suffer greater power consumption, lack adequate chromaticity, and require much larger driving voltages. The strong interaction of "hot" electrons with lattice phonons and crystal imperfections renders high-field EL an inefficient process, making it naturally more difficult to find sufficiently efficient phosphor materials for ACTFEL devices that emit in the primary colors. The best known ACTFEL phosphor to date is the yellow emitting ZnS:Mn, which can be filtered to give bright red and green emission.

## 1.1 STATE-OF-THE-ART

The generation of light in an electroluminescent device is achieved by transferring energy from charge carriers to luminescent centers in the phosphor. This requires that there are charge carriers in the phosphor and that those carriers have sufficient energy to excite the luminescent impurity to an excited state. The phosphor layer in an ACTFEL device is in series with at least one insulator, so light generation cannot be induced by a direct current flow through the phosphor layer.

In an ACTFEL device, light emission is produced when some type of alternating-current (AC) voltage waveform is applied to the electrically conducting layers of the thin-film stack. [5] In the basic model, the conduction of charge carriers in the phosphor layer of an ACTFEL device is usually assumed to originate from tunneling of electrons from insulator-phosphor interface states. [4,6,7] The energy depth of the states necessitates a high electric field be present at the phosphor-insulator interface for injection to occur. This field also serves to accelerate the carriers to energies sufficient to excite the dopant in the phosphor.

Upon application of an AC voltage waveform to the electrical contacts of an ACTFEL device, an electric field is set up in the phosphor layer. In an ideal device, the field is constant throughout the phosphor layer. If the field in the phosphor is insufficient for injection of charge carriers from interface states, the phosphor layer behaves like a dielectric and the device behaves like a capacitor with a capacitance equal to the capacitance of the phosphor and insulator layers in series [A1],

$$C_{tot} = \frac{C_{ins} C_{ph}}{C_{ins} + C_{ph}} . \tag{1}$$

The field in the phosphor layer is then given by

$$f_p = \frac{C_{ins}}{C_{ins} + C_{ph}} \frac{V_{applied}}{t_{ph}} , \tag{2}$$

where $V_{\text{applied}}$ is the voltage applied to the device and $t_{\text{ph}}$ is the thickness of the phosphor layer. The applied voltage at which injection occurs and the purely capacitive behavior of the phosphor layer is no longer present is the threshold voltage, $V_{\text{th}}$. When a voltage is applied across the device with a magnitude greater than $V_{\text{th}}$, charge is transferred across the phosphor layer and light emission is observed, if the carriers excite luminescent impurities.

There are two regimes of operation when the applied AC voltage has a magnitude greater than the threshold voltage in an ideal ACTFEL device:

a) when the applied voltage is below the turn-on voltage, the device behaves as a capacitor as described above,

b) above the turn-on voltage, the following processes occur in the phosphor layer of the device, as illustrated in Fig.2. [6]

Above the turn-on voltage, the phosphor field at the phosphor/insulator interface on the cathodic side of the device is large enough that electrons trapped in interface states or bulk traps are tunnel emitted into the phosphor conduction band, as illustrated by **process 1** in the energy band diagram representation shown in Fig.2. The injected electrons gain kinetic energy from the electric field and drift across the phosphor layer (**process 2**). As electrons transit across the phosphor, collisions with the host lattice atoms and the impurity atoms may occur. After undergoing a collision with an electron, a luminescent impurity could absorb some of the energy and become excited from its ground state to its excited state (**process 3**). The luminescent impurity subsequently relaxes back to its ground state, either radiatively by emitting a photon with energy equal to the energy level difference (**process 4**), or non-radiatively through phonon emission. Optical device efficiency is maximized when all of the excited impurity centers relax radiatively. After undergoing collisions, electrons continue to be transported across the remainder of the phosphor, gaining energy and possibly undergoing more collisions, until reaching the anodic phosphor/insulator interface, where they are captured in electron traps (**process 5**). A plethora of traps exist at the interface due to the disorder of the phosphor/insulator heterojunction. Some of the photons released during the luminescent impurity relaxation outcouple from the device and are observed by the viewer (**process 6**).

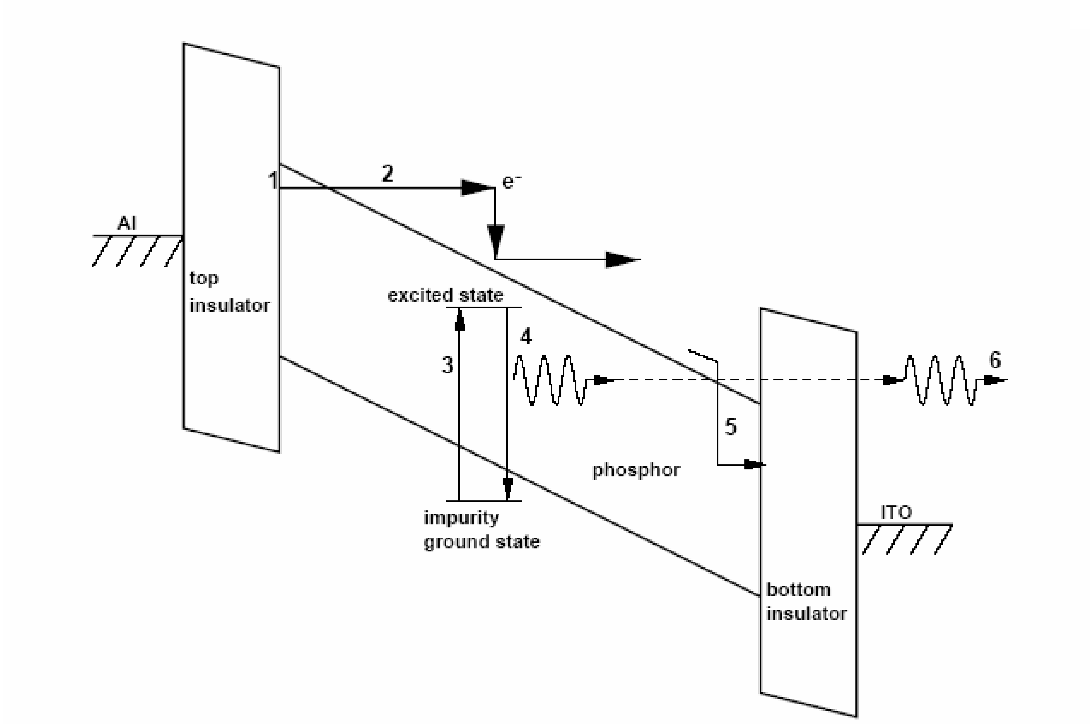


**Fig.2**: An energy band diagram of an ideal ACTFEL device under applied voltage, illustrating the primary physical properties involved in its operation.[6]

The simple model described above is acceptable as a basic description of ACTFEL operation; however, actual devices are more complicated. One of the most extensively researched departures from the simple ACTFEL device model is the presence of space charge in the phosphor bulk. A phosphor field dependent on both position and time complicates ACTFEL device operation.

If space charge exists in the phosphor, there is a field due to this charge, and the bands become bent when this field is represented in the energy band diagram.

Space charge is created in the phosphor bulk via

1) the trapping of holes generated by band-to-band impact ionization [8],

2) impact ionization of trapped electrons [9], and

3) field emission of trapped electrons to the conduction band, as depicted in Fig.4. [10]. The mechanism of space charge generation varies depending on the phosphor host, luminescent impurities, and codopants. Space charge in ACTFEL devices is ordinarily assumed to be positive because all of the II-VI wide bandgap semiconductors commonly used for ACTFEL phosphors are typically n-type. [10]

Another effect that hinders the understanding of ACTFEL operation is the dependence of the emission rate of electrons into the phosphor on the density of interface states. Emission from the insulator-phosphor interface is dependent on the field in the phosphor layer adjacent to the interface and on the temperature. A higher field is required for electron emission from a deeper state. Measurement of the interface state depth is complicated by the fact that space charge in the phosphor creates a higher field at the cathodic interface where emission occurs. In addition, electron multiplication due to impact ionization in the phosphor causes the measurement of more charge than is actually sourced from the interface states, making it appear that there are more interface states than actually exist. The interface state distribution assumed in the zero-order model does not simultaneously predict experimental leakage charge and turn-on voltage trends. [6,10]

## 1.2 OBJECTIVE OF THE DISSERTATION

The objective of this thesis is to **study the electrical and optical characterization** of ACTFEL display, and specifically the **aging process** of materials that comprise the ACTFEL display in an effort to improve the overall performance of the primary phosphor colors in terms of brightness, efficiency and stability. Since the dominant flat-panel display technology is the LCD, an alternative flat-panel display technology must gauge itself in terms of the LCD. The advantages of ACTFEL displays in comparison with LCDs are the ability to pattern much smaller pixel, performance over a wider temperature range, full-viewing angle, and readability with much greater intensity background light. The disadvantages of ACTFEL displays in comparison with LCDs are larger power consumption, lack of adequate chromaticity of the three primary colors, and much larger driving voltages.

Although the use and importance of green phosphors looked to be overcome, the target for the near future is the investigation of a green phosphor with enough brightness to maintain the correct ratio of brightness between the red, green and blue phosphors. For this reason, the **development of green ZnS:Mn ACTFEL phosphors** and **their characterization** is the main emphasis of this thesis although phosphors of other colors have not been entirely ignored.

Because limited funds for this investigation, which was marginal in the mainstream of the research in the Department of Physics, the realistic goals of the thesis was to provide an improved understanding of luminescent materials, and to exploit their properties to achieve bright, efficient green phosphors for use in full-color at-panel displays. Fortunately, a high-luminance, high-efficiency ACTFEL phosphor system, capable of being processed at temperatures below the glass substrate melting temperature, has been study on the different ACTFEL samples prepared by French colleagues from University of Technology of Troyes. The development of ACTFEL phosphors has also been advanced through the exploration of other phosphor materials, such as $Zn_2GeO_4$:Mn and ZnS:Mn doped with KCl.

# 2 SELECTED METHODS OF INVESTIGATION

To understand the results of the current study, previous studies of some optical and electrical characteristics of ACTFEL devices are shortly reviewed from the experimental point of view. The interested reader is also referred to the critical review article on this subject by Wager et al. [10] The methods used in this thesis will be explain more in detail in following chapter.

## 2.1 STANDARD MEASUREMENTS

The Figure 3 shows a block diagram of different set-ups used in this thesis for the measurement of optical and electric characterizations [A3].

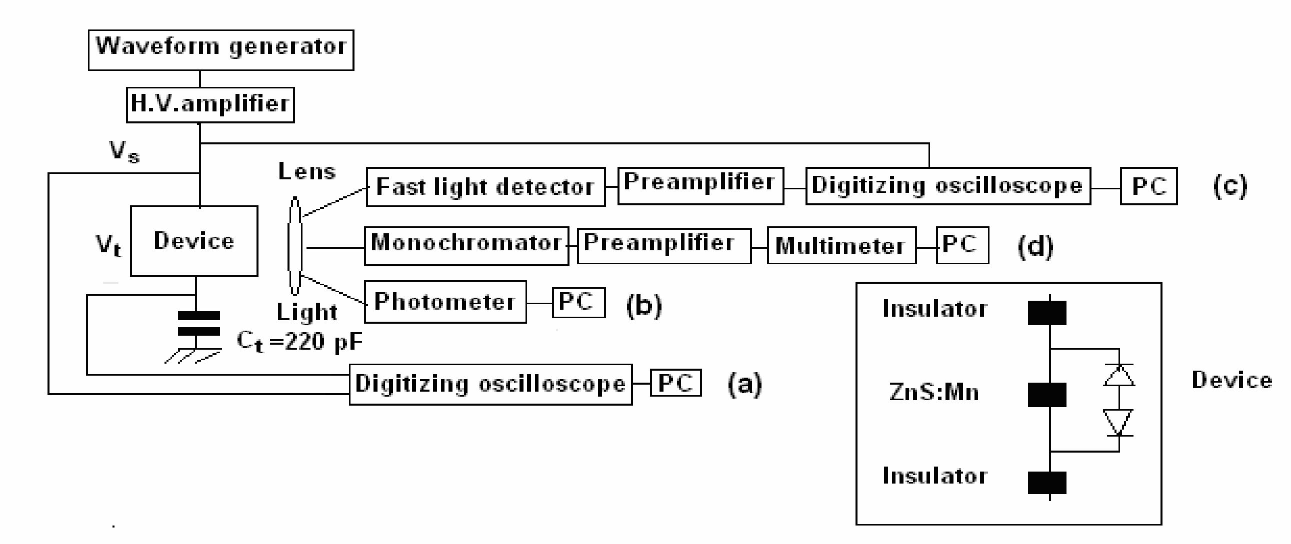


**Fig.3** Block diagram of the different set-ups used in this work: (a) *Q–V* loop evaluation, the typical equivalent circuit of the EL device is depicted in the detail; (b) *L–V* characteristic and efficiency; (c) Time relationship between $V_s$ waveform and the EL light pulse; (d) Emission spectra measurement [A3].

Since the ACTFEL device is an optoelectronic device, it is necessary to measure certain properties in terms of optical parameters like

- luminance,
- luminous efficiency,
- emission spectrum,
- latent image,
- color of the light

as well as electric parameters such as

- charge-voltage (Q-V),
- capacitance-voltage (C-V),
- internal charge-phosphor field ($Q_{int}$-$F_p$) and
- maximum charge-maximum voltage ($Q_{max}$-$V_{max}$).

A non-negligible and important property of each ACTFEL device is its aging process.

## 2.2 OPTICAL CHARACTERIZATION

For practical applications, the optical output of EL devices is a critical parameter.

Two systems units for quantifying optical output are used:

- Radiometric (optical power) units are used to quantify all electromagnetic radiation. These units quantify the photon flux density (radiant flux density) at a given wavelength.
- Photometric units are used to quantify light only in the visible part of the spectrum. The photometric system takes into account the spectral response of the human eye.

The most important properties of an ACTFEL device are

- the intensity of the light output, [11, A2]
- the power required to generate that light, and
- the color of the light.

As a result of this, the most commonly performed characterization experiments measure the luminance (brightness), the luminous efficiency, and the color spectrum of an ACTFEL device.

## 2.3 ELECTRICAL CHARACTERIZATION

Measuring the optical output of an ACTFEL device is useful for evaluating its potential as a display product, but does not provide adequate information regarding the physics of device operation. More insight into the physics of ACTFEL operation is gained with the use of various electrical characterization techniques [10, 12, 13]. This section describes electrical characterization techniques commonly used to investigate the physics of ACTFEL devices.

## 2.4 AGING CHARACTERIZATION

The importance of the aging characteristics of ACTFEL devices is underscored by the fact that device stability with aging tend to stabilize after a few tens of hours of burn-in, but can exhibit complex aging behavior during the burn-in process [14]. The aging is done by continuously operating the device at a fixed voltage or at a fixed voltage above threshold [15]. The aging process can be accelerated by operating the device at higher frequency or at higher temperature regime.

# 3 EXPERIMENTAL RESULTS

In this chapter, we present only most important results of the thesis. Because it is difficult to clearly separate optical, electrical and aging characterization methods, they are considered together.

## 3.1 PHOTO-INDUCED CHARGE AND HOLE DRIFT LENGTH

The photo-induced charge (PIQ) experimental set-up is modified scheme shown in Fig.3d [A3]. The ultraviolet radiation is generated by a nitrogen laser at a wavelength of 337 nm pumping a dye laser tuned to 500 nm, which then passes through a doubling crystal to create 250 nm wavelength pulses of 2-3 ns duration. Since the band gap of ZnS is 3.7 eV (330 nm), this photon energy is sufficiently large to create electron-hole pairs by band-to-band generation. The DC voltage applied to the ACTFEL device is generated by an arbitrary-waveform generator (Wavetek model 395) and amplified by a high-voltage amplifier. The PIQ signal is measured by means of a 100 pF sense capacitor in series with the ACTFEL device via a digitizing oscilloscope (Tektronix model TDS 420A) [A4].

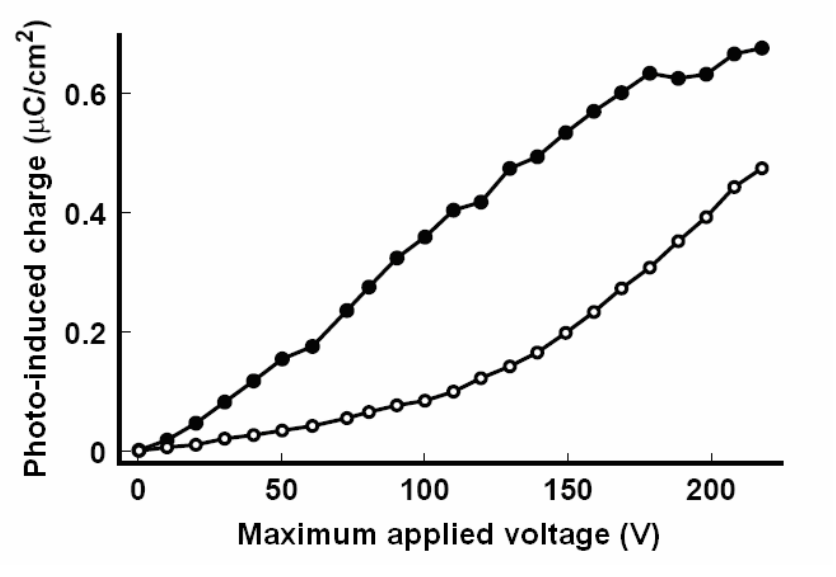


**Fig.4:** PIQ curves for ZnS:$Mn^{2+}$ ACTFEL device (Thickness of phosphor is of 700 nm). • - electrons, o – holes [A4].

The samples used in this study consist of a standard ACTFEL structure with SiON top and bottom insulators, evaporated ZnS:Mn as the phosphor layer, an indium-tin oxide bottom contact, and aluminum top contact. The top and bottom insulator thicknesses are approximately 110 nm and 180 nm, respectively, for all three of the ACTFEL devices used in this study. Phosphor thicknesses are 300, 700, and 950 nm. For PIQ experiments, an ~15-nm-thick semi-transparent layer of aluminum is thermally evaporated onto the sample so that a small portion of this layer overlaps neighboring thick aluminum dots, but the majority of the thin contact covers the uncontacted ACTFEL stack.

The experimental results of this study are presented in Fig. 4 in which PIQ is plotted as a function of the maximum voltage applied to the ACTFEL device with phosphor thickness of 700 nm. The PIQ curves for phosphor thicknesses of 300 and 950 nm exhibit trends similar to those shown in Fig.4.

Fig. 5 is a plot of the drift length as a function of the internal phosphor field. Note that the lowest field points are not reliable because of the PIQ uncertainties. Also, the upward trend in the hole drift length for phosphor fields greater than ~0.8 MV/cm arises from the onset of backside electron injection, not from an enhancement in the hole drift length. Thus, taking the relatively constant, low-field portion of Fig. 5 as a measure of the drift length, the hole drift length is estimated to be 180 ± 70 nm. If holes are assumed to travel at a saturated drift velocity of $\sim 10^{7}$ cm/s, then the drift distance can be used to deduce an average hole lifetime of ~2 ps. Furthermore, if the hole trap density is assumed to be $7\times10^{16}$ $\mathrm{cm}^{-3}$ [A3], the hole trap capture cross section can be estimated from [17]

$$\sigma = \frac{1}{\tau v_{\mathrm{sat}} N_{\mathrm{t}}} \sim 7 \times 10^{-13}\ \mathrm{cm}^{2}, \tag{3}$$

where $\tau$ is the hole lifetime, $v_{\mathrm{sat}}$ is the saturated drift velocity, and $N_{\mathrm{t}}$ is the trap density.

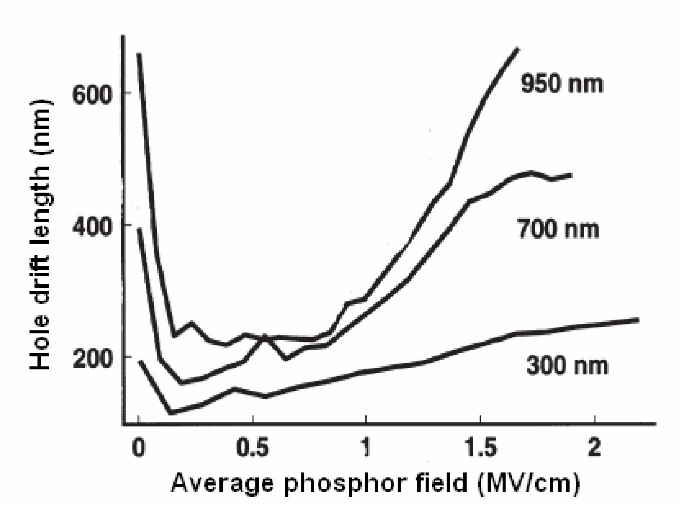


**Fig.5:** Hole drift length versus average phosphor field for evaporated ZnS:Mn ACTFEL devices with phosphor thickness of 950 nm, 700 nm and 300 nm [A3].

## 3.2 BRIGHTNESS AND THRESHOLD VOLTAGE AS A FUNCTION OF PHOSPHOR THICKNESS

Memory ACTFEL devices show hysteresis in their brightness-voltage (B-V) response curve [A5, A6]. The hysteresis voltage margin, $\Delta V$, and saturation brightness $B_s$, can be considered as the figures of merit for memory ACTFEL displays.

As an example of obtained results, the measured relations of the B-W response curves at various peak-to-peak voltages for the ZnS:Mn film thickness of 700 nm are shown in Fig. 6. As can be seen, a pronounced hysteresis effect is observed for the device driven near the threshold voltage.

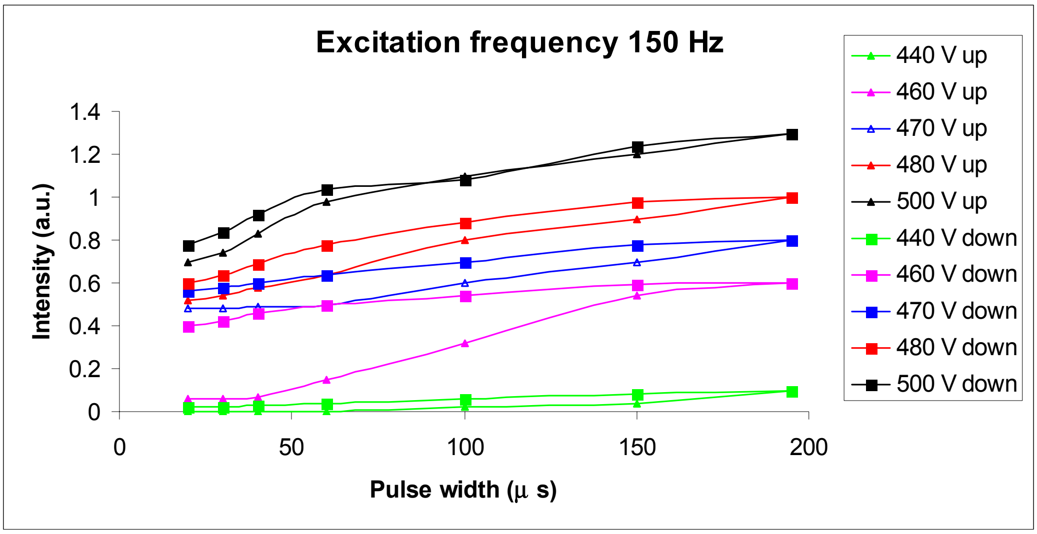


**Fig.6:** The measured relation of the brightness versus pulse width (B-W) at various peak-to-peak voltage of the memory EL device at excitation frequency 150 Hz [A6].

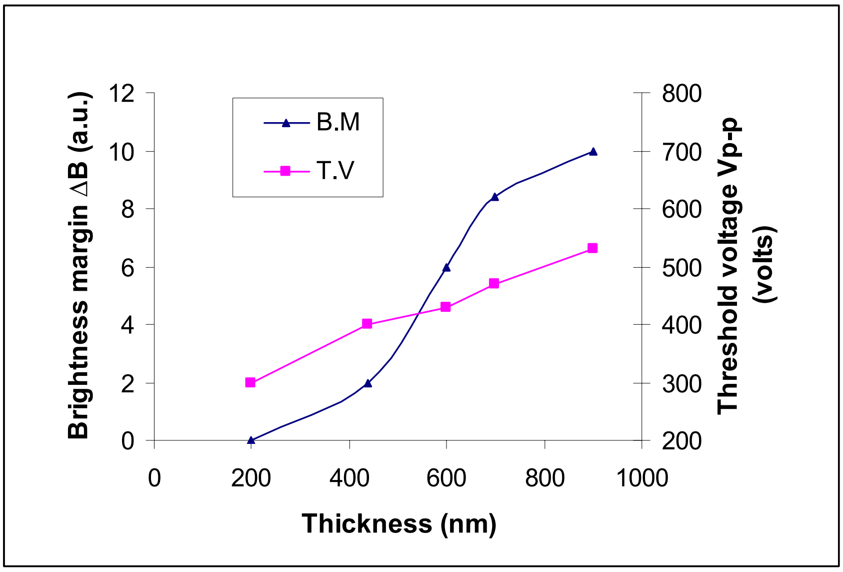


**Fig.7:** The observed variations of brightness margin, ΔB (curve BM) and threshold voltage $V_{p\text{-}p}$ (curve TV) with respect to the film thickness of ZnS:Mn layer [A6].

Let the brightness margin, Δ*B,* be defined as the hysteresis width at pulse width 20 µs, the observed variations of Δ*B* and the threshold voltage with respect to the ZnS:Mn film thickness are shown in Fig.7 [A6]. It is noted that the hysteresis appears only if the ZnS film is thicker than 200 nm. Above it, the hysteresis width Δ*B* increases with the film thickness.

## 3.3 BRIGHTNESS AND LUMINOUS EFFICIENCY OF ZnS:Mn DOPED WITH KCl

The grain structure from as deposited ZnS:Mn is shown in Fig.8 by TEM photomicrographs taken from an ACTFEL device [A7]. In Fig.8a, a layer of very fine equiaxed grains (10 nm grain diameter, 100 nm thick) is observed close to the insulator/phosphor interface. The grain boundaries of most of the columnar grains in the balance of the cross section are barely definable. The columnar grain diameter measured by the mean linear intercept from plan-view TEM photomicrographs is 90 nm.

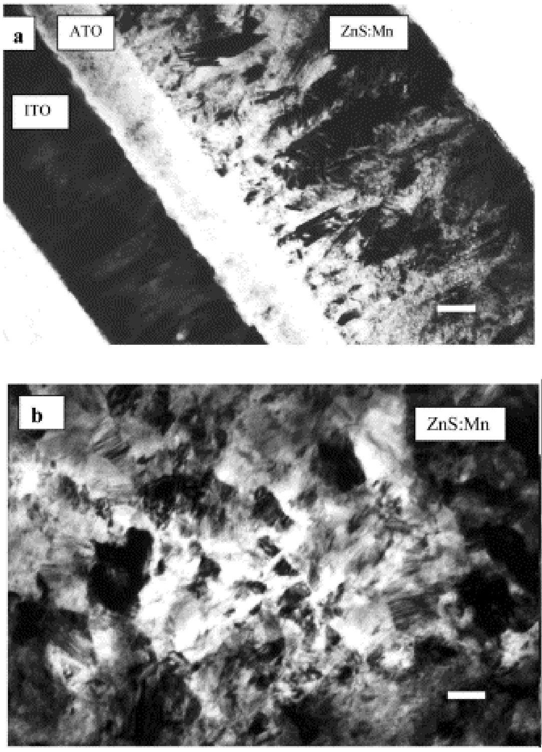


**Fig.8:** TEM micrographs taken from the ACTFEL device with as-deposited ZnS:Mn phosphor [A7].
(a) cross-section,
(b) plan-view (bar=100nm).

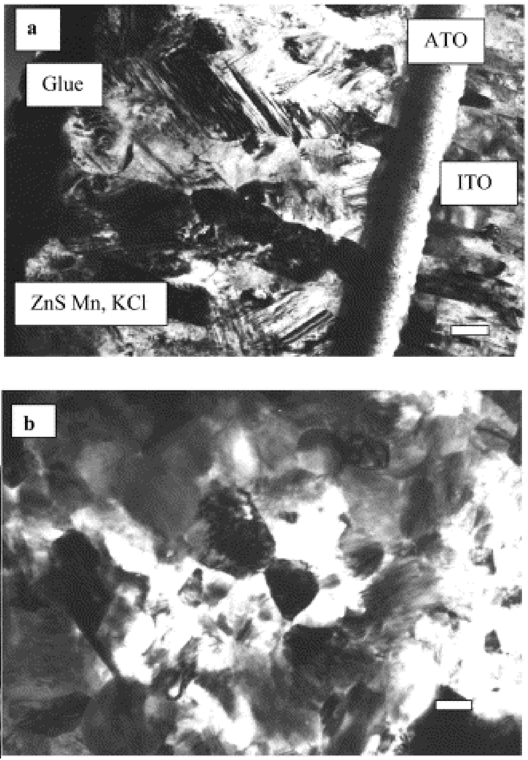


**Fig.9:** TEM micrographs taken from ZnS:Mn, KCl after 5min of annealing at 700°C [A7].
(a) cross-section,
(b) plan-view (bar=100nm).

Contrast bands in the columnar grains are obvious. After an RTA at 700 °C for 5 min, KCl co-doped ZnS:Mn phosphor exhibited enhanced columnar grain growth (to a grain diameter of 190 nm) which also consumed the equiaxed grain layer at the ZnS/ATO interface (Fig.9). The density of the contrast bands was still high in this sample, independent of whether or not KCl was co-doped. Finally, KCl co-doped ZnS:Mn thin films annealed to T ≈ 900 °C resulted in very large grains which approached equiaxed geometries with diameters >1 μm.

The luminous efficiency and brightness from samples as-deposited or annealed at 700 °C with or without KCl are plotted in Fig.10. In all cases, the brightness first increases almost linearly with the applied voltage, then tends to saturate in the high voltage regime. This behavior is characteristic of ZnS:Mn devices [14]. Data in Fig.10 also show that the slope of the *B–V* curve from KCl doped sample is larger than for undoped samples, indicating a sharper turn-on behavior. Neither annealing nor incorporation of KCl changed the color of ZnS:Mn thin films, since all the EL emission spectra exhibit a peak at 580–584 nm, and no changes in CIE coefficients are detected.

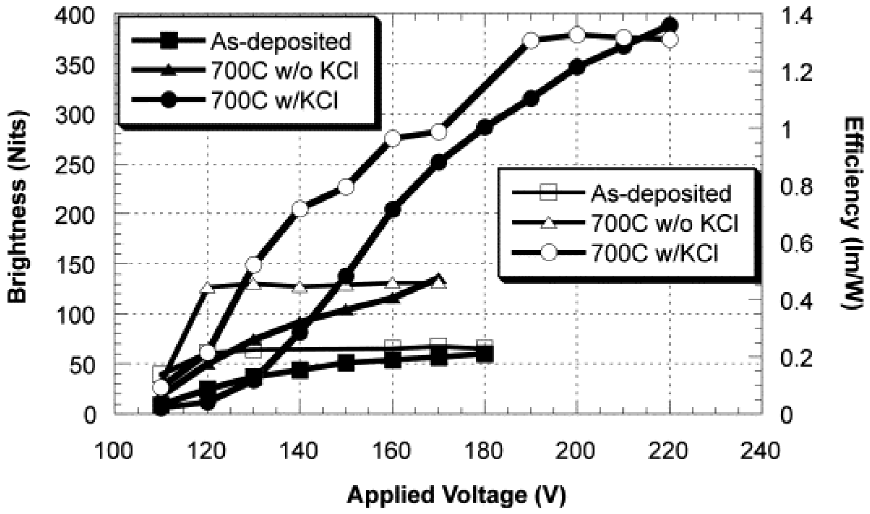
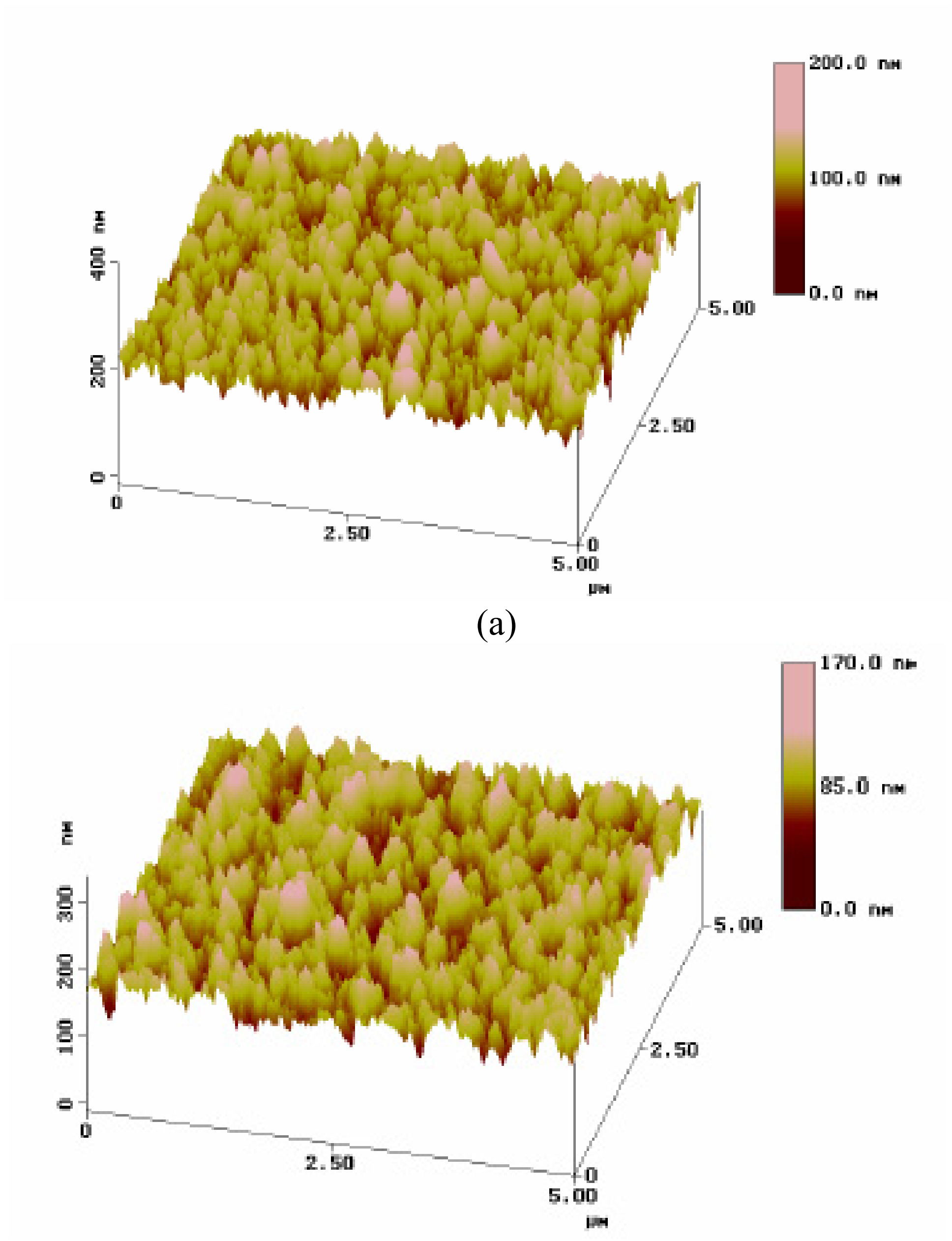


**Fig.10:** Effects of RTA and KCl co-doping on EL brightness (solid circles) and luminous efficiency (open circles) [A7].

## 3.4 AGING OF GREEN-EMITTING $Zn_2GeO_4$:Mn PHOSPHOR

Oxides were among the first and more extensively researched luminescent materials, and they comprise a substantial portion of important phosphors for electro-luminescent lamp, cathode ray tube (CRT), and other applications [16]. Research on alternating-current thin-film electroluminescence (ACTFEL) [6], however, has generally been focused on sulfide-based phosphor systems, particularly ZnS and SrS. Oxide phosphor materials have been thought to be poorly suited for ACTFEL applications because of their typically large bandgaps and their refractory nature. The last decade, however, has seen an increase in oxide thin-film phosphor research with several groups reporting success in manufacturing oxide-based ACTFEL devices [10].



(a)

(b)

**Fig.11:** Apertureless SNOM surface morphologies of
(a) as-deposited and (b) annealed at 425 ºC for 1 hr $Zn_2GeO_4$:Mn thin films [A8].

Surface roughness can significantly affect the brightness of the device by affecting the outcoupling efficiency. As-deposited films and films annealed at 425 ºC for 1 hr films were quantitatively analyzed to study changes in surface roughness. Figure 11 shows surface morphology from apertureless Scanning near-field optical microscopy for (a) as-deposited and (b) annealed $Zn_2GeO_4$:Mn samples. The root mean square (RMS) surface roughness measured was 16 -16.5 nm for the as-deposited films and 15-15.5 nm for the annealed films [A8]. Negligible change (±10%) in the surface roughness was observed between the two, suggesting that the outcoupling efficiency of EL emission was not changed by annealing [18].

To resolve the cubic and hexagonal phases, TEM was used to investigate the structure of the $Zn_2GeO_4$:Mn thin films on a microscopic scale. A JOEL 200 CX TEM operating at 300 keV was used for characterization and cross section of samples. Figure 12 shows cross section TEM micrographs for $Zn_2GeO_4$:Mn thin films in the as deposited (Fig.12a) and the annealed conditions (Fig.12b) which clearly shows the multi-stacked ACTFEL structure. To study the structure of the thin film device, electron diffraction patterns were collected from various parts of the $Zn_2GeO_4$:Mn film. TEM revealed a mixture of two structures (cubic and hexagonal) though it was difficult to resolve one from the other. In one area of the film a predominantly cubic structure (Fig.12d) was observed whereas in other areas it was predominantly hexagonal (Fig.12c). On the whole a rather non- homogenous film was observed.

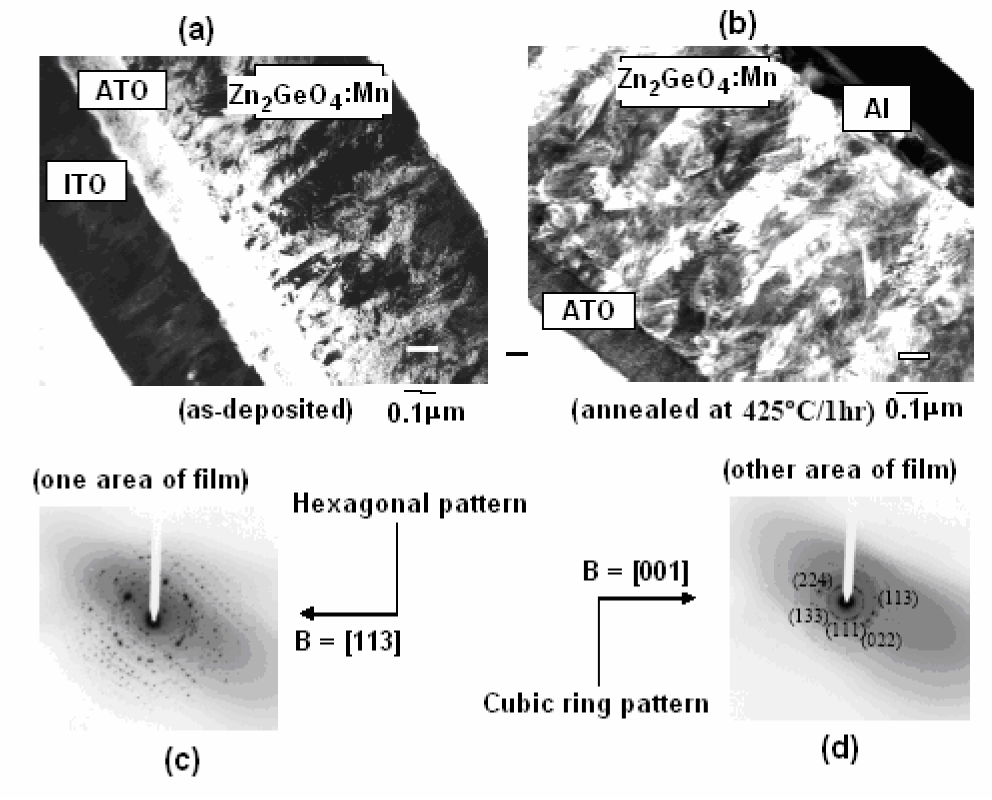


**Fig.12:** TEM micrographs for $Zn_2GeO_4$:Mn thin films [A8].

One of the more important attributes of an ACTFEL phosphor material is its luminance stability [19]. The luminance-voltage (*L-V*) and luminous efficiency-voltage ($\eta$-*V*) characteristics of a $Zn_2GeO_4$:Mn (2% Mn) ACTFEL device operated at 50 Hz are shown in Fig.13. $L_{40} = 10^5$ cd/m$^2$ and $\eta_{40} = 0.33$ lm/W are observed for the brightest device; other devices exhibit lower luminance levels ($L_{40} = 80$cd/m$^2$) but better efficiency ($\eta_{40} = 0.45$ lm/W). These numbers can be compared to the brightest reported saturated green ACTFEL phosphors, ZnS:Tb and ZnS:TbOF, which have 50 Hz $L_{40} = (90 – 100)$ cd/m$^2$ and $\eta_{40} = (0.6 - 1.0)$ lm/W, respectively, and CIE coordinates of 0.30; 0.60. These ZnS:Tb EL phosphors, however, have been hindered by stability problems; four prominent emission peaks also limit color purity. Also, the use of $BaTa_2O_6$ as a top insulator material would double the insulator capacitance and therefore is expected to double the $L_{40}$ value for the $Zn_2GeO_4$:Mn devices to $\eta$ = 200 cd/m$^2$ [A3].

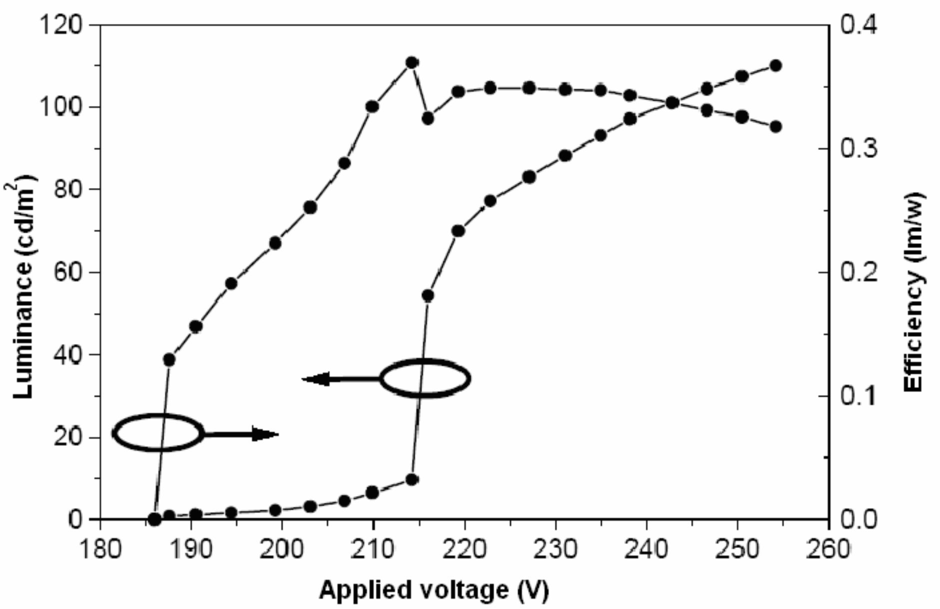


**Fig.13:** Luminance-voltage (L-V) and efficiency-voltage ($\eta$-V) plots of a $Zn_2GeO_4$:Mn (2% Mn) ACTFEL device driven at 50 Hz. ($L_{40} = 10^5$ cd/m$^2$ and $\eta_{40}$ = 0.33 lm/W) [A3].

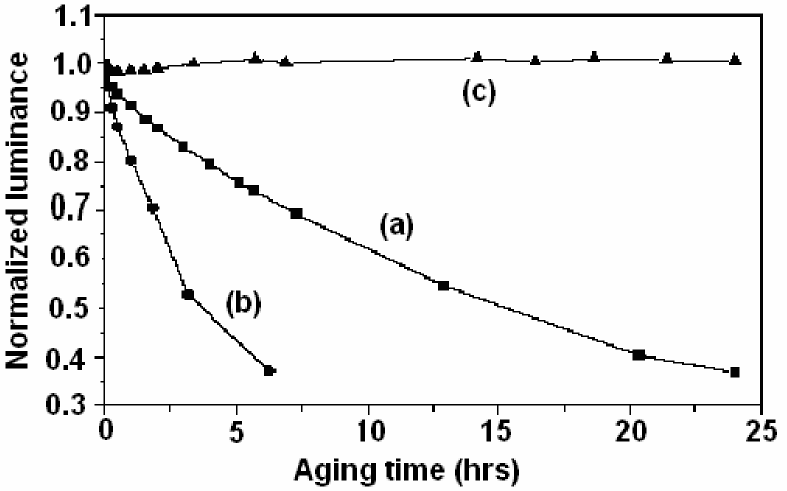


**Fig.14:** Normalized luminance vs. aging time for three devices on two substrates, as described in the text. Devices (a) and (c) are aged at 300 K, while (b) is aged at 125 K [A8].

Constant voltage aging behavior typical of the devices manufactured during this study with the standard structure is indicated by curve (a) in Fig.14, which shows the normalized luminance of a 3% doped Mn $Zn_2GeO_4$:Mn device operated at 40 V above the initial threshold voltage at 1 kHz as a function of time [A8].

## 4 CONCLUSIONS

Although the use and importance of green phosphors looked to be overcome, the target for the near future is the investigation of a green phosphor with enough brightness to maintain the correct ratio of brightness between the red, green and blue phosphors. For this reason, the **development of green ACTFEL phosphors** and **their characterization** is the main emphasis of this thesis although phosphors of other colors have not been entirely ignored.

Having this in mind, the principal **objectives** of this thesis were to **study the electrical and optical characterization** of ACTFEL devices, and specifically the **aging process** of materials that comprise the ACTFEL display. Short-term and long-term ACTFEL aging studies has been provided and an attempt to visualize locally the structure of phosphor with a subwavelenght resolution using Scanning near-field optical microscope (SNOM) has also been presented.

The important results of this study are:

**1) Luminance-voltage** (*L-V*) and **luminous efficiency-voltage** ($\eta$ *-V*) characteristics are dependent on several factors [A1, A2]:
- type of driving waveform, - shape of the waveform, and - frequency of the waveform.

The *L-V* characteristics are also dependent on
- ambient temperature [A2], - dopant concentration [A5], and - thickness of the phosphor layer [A6].

**2) Photo-induced charge** (PIQ) and p**hoto-induced luminance** (PIL) experiments show that e*lectron and hole transport may be studied independently* by simply changing the polarity of the DC bias. In ZnS:Mn$^{2+}$ ACTFEL devices the hole transport may give rise to impact excitation-induced electroluminescence, holes are approximately half as efficient as electrons in contributing to the transferred charge, and that the efficiency of transport is significantly greater for holes than electrons [A3, A5].

The fact *that photo-induced hole efficiency is greater than the photo-induced electron efficiency was very surprising.* This result can be interpreted as arising from differences in the electric field profile in the phosphor for the cases of hole and electron transport. The further study suggests that hole transport is not effective in ZnS, and that what appears to be hole-induced effects are actually due to whole trapping-induced back injection of electrons [A2, A9].

**3) Influence of KCl co-doping on the microstructure and the EL properties of ZnS:Mn phosphors**:
At temperatures of 700 °C, the incorporation of KCl *improves the crystallinity of the ZnS:Mn* phosphors by enhancing a grain growth in the columnar grains.

Co-doping with KCl *improves the brightness and efficiency by ≈ 100 %,* and *increases the threshold voltage* and makes the slope of the *B–V* plot much larger.

The EL data show that while improved crystallinity may reduce non-radiative recombination, the *most important effects* of KCl co-doping are a *reduction of space charge* and *band bending* with a resulting l*arger, hotter electron population in the EL phosphor* [A7].

**4) ACTFEL devices aging trends**

Most of this work has involved characterization of the electric and/or luminescent properties of the ACTFEL devices as a function of aging time.

ACTFEL devices tend to stabilize after a few tens of hours of burn-in, but can exhibit **complex aging behavior** during the burn-in process. This study is unique in that the aging characteristics are monitored, as a *function of temperature* and *aging time*, using the *capacitance-voltage (C-V) technique*, which offers several advantages for ACTFEL aging studies [A10, A11, A12].

The luminance-voltage curves for ZnS:Mn devices in which the phosphor layer was deposited, tend to shift to slightly higher voltage during burn-in [A13, A14].

The experimental results are the following:

- Insulator and phosphor capacitances are constant with respect to aging time; this suggests that the *perturbation in the electrostatic charge distribution* which is *responsible for aging occurs near the SiON/ZnS interfaces*.
- *C-V* curve shifts rigidly with aging time; a rigid shift indicates that *changes in the fixed charge density*, not the interface charge density, *give rise to aging*.
- Activation energy for short-term aging is found to be approximately 0.2 eV. *Atomic rearrangement at SiON/ZnS interfaces leads to the formation of deep level*, *fixed charge states* which *trap transported conduction electrons*. Such electron trapping l*eads to a reduction of the conduction and polarization charges* and an *increase in the turn-on voltage*.
- The most striking implication of the **aging trends** is that the *interface state distributions* at the *top and bottom interfaces* are *asymmetric* and *exhibit highly asymmetric aging characteristics*.

A short study of aging characteristics of borrowed sputtered $Zn_2GeO_4$:Mn ACTFEL device is also presented [A8, A15]. Although the electro-optic performance and aging behavior of this phosphor was rather good, the luminous efficiency was currently not sufficient to justify commercialization of this phosphor.

Future efforts to improve the luminous efficiency of this phosphor should focus on alternatives to field-ionization of impact-excited $Mn^{+2}$ luminescent impurities as a means of introducing space charge into the phosphor.

Perhaps this could be accomplished via co-doping or the use of alternative annealing procedures. Also, the use of luminescent impurities with shorter lifetimes could be advantageous since this would minimize transient luminance annihilation.

# 5 REFERENCES

[1] KOBAYASHI, H., TANAKA, S. The present and future prospects of electroluminescent phosphors, *Journal of SID*, 1996, Vol. 4, No.3, p. 157-163.

[2] DESTRIAU, G., Recherches sur les scintillations des sulfures de zinc aux rayons, *Journal de la Chimie et de la Physique*, 1936, Vol. 33, No. 9, p. 587-625.

[3] VLASENKO, N.A., POPKOV, Y.A., The electroluminescence of sublimate phosphor ZnS:Mn, *Optika i Spektroskopiya*, 1960, Vol. 8, No. 1, p. 81-88.

[4] INOGUCHI, T., TAKEDA, M., KAKIHORA, Y., YOSHIDA, M., Stable high luminance thin-film electroluminescent panels, *SID Digest*, 1974, Vol. 5, No. 1, p. 84 - 92.

[5] MAUCH, R.H., The current status of thin-film electroluminescence, *Journal of SID*, 1997, Vol. 5, No. 3, p. 173-178.

[6] ONO, Y. A., *Electroluminescent display*, World Scientific, Singapore, 1995.

[7] HITT, J.C., BENDER, J.P., WAGER, J.F. Thin-film electroluminescent device physics modeling, *Critical Review of Solid State Materials Science*, 2000, Vol. 25, No. 1, p. 29-85.

[8] STUYVEN, G., De VISSCHERE, P., NEYTS, K., HIKAVYY, A., Hybrid electroluminescent devices with atomic layer deposited thin films on a screen printed dielectric, *Japanese Journal of Applied Physics*, *part 1-regular papers short notes & review papers*, 2002, Vol. 41, No. 8, p. 5702 -5705.

[9] BRINGUIER, E., Statistical mechanics of high-field transport in semiconductors, *Physical Review*, 1995, Vol. B 52, No. 11, p. 8092 – 8105.

[10] WAGER, J. F., KEIR, P. D. Electrical characterization of thin-film electroluminescent devices In *Annual Review of Materials Science*, Palo Alto, 1997, Vol. 27, p. 223-248.

[11] DOBIS, P., BRÜSTLOVÁ, J., GRMELA, L., TOMÁNEK, P. Electrooptical characterization of ZnS:Mn thin-film electroluminescent devices, In *10th EDS 2003 Electronic Devices and Systems Conference*, Brno, Ing. Zdeněk Novotný, CSc., 2003, p. 287 - 290, ISBN 80-2142452-4.

[12] BHATTACHARYYA, K., GOODNICK, S.M., WAGER, J.F., Monte Carlo simulation of electron transport in alternating-current thin-film electroluminescent device, *Journal of Applied Physics*, 1993, Vol. 73, No. 7, p. 3390-3395.

[13] NEYTS, K. A., CORLATAN, D., VISSCHERE, P.D., DEN BOSSCHE, J. V., Observation and simulation of space-charge effects and hysteresis in ZnS:Mn

ac thin-film electroluminescent devices, *Journal of Applied Physics*, 1994, Vol. 75, No. 8, p. 5339-5346.

[14] SOENEN, B., VAN DEN BOSSCHE, J., DE VISSCHERE, P., Kinetics and aging in atomic layer epitaxy ZnS:Mn AC thin-film electroluminescent device, *Journal of Applied Physics*, 1997, Vol. 82, No. 8, p. 5241-5246.

[15] SHIH, S.-P. *Electrical characterization and aging studies of ALE ZnS:Mn ACTFEL devices with varying phosphor thickness,* M.S. thesis, Oregon State University, 1996.

[16] BLASSE, G., GRABMAIER, B.C., *Luminescent materials*, 1994, Berlin: Springer-Verlag.

[17] CLEARY, B.A., HITT, J.C.,KEIR, P.D., PLANT, T.K., WAGER, J.F., SUN, S.S., Photo-induced charge and luminescence measurements of evaporated ZnS:Mn alternating-current Thin-film electroluminescent devices*, Journal of SID*, 2000, Vol. 51, Suppl-1, p. 51-56.

[18] LEWIS, J.S., DAVIDSON, M., HOLLOWAY, P., Control of point defects and space charge in electroluminescent ZnS:Mn thin films, *Journal of Applied Physics*, 2002, Vol. 27, No. 12, p. 6646-6657.

[19] WILLIAMS, L.C, NORTON, D., BUDAI, J., HOLLOWAY, P.H. Cathodoluminescence from thin film $Zn_2GeO_4$:Mn phosphor grown by pulsed laser deposition, *Journal of Electrochemical Society*, 2004, Vol. 151, No. 8, p. H188-H191.

# 6 OWN PUBLICATIONS

[A1] AHMED, M., TOMÁNEK, P., *Luminance-voltage and efficiency-voltage characterization of* $ZnS:Mn^{2+}$ *alternating-current thin-film electroluminescent device,* In Proceedings EDS' 04. The 11th Electronic Devices and Systems Conference. Brno: Vysoké učení technické v Brně, 2004, p. 76 - 79, ISBN 80-214-2701-9

[A2] AHMED, M., TOMÁNEK, P., Influence of charged centers on transport characteristics of alternating current thin film electroluminescent devices, *Proceedings of SPIE*, ISSN 0277-786X, 2006, Vol. 6018, p. 61 - 65.

[A3] AHMED, M., *Photo-induced charge and hole drift length measurement of evaporated ZnS:Mn alternating-current thin-film electroluminescent devices,* In Elektrotechnika a informatika 2004. Plzeň: Fakulta elektrotechnická, Zapadočeská univezita v Plzni, 2004, p. 63 - 66, ISBN 80-7043-300-0

[A4] AHMED, M., *Photo-induced charge and luminescence measurements in* $ZnS:Mn^{2+}$ *ACTFEL,* In New trends in Physics NTF 2004. Brno: Ing. Zdeněk Novotný, CSc., 2004, p. 200 - 203, ISBN 80-7355-024-5

[A5] AHMED, M., *Phosphor materials and luminescent impurities for ACTFEL device,* In Workshop NDT 2004 Non destructive testing. Brno: Brno University of Technology, 2004, p. 8 - 13, ISBN 80-7204-371-4

[A6] AHMED, M., *The dependence of brightness and threshold voltage of memory ZnS:Mn thin film electroluminescent device upon its thickness,* In Proceedings of the 12th Conference Student EEICT 2006. Brno: Vysoké učení technické v Brně, FEKT a FIT, 2006, p. 128 - 132, ISBN 80-217-4-3162-8

[A7] AHMED, M., *Electroluminescence brightness and luminous efficiency of ZnS:Mn doped with KCl,* In Proceedings of the 13th Conference STUDENT EEICT 2007. Ing. Zdeněk Novotný, CSc., Ondráčkova 105, Brno, 2007, p. 210 - 214, ISBN 978-80-214-3409-7

[A8] AHMED, M., Aging characteristics of green-emitting $Zn_2GeO_4$:Mn alterating-current thin-film electroluminescent devices, *Transactions of the VŠB – Technical University of Ostrava, Mechanical Series,* 2005, Vol. LI, No. 2, p. 1-6, ISSN 1210-0471

[A9] AHMED, M., *Subtreshold voltage-induced transferred charge aging analysis of alternating-current thin-film electroluminescent device,* In New trends in Physics NTF 2004. Brno: Ing. Zdeněk Novotný, CSc., 2004, p. 196 - 199, ISBN 80-7355-024-5

[A10] AHMED, M., TOMÁNEK, P., *Local opto-electronic characteristics of alternating current ZnS:Mn thin-film electroluminescent devices* In Mikrosyn-

2006. Nové trendy v mikroelektronických systémech a nanotechnologiích: Moderní diagnostika materiálů a součástek-2006. Brno: Ing. Zdeněk Novotný, CSc., Ondráčkova 105, Brno, 2007, p. 93 - 102, ISBN 978-80-7355-075-2

[A11] AHMED, M., TOMÁNEK, P. DOBIS, P., BRÜSTLOVÁ, J., *Local investigation on alternating current ZnS:Mn thin-film electroluminescent devices,* In CoPhys 2006, International Physics Workshop. Nitra: Constantine the Philosopher University, 2007, p. 53 - 63, ISBN 978-80-8094-084-3

[A12] AHMED, M., TOMÁNEK, P., *Influence of charged centers on transport properties of thin film electroluminescent devices,* In Photonics Prague 2005. Prague: Zeithamlová Milena, Ing. - Agentura Action M, 2005, p. 145 - 146, ISBN 80-86742-08-3

[A13] AHMED, M., *Aging study of evaporated ZnS:Mn alternating-current thin-film electroluminescent devices,* In Proceedings of the 11th conference STUDENT EEICT 2005. Brno: FEKT VUT, 2005, p. 193 - 197, ISBN 80-214-2889-9

[A14] AHMED, M., *Aging studies of atomic layer epitaxy ZnS:Mn alternating-current thin-film electroluminescent devices* In Proceedings of the 11th Conference STUDENT EEICT 2005. Brno: FEKT VUT, 2005, p. 188 - 192, ISBN 80-214-2889-9

[A15] AHMED, M. *Aging characteristics of green-emitting* $Zn_2GeO_4$*:Mn alternating-current thin-film electroluminescent devices,*In Proceedings of XXXth Seminary XXX ASR'05 INSTRUMENT and CONTROL'05. Ostrava: VŠB-TU Ostrava, 2005, p. 10 - 11, ISBN 80-248-0774-2

# 7 CURRICULUM VITAE

**Name:** AHMED Mustafa M. Abdalla
**Date and place of birth**: November 11, 1965, Bergen, Libya
**Citizenship**: Libyan
**Contact**: Mustafa_phy2005@yahoo.com

## Education

| | |
|---|---|
| 2003-2008 | Technical University of Brno, Department of Physics<br>Ph.D. study of Microelectronics and Technology |
| 1996-2000 | University of Nicolas Copernicus, Toruň, Poland<br>M.Sc. study of Physics and Astronomy |
| 1996 | University of Science Malaysia<br>English Language Course |
| 1987-1991 | Sebha University, Libya<br>BSc. Study of Physics |

## Working experience

| | |
|---|---|
| 1991-1995 | Sebha University, Libya<br>Assistant Lecturer, Department of Physics |
| 2000-2003 | Sebha University, Libya<br>Lecturer, Department of Physics |

## Award

| | |
|---|---|
| 2005 | Technical University Ostrava – laureate’s award at XXXth Seminary ASR´05 “Instruments and Control” – best paper “Aging characteristics of green-emitting $Zn_2GeO_4$:Mn alternating-current thin-film electroluminescent devices” |

## Language

Arabic – native
English

## Project

MSM 0020630503 – New Trends in Microelectronic System and Nanotechnologies

# 8 ABSTRACT

The **objective** of this thesis is to **study the optical and electrical characterization** of Alternating-Current Thin-Film ElectroLuminescent (ACTFEL) devices, and specifically the **aging process** of phosphor materials that comprise the ACTFEL display in an effort to improve the overall performance of the primary phosphor colors in terms of brightness, efficiency and stability. Since the dominant flat-panel display technology is the LCD, an alternative flat-panel display technology must gauge itself in terms of the LCD. The advantages of ACTFEL displays in comparison with LCDs are the ability to pattern much smaller pixel, performance over a wider temperature range, full-viewing angle, and readability with much greater intensity background light. The disadvantages of ACTFEL displays against are larger power consumption, lack of adequate chromaticity of the three primary colors, and much larger driving voltages.

To achieve these objectives, the optical, electrical, and opto-electric measurements of the ACTFEL structures and ZnS:Mn phosphor hosts were carried out. Moreover, the effect of KCl co-doping on the microstructure and the electroluminescent properties (mainly brightness and luminous efficiency) of ZnS:Mn phosphors has been investigated, too. A non-common electrical characterization of ACTFEL devices has also been provided. We also calculated charged center scattering rates, and simulated the electron transport process in an ACTFEL device

The study of the aging characteristics of evaporated and atomic layer epitaxy ZnS:Mn phosphors has been undertaken by monitoring the luminance-voltage ($L$-$V$) internal charge-phosphor field ($Q$-$F_p$) and capacitance-voltage ($C$-$V$) electrical characteristics at in selected time intervals during aging. Short-term and long-term ACTFEL aging studies has been provided and an attempt to visualize locally the structure of phosphor with a subwavelenght resolution using Scanning near-field optical microscope (SNOM) has also been presented.

The practical case of a green $Zn_2GeO_4$:Mn (2% Mn) ACTFEL device operated at 50 Hz has been studied and a luminance stability by a measurement of luminance-voltage ($L$-$V$) and luminous efficiency-voltage ($\eta$-$V$) characteristics evaluated.

A non-negligible and indiscreptible task of this thesis was also its pedagogical aspect. Therefore, the presented text can be considered as a textbook suitable for our students in Libya.