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Miniature field emission light sources for bio-chips

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Abstract. A concept based on preparation of miniature field emission light sources (FELS) for integration with bio-chips is presented. Glass and silicon-glass micro-fluidic systems (bio-chips) with spectrofluorometric detection are designated for this solution. Planar, miniature silicon-glass field emission light sources were designed and fabricated for this conception. Carbon nanotubes (CNTs) have been used as a low-voltage electron emissive layer. Nanocrystalline yttria matrices doped with rare earth (Re) ions (Re: Eu$^{3+}$, Tb$^{3+}$) have been synthesized and utilized as phosphor layers. Light emission spectral characteristics of fabricated sources allow to couple them with typical fluorescent markers as e.g. Alexa, Fluorescein or TO-PRO, used on the wide scale in biochemical researches. Fabricated FELSs are characterized by the intensive and homogenous light emission with well defined sharp emission lines. The efficient and stable field emission from carbon nanotubes has also been noticed. Fabricated FELS are technologically compatible with highly developing micromachined fluidic systems and are able to direct on-chip integration with these microsystems.

1. Introduction
Identification and characterization of functional subsets of bio-particles carried out in bio- or cyto-chemistry research involve usage of chemical markers (fluorophores). Such a biological marker manifests his presence in terms of fluorescence phenomena initiated by an external light source (typically laser diodes) tailored to an individual fluorophor. The fluorescent marker will absorb energy from the external light source and re-emit light at a different wavelength but equally specific for each type of the fluorescent marker. Miniaturization and intensive development of microfluidic systems for chemical analysis, enforce the integration of the pumping light source directly on-chip [1]. Large and incompatible with micromechanical system (MEMS) technology, external optical devices cannot take such a challenge.

Interesting solution of the described problem can be relied on application of a miniature silicon field emission light source (FELS). Such a source is fabricated of silicon and is able to be integrated directly (on-chip) on the surface of glass micro- bio-chip. Utilizing carbon nanotubes (CNTs) as low-voltage and ultra sharp - tens of nanometers of diameter for individual multi-walled carbon nanotubes - electron emitting material as well as micrometer distances, micromachined in silicon will minimize the threshold voltage needed to observe the field emission phenomena. Light exited from such a light source can be tailored to particular group of fluorescent markers by changing a deposited phosphor layer.

All of these advantages enclose possible application of FELS to integration with microfluidic systems.
2. **Experiment**

Field emission light sources were fabricated in typical two electrode system with electron emissive silicon cathode and excited light emissive glass anode (Fig. 1).

### 2.1 Cathode

Cathodes were fabricated in 3” silicon substrates. Shallow cavities were micromachined in n-type silicon substrates with <100> crystallographic orientation. Resistivity of silicon wafers was in the range of 1-5 Ω·cm. Dimensions of micromachined pattern were set to 5×10 mm². Micromachining was performed by wet anisotropic etching in 10 M KOH solution through a 1µm wet silicon oxide mask (Fig. 1). The depth of etched cavity was fixed to 70 µm. Following, thin indium-tin oxide (ITO) layer which served as the low resistive contact electrode was deposited on micromachined substrates (Fig. 1c). Deposition of the ITO layer was performed in pulsed magnetron sputtering method from ITO (90% In₂O₃, 10% SnO₂) target [1]. This method can ensure a room temperature deposition with deposition rates (5 nm/min), low resistivity (10⁻⁴ Ω·cm) and high transparency in visible region (> 80%). Patterning of the ITO thin film was performed in a water solution of hydrochloric acid (HCl:H₂O 1:1), through mechanical mask to define the shape of emissive area (Fig. 1d). Dimensions of ITO contact electrode were set to 3×9 mm². The next step involved electrophoretic deposition of carbon nanotubes (CNTs).

Carbon nanotubes in form of multi-wall (MWNT) and single-wall (SWNT) were supplied by Shenyang National Laboratory for Material Science in China. Obtained raw nanotubes were purified by thermal annealing in air atmosphere and by diluting in highly oxidizing solution of nitric acid [2].

Purified material – MWNTs and SWNTs – was dispersed in isopropyl alcohol (IPA) with addition of magnesium salt (Mg(NO₃)₂•6H₂O). Addition of magnesium salt will facilitate electrophoretic deposition and ensure also deposition of magnesium hydroxide which is transformed to magnesium oxide and act as a binder for deposited carbon nanotubes. Electrophoresis of carbon nanotubes from prepared colloidal suspension was performed on micromachined silicon substrates with the deposited ITO layer (Fig. 1e).

### 2.2 Anode

The anode of presented field emission light sources was fabricated as a glass substrate covered with an ITO thin film and phosphor layer (Fig. 1f). Different types of phosphors were deposited on ITO anode surface. We have synthesized nanocrystalline phosphors based on Y₂O₃ doped with rare earth ions (Eu³⁺ and Tb³⁺). Commercially available, ZnS:Ag phosphor have also been used in FELS fabrication. Yttrium oxide based nanophosphors were synthesized in combustion method [3] and were doped by europium or terbium ions (Y₂O₃:Eu 5 at%, Y₂O₃:Tb 1 at%). Yttrium oxide, europium oxide and terbium oxide (Sigma-Aldrich) were used as starting materials for combustion synthesis. Following, starting oxides reacted with hot concentrated nitric acid to form nitrates. According to particular phosphor, corresponding nitrates (europium nitrate or terbium nitrate) were diluted in de-ionized water and mixed with a water solution of yttrium nitrate. After this, suitable amount of urea (CO(NH₂)₂) was...
added to the prepared solution which acted as a fuel for combustion synthesis. The combustion synthesis of $Y_2O_3$:Eu with urea, can be described as follows [3]:

$$(2 - 2x)Y(NO_3)_3 + 2xEu(NO_3)_3 + 5(NH_2)CO \rightarrow (Y_{1-x}Eu_x)_{2}O_3 + 5CO_2 + 8N_2 + 10H_2O$$

After the addition of urea, the solution was heated over 80°C to evaporate free water and concentrate the nitrates solution. Heating the prepared nitrate solution over 500°C initiated the combustion synthesis and production of a white residue. The crucible with obtained white residue was annealed at 1000°C for 5 hours. Obtained nanopowder was dispersed in IPA with an addition of magnesium salt, as it has been done for dispersion of carbon nanotubes. Electrophoretic deposition of fabricated or commercially available phosphor finished preparation of the anode part.

3 Results and discussion

Structural analysis of synthesized phosphors was made with the XRD diffractometer (HR XRD Philips, $K_{\alpha_1}, \lambda = 1.5405\text{Å}$). Obtained powder diffraction spectra of our luminescent materials shown in Fig. 2a and b reveal well crystallized $Y_2O_3$ phase. The XRD patterns of all resultant products $Y_2O_3$:Eu 5 at% and $Y_2O_3$:Tb 1 at% were indexed to cubic phase. The broadening of diffraction peaks of fabricated powders suggests a nanometric particle size. The particle size can be estimated from half-width at half-intensity (FWHM) of X-ray diffraction lines by the Sherrer’s formula: $D = (0.94\cdot\lambda)/(\beta\cdot\cos\Theta)$ where $D$ is the average diameter, $\lambda$ is the wavelength of X-ray, $\beta$ and $\Theta$ are width at half height and Bragg angle, respectively. An estimated grain size for synthesized powders was in the range of 25-30 nm.

Usage of the nanocrystalline phosphors can improve optical properties such as cathodoluminescent intensity in comparison to standard micrometer-size phosphors [4]. In addition, usage of combustion synthesis against traditional high temperature solid state synthesis can simplify and lower the costs of fabrication.

Electrophoretic deposition of carbon nanotubes can ensure good film properties without high complexity of technological process as it is for chemical vapor (CVD) method. EDP is based on the movement and deposition of small electric charged particles caused by the DC electric field. This method has advantages of short formation time, simple deposition apparatus and low cost and suitability for mass production in coating industry [4]. The uniformity of deposited CNTs film is dependent on applied voltage and time of deposition process. Future technological optimization steps are needed to improve morphology of deposited films.

Single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes were deposited on fabricated silicon cathodes. Fabricated field emission cathodes with carbon nanotubes provided high and stable emission currents at low voltages. All measurements were carried out in oil free vacuum at the vacuum level of $2\times10^{-3}$ hPa (measured in vacuum chamber). Typical emission currents for emission...
area $3\times9\ \text{mm}^2$ oscillate around $10\ \mu\text{A}$ at $700\ \text{V}$ for MWNTs and $40\ \mu\text{A}$ at $850\ \text{V}$ for SWNTs (Fig. 3a and b).

![Fig 3. Current – voltage characteristics of cathodes with MWNT a) and SWNT b) carbon nanotubes film.](image)

It has been observed that active emitting centers are usually increased with measurement time. Taking the pre-emitting conditions can also prevent from higher and very unstable emitting currents measured at the first time when a new cathode has been made and measured. It is likely that high emission current noticed for newly made cathodes is caused by degassing of carbon nanotubes film. This current push up effect has been noticed also for single-walled and multi-walled carbon nanotubes and needs future investigation. Emission currents obtained from fabricated cold cathodes are sufficient to excite commercially available phosphors such as ZnS:Ag or nanocrystalline phosphors synthesized in combustion synthesis (Fig. 4).

4 Conclusions

Silicon field emission light sources for integration with the glass microfluidic system have been presented. Carbon nanotubes were used as an electron emissive film deposited on micromachined silicon substrates. Electrophoretic deposition process can provide quite a good morphology of deposited films which can be improved by adjustment of deposition parameters as voltage etc. Obtained field emission currents are able to excite typical commercially available phosphors as also nanocrystalline phosphors based on yttria doped with rare earth ions, fabricated in combustion synthesis. Light emission spectral characteristics are in a good agreement with absorption lines of fluorescent markers typically used in cytochemical or biochemical researches. It seems that technological compatibility allows future integrating fabricated FELS with glass-silicon bio-chips.

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