Application of multiwall carbon nanotubes to microfluidic systems

B. CICHY1*, W. STRĘK2, J. DZIUBAN1, A. GÓRECKA-DRZAZGA1

1Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, ul. Janiszewskiego 11/17, 50-372 Wroclaw, Poland

2Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-422 Wroclaw, Poland

A new idea of potential application of miniature light sources (micro-FED) have been presented for excitation of fluorophore dyes used in biochemical investigations. Such light sources are based on field emission phenomena in diode type structures. Surfaces of cold cathodes were modified by electrophoretic deposition of multiwall carbon nanotubes, whereas anode surfaces utilize nanocrystalline phosphors with lanthanide-doped YAG matrices. Spectral characteristics of the light sources are in a good agreement with excitation spectra of a series of well known fluorescent dyes.

Key words: nanotubes; nanoparticles; lab-on-a-chip; fluorescent dyes

1. Introduction

There has been a great interest in identification and characterization of various functional molecules in the field of biochemistry and protein studies. Specialized techniques, e.g. flow cytometry allow one to group heterogeneous population of cells to functional subsets [1]. Identification of a variety of functionally distinct cells and their localization in the environment is also essential in lots of studies, e.g. estimating events occurring in vivo. The identification and localization is usually performed by use of fluorophore dyes. Their molecules chemically attached to investigated particles serve as fluorescent markers that can be detected by dedicated hardware. An impressive amount of fluorophores with various excitation energies have been characterized in literature, according to fluorescence specificities and binding properties to various particles [2]. An example of popular dyes is the rhodamine family, commonly used

*Corresponding author, e-mail: bartlomiej.cichy@pwr.wroc.pl
due to their high resistance to photodegradation, high emission intensity and pH insensitivity [3]. Long-wavelength emitting carbocyanines (Cy3, Cy5, Cy5.5, Cy7) are also used in fluorescence microscopy or flow cytometry [4] as well as fluorescein, Lucifer yellow or Alexa dyes, more photostable and fluorescent than the spectral analogues listed above. It is also worth noting that Alexa dyes exhibit very broad range of pH insensitivity (4–10) and retain very bright light emission on conjugation [3].

The aim of this work was to develop efficient miniature light sources based on field emission effect whose fabrication process is simple in comparison to solid state p-n junction devices. Such a light source should also provide an effective light emission and its luminescence spectra have to cover excitation lines of particular fluorophore dyes. Finally, the construction of pondered light sources should allow to “on-chip” assembly with portable micromechanical real time bio-analysers.

2. Experimental

Light sources have been prepared as diode type field emission devices. Cathode surfaces have been modified by electrophoretical deposition of distinct nanoparticles. Multiwall carbon nanotubes (MWNT) were used to prepare the cathode. Nanotubes received from Shenyang National Laboratory for Materials Science, Shenyang, China (SNL) were delivered as raw material, containing large amounts of amorphous carbonaceous particles and catalyst impurities (Fig. 1a). Beside impurities, the raw material was also characterized by a considerable inhomogeneity, mainly due to the presence of carbon fibres and various types of nanotubes (Fig. 2). It is important for future applications to have the tubes pure enough for the following electrophoretical deposition. Therefore it was necessary to employ certain purification procedures.

Two methods were used to purify raw tubes. The first of them included thermal annealing of raw MWNTs in air at 250 °C for 12 hours. This purification method presumably utilizes the fact that MWNT and other carbonaceous particles have different thermal oxidation rates [5]. It is considered that carbonaceous particles are burned first out due to faster selective etching. However, as time proceeds, more carbon nanotubes are exposed and have more chance to be attacked by oxygen molecules. A possibility of oxidation of the nanotubes being the main disadvantage, nevertheless the method theoretically is able to eliminate amorphous carbon impurities [6]. The other approach consists in purification in acidic solution [7]. The tubes were treated for few hours with diluted solution of nitric acid to dissolve iron compounds and oxidize amorphous carbon particles. Temperature of the reaction was maintained at 60 °C with intensive ultrasonic stirring. Finally, the samples were washed a few times with deionized (DI) water and immersed in isopropyl alcohol (IPA).

X-ray diffraction analysis was used to determine impurities in the material before and after purification. The morphology of cleaned MWNT was examined by the AFM microscopy. Nanotubes immersed in IPA were enriched by addition of magnesium nitrate hexahydrate (Mg(NO3)2·6H2O) in order to facilitate electrophoretic deposition.
The salt served as a binder necessary in electrophoretic deposition to glue the tubes to selected substrates and imposed positive charge onto suspended particles. The sol prepared in such a way was used to deposit the tubes on selected substrates. Two classes of substrates were used: plane substrates as glass slices with ITO layer used also for cathode and anode electrodes, and patterned substrates which contained mainly porous silicon (PS) and Si substrate with array of dry etched silicon tips covered with thin Cr layer (used only as cathode substrates).

Electrodes were prepared by electrophoretical modification of the surfaces. As deposited phosphors, we chose widely used YAG:Re (Y₃Al₅O₁₂: Re = Ce³⁺, Tb³⁺, Eu²⁺) doped matrices [8]. Yttrium aluminum garnet (YAG) is a very promising host for rare-earth-doped phosphors [9]. Its typical synthesis route is based on solid state reaction and requires high temperatures of 1600 °C and prolonged heating to obtain pure phases [10]. Therefore, the main effort has been focused on wet chemical methods such as sol-gel synthesis. Its advantages are inexpensive precursors, convenient process control, low sintering temperatures and large mass production [11]. The starting materials
for the combustion synthesis method were as follows: Al(NO₃)₃·9H₂O, Y₂O₃, citric acid (C₆H₈O₇·H₂O) and lanthanide oxides as dopant sources. The oxides were diluted in concentrated nitric acid to obtain corresponding nitrate solutions. Stoichiometric amounts of the nitrates were dissolved in DI water and mixed together. The ratio of citric acid to nitrate was maintained at 1:1. The solution was continuously stirred at 60 °C until it turned to yellowish sol. In the next step, the sol was rapidly heated to about 200 °C to initiate the autocombustion process, i.e., a self-propagating process between the reducing citrate and oxidizing nitrate groups [9]. The product looked like brown fluffy foam and did not reveal any crystal structure (Fig 3).

The precursor was sintered at various temperatures in a muffle furnace in ambient atmosphere to transform the amorphous precursor to YAG phase (Fig. 4). As prepared phosphor was then dispersed in IPA with addition of magnesium nitrate and likewise nanotubes were electrophoretically deposited on ITO substrates. Anodes and cathodes were assembled together with 250 μm mica or 400 μm silicon spacers. As
prepared sources were placed in a vacuum chamber and pumped out to $10^{-3}$ hPa followed by the field emission and cathodoluminescence measurements.

Fig. 4. XRD spectra of the combustion YAG precursor sintered at: a) 800 ºC, b) 1100 ºC

3. Results and discussion

The results of applied purification procedures have been assessed by the X-ray diffraction and morphology of the nanotubes was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM) (Fig. 5). The obtained carbon nanotubes can be purified also by thermal annealing and by liquid phase purification in acidic solutions, as was mentioned in the preceding section. Thermal annealing of raw samples eliminated much of amorphous carbonaceous particles (Fig. 1b). However, the diffraction spectra still contain peaks from catalyst compounds. After the liquid phase purification, the diffraction intensities of iron compound peaks were significantly reduced. Therefore, good results can be achieved by the multi-technique purifica-
tion procedures. None of these procedures were able to improve the homogeneity of the purified material, what is still a weak point of these samples. AFM scans show that the purified samples contain mainly straight multiwalled carbon nanotubes. It is likely that beyond straight MWNTs, the material contained also Y shaped tubes (Fig. 6).

![Fig. 5. MWNT morphology after purification examined by a) AFM microscopy, b) SEM microscopy](image1)

![Fig. 6. AFM image of a possible Y shaped nanotube](image2)

Major diameters of the MWNT tubes amount to ca. 30 nm and carbon fibre diameters to a few hundreds nanometers. It is obvious that more demanding applications or deposition procedures will require very homogeneous phases. X-ray spectra of purified MWNT show also (002) peaks slightly shifted to higher angle values (Fig. 1b). This feature is presumably connected with tensions in the structure after intensive sonication during the purification procedure. Moreover, it is also likely that the intensive sonication could lead to breaking up the outer walls of the tubes. The sol-gel combustion method for preparation of phosphors is well known and can provide quite a good alternative for the solid state synthesis. The obtained YAG matrices did not contain other stable phases as YAM (Y₂Al₂O₉) or YAP (YAlO₃) in the system of Y₂O₃–Al₂O₃ (Fig. 4). Taking advantage of the Scherrer–Debye formula, it is possible to estimate the grain size of prepared YAG matrices to amount to ca. 65 nm after annealing at 1100 °C.
Fig. 7. Field emission characteristics: a) $I-V$ characteristic, b) Fowler–Nordheim plot; cathode covered by deposited of MWNT tubes. The distance between cathode and anode fixed at 250 μm.

4. Conclusions

Field emission characteristics of the prepared sources show very high current densities even if the deposited layers of the tubes on every substrate are very inhomogeneous and
messy. It is also quite possible that the deposited layer can provide some type of reorganization on impact of the electric field what can explain a high field amplification factor (Fig. 7).

Such a flat light source after few changes can be assembled to an appropriate microfluidic system utilizing optical detection with fluorescent dyes (Fig. 8). Preparing the cathode in silicon with microengineering techniques allows one to bond the electron source to an appropriate borosilicate glass thereby obtaining solution ready for use. Spectral characteristics of obtained phosphors are in a good agreement with absorption spectra of well known fluorophores such as Rhodamine 6G, Alexa dyes or carbocyanines. Further work of the present authors will aim at designing sources allowing for efficient field emission and at obtaining efficient phosphors with low emission thresholds.

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