

ORAL SESSION: MATERIALS 2

ZnO NANOCRYSTALS VIA CHEMICAL ROUTE: GAS INFLUENCE ON PHOTOLUMINESCENCE PROPERTIES

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Abstract

In this work we studied the optical properties of new ZnO nanocrystal synthesized via chemical method and their interaction with gases in the surrounding environment.

Photoluminescence (PL) is a powerful tool to study the quality of oxide prepared, since PL spectrum of ZnO depends on the crystalline quality of the material as well as on the surface states. ZnO nanocrystals prepared via chemical route can show properties that are different from ZnO grown via vapour solid technique, regardless of the similarity in nanowire radius^[1,2].

It has been demonstrated that ZnO nanostructures^[3] exhibit interesting gas-sensitive photoluminescence properties: exposure to low concentrations of nitrogen dioxide (few ppm concentrations) significantly quenched the visible PL emission of nanowires in a reversible way.

ZnO nanostructures were prepared through a wet chemical approach, using different amines as template agents in order to tune the morphology of the final material. The chosen approach allows preparing ZnO nanocrystals under very mild conditions (aqueous bath kept at 95°C for 1 to 4 hours); organic templates were then removed by calcination.

The template effect exerted by amines is clearly visible when analyzing the samples by scanning electron microscopy: sample morphology varies from star-like (Figure 1, a) to rice-like (Figure 1, b) structures depending on the amine used in the synthesis.

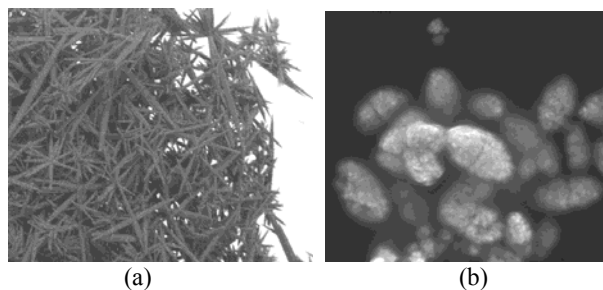


Figure 1: SEM images of ZnO nanocrystals, grown with different templates: (a) hexamethylenetetramine and (b) 1-adamantanamine.

ZnO nanocrystals PL spectrum (Figure 2), tested using 325 nm He-Cd laser line as excitation source, shows a UV peak at about 365 nm, attributed to free exciton recombination, and a visible broad band, ranging from green to yellow, which is probably the convolution of multiple peaks.

The ratio between the UV and visible emission, which is commonly used to estimate sample crystalline quality, is here very high.

UV photoluminescence of ZnO nanocrystals was studied in gaseous atmosphere, targeting mainly NO₂ sensing applications. We observed a strong and reversible PL enhancing with different concentrations of NO₂ (Figure 3).

We also tested the effect of interfering gases, such as ethanol and humidity. A small response was found in both cases: these measurements highlighted that the role of interfering species must be always taken into account.

The effect of gaseous species is opposite to that generally reported for ZnO nanowires^[2]; a possible explanation is still under investigation.

Nonetheless, the reversible PL response to gases at RT is extremely appealing for novel gas sensing applications: the PL properties of ZnO nanocrystals obtained via chemical route, under very mild conditions, can be exploited to develop an all optical gas sensor, inexpensive and working at room temperature, with no need of electrical contacts.

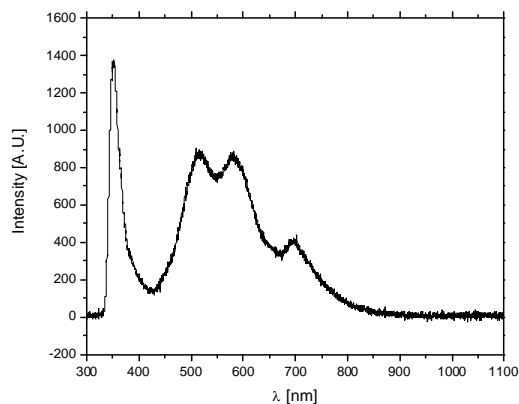


Figure 2: PL emission spectrum of ZnO nanocrystals at RT in dry air

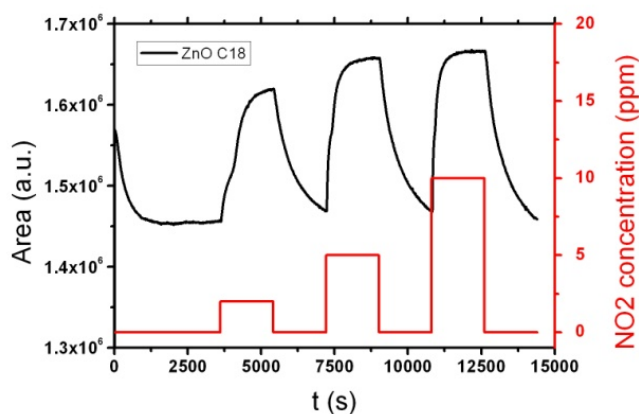


Figure 3: PL response to different concentrations of NO₂ (2, 5, 10 ppm)

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Synthesis of lithium fluoride nanopowders in a polymeric matrix for dosimeter applications

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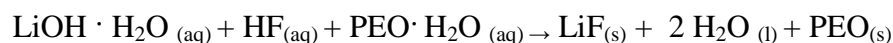
Abstract

Since many decades lithium fluoride (LiF) is receiving considerable attention because of its interesting and unique properties: it is a large band gap material, has got a large negative electron affinity, a high hardness, a high chemical stability and a low water solubility. Moreover, LiF is a radiation sensitive material because of the generation of point defects (color centers, CCs) which can be induced by ionizing radiation such as electrons, neutrons or ions. Thanks to these optically active defects several applications are possible such as solid state tunable colour centres lasers, radiation dosimeters, optoelectronic devices, nuclear sensors, etc.

In this work we propose a LiF based nano-composite film for dosimeter applications. Synthesis of LiF nanoparticles will be performed directly in a polymeric matrix for a better control of growth and dispersion of nanoparticles.

It is well known that colour centre formation efficiency is higher in thin films than in the bulk and we expect even higher colour centre formation efficiency in nanocrystals. Particles sizes can be controlled by changing the pH of the solution and/or the polymeric matrix.

Preliminary LiF particles synthesis has been performed in a solution of water and fluoridric acid containing dispersed Polyethylene Oxide (PEO). A composite film was formed in which LiF is dissolved in the polymeric matrix according to the following reaction:



Structural characterization of the films is done by X-ray diffraction using a Philips X-Pert Pro 500 Diffractometer with Cu K_α radiation in the conventional θ–2θ geometry. The microstructure of the films is observed by a field emission scanning electron microscope (Leo Supra 35).

Figures 1 and 2 show respectively, the X-ray diffraction pattern of a LiF film and the SEM micrograph of a LiF-PEO composite thin film.

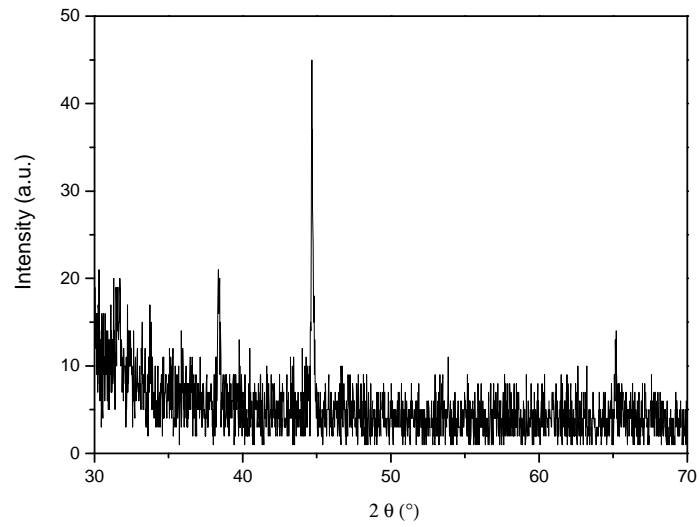


Figure 1. X-ray diffraction patterns of a LiF film deposited on a glass substrate by spinning

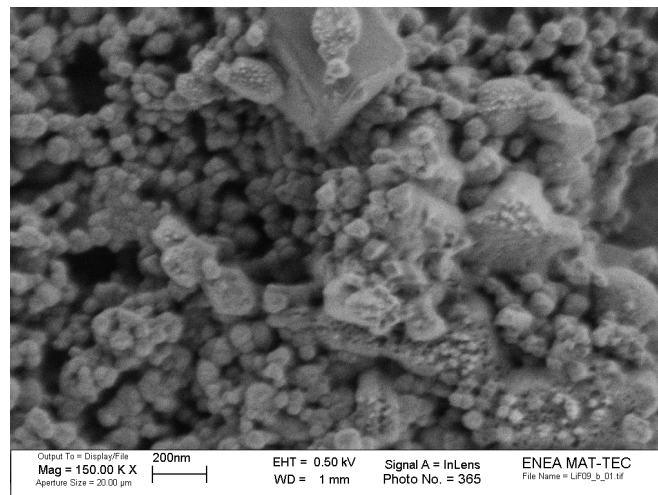


Figure 2. SEM micrograph of a LiF-PEO composite film deposited on a glass substrate by spinning

Testing of luminescent response of LiF-PEO composite under different doses of radiation is in progress to evaluate the performances of these films as radiation dosimeter.

SYNTHESIS, CHARACTERIZATION, AND AMMONIA SENSING PROPERTIES OF VANADIUM PENTOXIDE NANOCRYSTALS

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Abstract

Vanadium pentoxide is a versatile semiconductor, characterized by the property to change its optical and electronic behaviour reversibly, in response to a variety of stimuli including externally applied electric field [1], ultraviolet light irradiation [2], and thermal treatment [3]. In addition V_2O_5 is a promising candidate for gas sensing applications, because of its ability to change its electrical resistance when it is exposed to a variety of gas targets. In common with other transition metal oxides used in resistive sensors, the gas sensing performances of vanadium pentoxide in terms of sensitivity and response/recovery times, are found to improve by reducing the crystal size. V_2O_5 processed as nanotubes, nanowires, and nanobelts in order to maximize the surface area, has been used successfully to detect ethanol [4], ammonia [5], and amines [6]. This paper reports on a simple synthesis to prepare nanostructured vanadium pentoxide having excellent film forming property, and low temperature sensitivity towards ammonia. The material has been prepared using ammonium metavanadate as starting reagent. After heating the reaction product in air at 400°C , highly crystalline V_2O_5 nanoparticles were obtained, as it is evidenced by X-ray Diffraction (Fig. 1a) and Transmission Electron Microscopy (TEM) measurements (Figs. 1b, 1c).

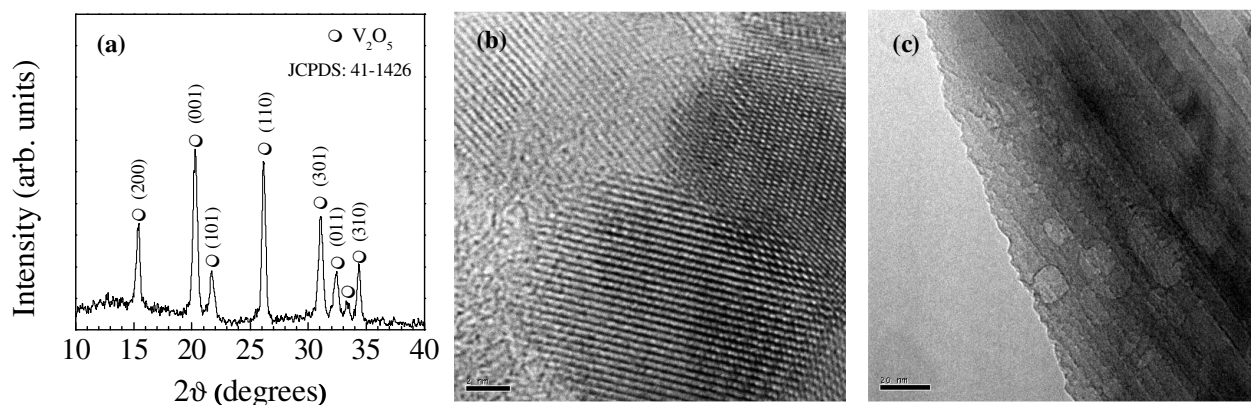


Fig. 1 - XRD spectrum (a), and TEM image (b) of the V_2O_5 nanoparticles (the scale bar is 2nm); (c) TEM image of V_2O_5 nanoparticles organized to form an agglomerate evidencing a certain degree of order (the scale bar is 20 nm).

The measurements reveal also that the nanoparticles have a trend to organize forming agglomerates consisting of planes superimposed one on each other, aligned along the same preferential direction (Fig. 1c). The film forming attitude shown by the nanoparticles, is confirmed by the results of direct deposition from ethanol nanoparticles suspensions, onto a variety of substrates including ITO coated PET, transparencies, glass, and silicon wafers. The developed films, obtained without the use of any binder or additive, and without the need of any substrate surface treatment, are found to be compact, and highly adherent to the substrates.

To investigate on the sensing properties of the nanostructured V_2O_5 , thin films have been deposited from ethanol suspensions of nanoparticles onto piezoelectric microbalances (QCM). Oscillation frequency of the coated quartzes changes reversibly as the relative humidity level changes. The response towards ammonia, at constant RH, is found to have irreversible components (data not reported). Optical and electrical measurements have been performed on films deposited from ethanol suspensions on glass substrates, on silicon, and on alumina substrates having platinum interdigitated electrodes on the top, before and after exposure to ammonia.

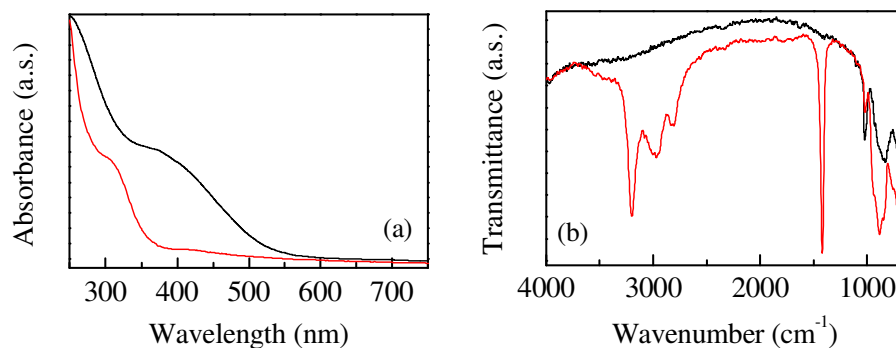


Fig. 2 – UV-VIS absorption spectrum (a) and FT-IR transmittance spectrum (b) of a V_2O_5 film before (solid) and after exposure to highly concentrated ammonia in air, at 28°C, 65% relative humidity.

The absorption spectrum of pale yellow V_2O_5 films deposited on transparent substrates (Fig. 2a) is characterized by a band positioned between 350 nm and 400 nm, superimposed on the tail of an intense UV absorption structure. The films bleach when exposed in air to concentrated ammonia vapour. Exposure to ammonia has remarkable effects on the FT-IR spectrum with the formation of peaks attributed to ammonium metavanadate (Fig. 2b).

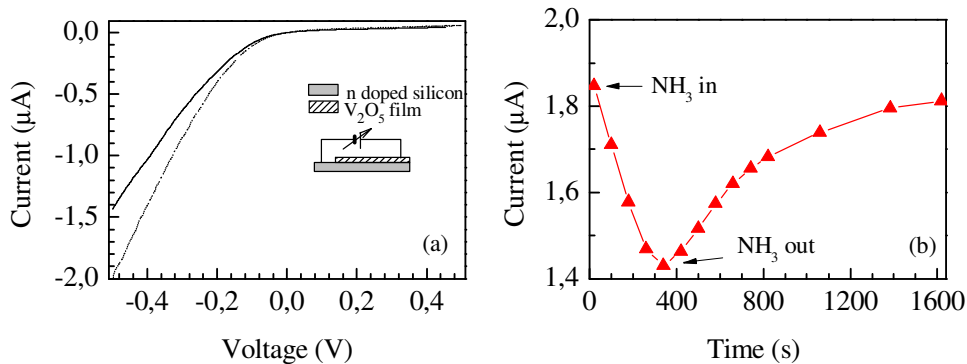


Fig. 3 – (a) I-V plot measured on a junction between V_2O_5 and n-doped silicon as deposited (solid) and after 350 s exposure to 7 ppm of dry NH_3 ; (b) dynamic behaviour of the current through the $V_2O_5/n-Si$, in response to a 350 s lasting pulse of 7 ppm dry ammonia.

Electrical resistance, and current-voltage measurements carried out at low temperature and in dry condition, show that exposure to calibrated amounts of ammonia in the ppm range results in reversible decrease of the metal oxide conductivity.

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