Growth, Electrical and Optical Properties of SnO_2:F on ZnO, Si and Porous Si Structures

A.Ferreira da Silva[1], M.V. Castro Meira[1,2], G. Baldissera[3], C. Persson[3] , N. Gutman[4], A. Sa´ar[4], P. Klason[5], M. Willander[5,6], C.D. Canestraro[3,7], T.V. Moreno[7] and L.S. Roman[7]

1- Instituto de Física, Universidade Federal da Bahia, Ondina, Salvador-Ba, 40210-340, Brazil
2- CETEC-Universidade Federal do Recôncavo da Bahia, Cruz das Almas-Ba, 44380-000, Brazil
3- Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
4- Racah Institute of Physics and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904 Israel
5- Department of Physics, Göteborg University, SE-412 96 Göteborg, Sweden
6- Dept. of Science and Technology (ITN), Linköping University, SE-601 74 Norrköping, Sweden
7- Departamento de Física, Universidade Federal do Paraná, Curitiba-PR, 81531-990, Brazil

ABSTRACT

In this work we have analyzed the optical absorption of the ZnO and SnO_2:F (FTO) films and applied them in porous silicon light-emitting diodes. The absorption and energy gap were calculated by employing the projector augmented wave method [1] within the local density approximation and with a modeled on-site self-interaction-like correction potential within the LDA+U^{SIC} [2]. Experiment and theory show a good agreement when the optical absorption and optical energy gap are considered. A layer of FTO is deposited by spray pyrolysis on top of porous Si (PSi) or ZnO/(PSi) in order to make the LEDs. The morphology and roughness of the films are analyzed by Atomic Force Microscopy before and after the FTO deposition. The electrical and optical properties are studied by characteristics curves J × V, and electroluminescence intensity versus bias.

1 INTRODUCTION

Fluorine-doped Tin Oxide (FTO)- SnO_2:F and Zinc Oxide (ZnO) are of great interest due to their broad range of technological application such as optoelectronic nanodevices [3,4]. In this work we have presented the optical characteristics of the semiconductor ZnO and FTO oxides and have applied these materials in porous silicon light-emitting devices. The use of FTO as transparent electrode in such devices has been brought beneficial effects in terms of resistance to degradation in PSi devices [5].

2 EXPERIMENTAL AND CALCULATION METHOD

2.1 Materials, growth and characterization

PSi samples were obtained from ordered arrays of trenches and holes in silicon substrates by hydrofluoric (HF) acid based silicon electro-chemical etching [6-8]. This technique produces deep and uniform pattern of holes or pores that can be utilized to form two-dimensional (2D) and three-dimensional (3D) photonic crystals in silicon. Hence, we have utilized the fabrication techniques described in references [7,8] to fabricate 2D pore arrays on top of *n*-type silicon wafer. In brief, a standard photolithography followed by alkaline anisotropic etching has been used to define 2D pattern of inverted pyramids on top of silicon wafer. Electrochemical etching was performed at room temperature under backside illumination for the samples.

ZnO samples were grown on top of the silicon and PSi samples using an aqueous chemical growth method (ACG) and a vapor-liquid-solid

method (VLS). There is several different chemical growth methods used to produce ZnO nanostructures and the most common procedure is that described by Vayssieres *et al.* [9]. In the VLS method ZnO powder was mixed with C powder using a 1:1 weight ratio. The powder was placed in a quartz boat and the Si samples were placed on top of the powder with a powder-substrate distance of 5 mm. The FTO samples were prepared by spray pyrolysis technique onto glass (ordinary soda lime), Si (PSi) or ZnO/(PSi) substrates. This process is based on the pyrolitic decomposition of a metallic compound dissolved in a liquid mixture when it is sprayed onto a preheated substrate. The method depends on the surface hydrolysis of metal chloride on a heated substrate surface [10]. These films were produced at 400 ºC and had received a thermal treatment at 450 ºC during ten minutes.

The surface morphology of the samples was analyzed using Shimadzu SPM equipment in contact mode for several scans sizes.

The light emitting devices were constructed in a sandwich structure, where the bottom electrode is aluminum and the top electrode is FTO. The intermediate layers are composed by Si/PSi or Si/PSi/ZnO. The electrical responses were acquired by Keithley 6487 Picoammeter equipment, a Termo Oriel photodetector and a voltage source. The aluminum electrode was positively and the FTO electrode negatively polarized in forward bias. The voltage range applied was –8 to 8 V.

To determine the optical absorption of ZnO sample the photoacoustic technique was used. The Photoacoustic spectroscopy (PAS) consists in illuminating a given material with a modulated light beam and measuring the subsequent temperature fluctuation induced in the sample resulting from the light absorption, due to nonradiative de-excitation processes within the sample. The intermittent heat is transferred into the sealed gas chamber generating an acoustical signal that can be detected by a microphone. We use a high-pressure 1000W xenon arc lamp (Osram), modulated to 20 Hz by a chopper (HMS Elektronik, model 220A) and monochromator (Sciencentech, model 9010) scanning a region from 350 nm to 700 nm, corresponding to energies from 3.54 eV to 1.77eV. The incident monochromatic light in the cell produces a photoacoustic signal detected by a microphone attached to the cell and it is connected into a Lock-in amplifier (Stanford Research System, model SR530) which synchronizes the PA signal with the reference pulse from the chopper. The measurements have been used the band pass filters, which aim to eliminate the contribution of the second order of diffraction of a wavelength smaller than 570 nm.

2.2 Theoretical analysis

The theoretical analysis is performed with the PAW/LDA+U^{SIC} method [1] as described in [2,11,12]. Optical absorption of ZnO is obtained from a four atom wurtzite unit cell, and flourine doping rutile SnO_2 is modeled by 216 atom supercells, implying TO with a F substituting oxygen with F concentration of $n_F = 3.9\times10^{20}$ cm^{-3}. Absorption coefficient is obtained from $\alpha(\hbar\omega) = \omega/c\cdot(2|\varepsilon(\hbar\omega)| - 2\varepsilon_1(\hbar\omega))^{1/2}$ where c is the speed of light, and the dielectric function is obtained from the joint density-of-states, the Fermi distribution, the momentum matrix elements $\langle \mathbf{k},j\left|\hat{p}\right|\mathbf{k},j'\rangle$, and the Kramers-Kroning transformation relation [11–13].

3 RESULTS AND DISCUSSION

The theoretical and experimental absorption spectra of the FTO and ZnO materials are depicted in the figure 1. In both cases we have good agreement between measurements and calculations. FTO (black lines) have relatively strong absorption in the 2.0–3.0 eV and 3.0–4.0 eV regions. The calculated gap is estimated to be ~3.2 eV, which agrees well with the experimental data (dashed-dot lines). The absorption peaks at medium energy region (i. e., around 0.8, 2.2, and 3.8 eV) could be suggested as in-gap defects in the material. However, we find that the shallow F donor electron states hybridizes with the intrinsic SnO_2 host conduction band at energies about 0.6–0.8, 1.4–2.0, and 3.5–3.9 eV, and thus the low-energy absorption peaks originate from inter-conduction-band absorption [11,12].

The energy gap of ZnO was determined by Linear Method for direct optical transition $I(h\nu) = A(h\nu - E_g)^{1/2}$. Where I is the intensity of the absorption, $h\nu$ is the energy of photons and E_g is obtained by linear extrapolation of the best fit between $(I(h\nu))^2$ and $h\nu$ at the point where it meets the axis of the energy [14,15]. The value found by this method, (3.09 ± 0.03) eV, in close agreement to the proposed theoretical model, as shown in Figure 1(gray lines).

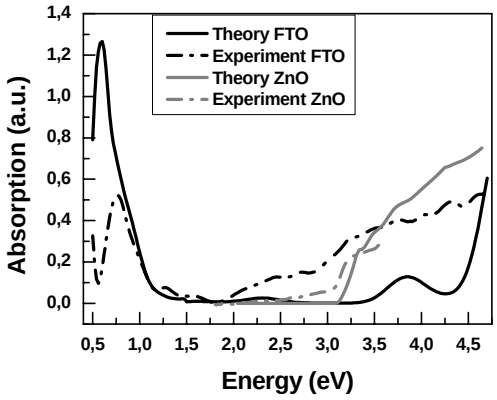

Figure 1. Absorption spectra for FTO (black lines) and ZnO (grey lines) oxides.

The figure 2 shows the AFM images of (a) PSi, (b) PSi/FTO, (c) PSi/ZnO and (d) PSi/ZnO/FTO. The surface homogeneity is slightly changed with the ZnO nanorods, which can be well visualized in the figure 2c. The roughness is increased about 4% in both cases after the FTO deposition.

The J × V curves of the lighting emitting devices are shown in the figure 3 and the electroluminescence intensity versus forward bias in the figure 4. The opened symbols correspond to the samples without the ZnO layer in both figures. From the figure 3 we can notice that both devices present rectification, as expected.

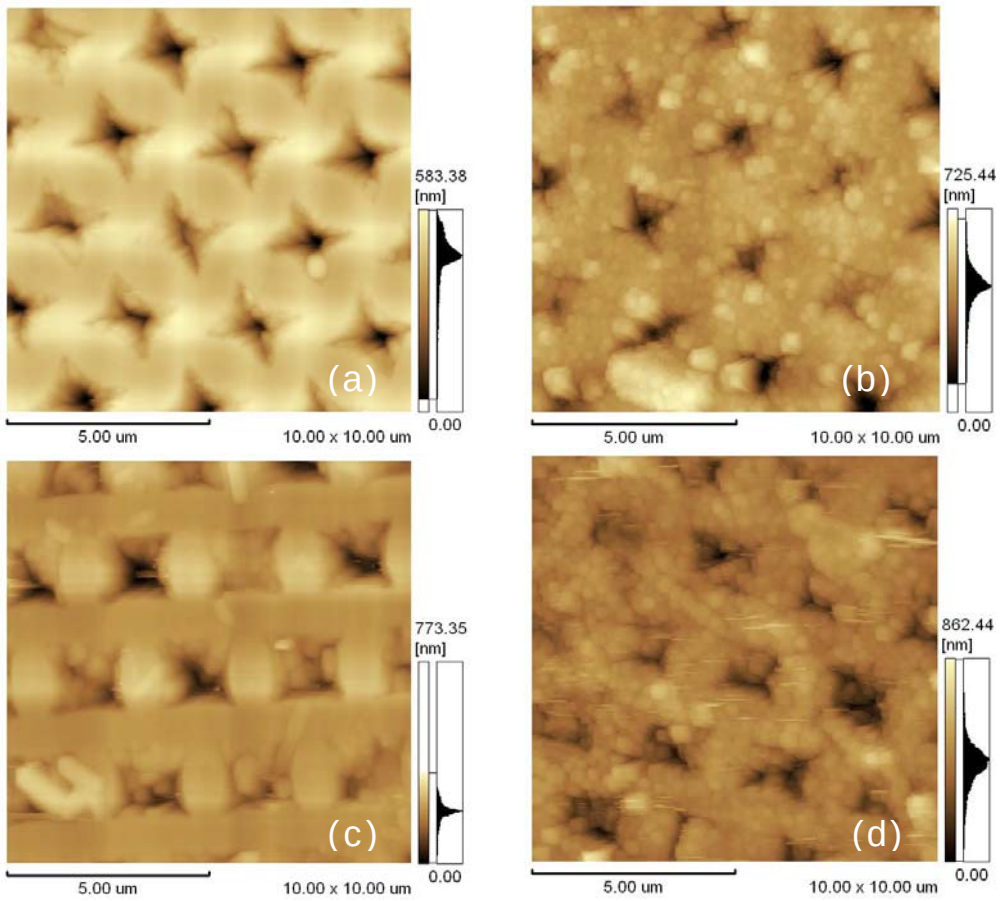

Figure 2. AFM surfaces images of Si/PSi (a), Si/PSi/FTO (b), Si/PSi/ZnO (c) and Si/PSi/ZnO/FTO (d). The roughness is increased about 4% for both samples after the FTO deposition.

The ZnO nanorods layer deposition on top of PSi reduced the conductivity of the device (closed symbols) suggesting a dependence of the surfaces morphologies with the electrical responses (c.f. fig. 2 a and c). The light intensity is also reduced for the device with a ZnO layer, which present an inset to light emission around 7 V, as shown in the figure 4. On the other side, the device without ZnO layer indicates a lower inset to the operating voltage (~ 5 V) plus a higher light intensity.

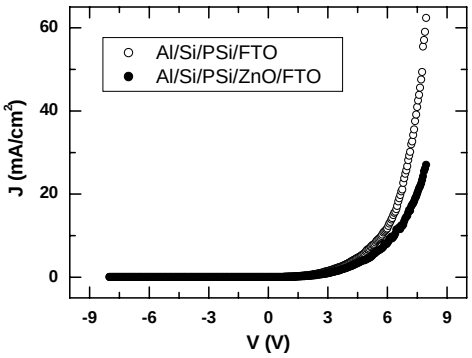

Figure 3. J × V curves of the devices with ZnO (full circles) and without ZnO layer (opened circles).

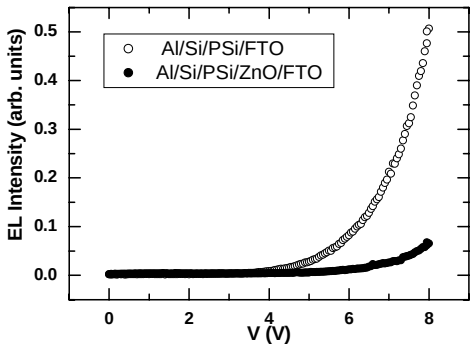

Figure 4. Electroluminescence intensity versus forward bias of the devices with ZnO (full circles) and without ZnO layer (opened circles).

4 CONCLUSIONS

Experiment and theory show a good agreement when the optical absorption and optical energy gap of the FTO and ZnO materials are considered. The construction of light emitting devices is possible when we deposit these layers on silicon/porous silicon substrates. Electrical responses show that the inset for light emission is increased by approximately 2 V when ZnO nanorods layers are deposited on top of silicon.

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