Highly efficient NIR to visible upconversion in ZnO:Er,Yb thin film deposited by AACVD atmospheric pressure process

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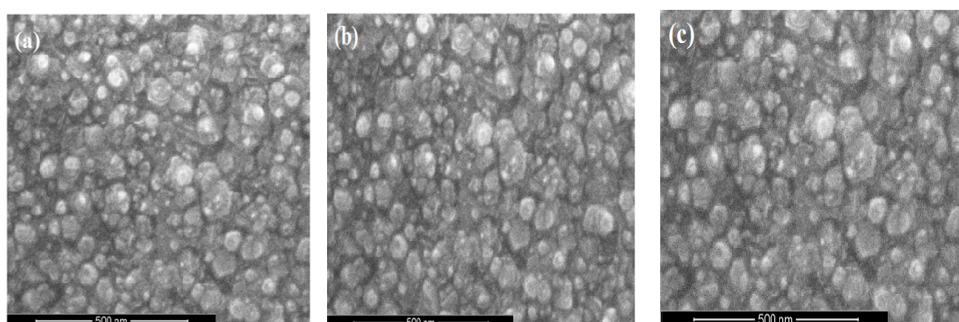E-mail : ridhaelleuch@yahoo.fr

FESEM images

Figure 1. FESEM images of ZnO:Er,Yb thin films deposited by AACVD process on Si(111) substrates with various Yb ion concentrations of: (a) 8 mol.%, (b) 9 mol.% and (c) 10 mol.%.

The FESEM images shown in Figure S1 presented the morphological state of the ZnO:Er,Yb film deposited at 430 °C using the AACVD process. These images were obtained by FEI Quanta FEG SEM 250 microscope, which equipped with a field emission gun hot cathode for emitting electrons. We used an accelerating voltage of 15 kV with high vacuum of 10^{-4} Pa to having high cleaning envirement. The images were obtained by the secondary electrons

detected with an Everhart-Thornley detector. It can be seen that the nanograins staged on films are about 120 nm.
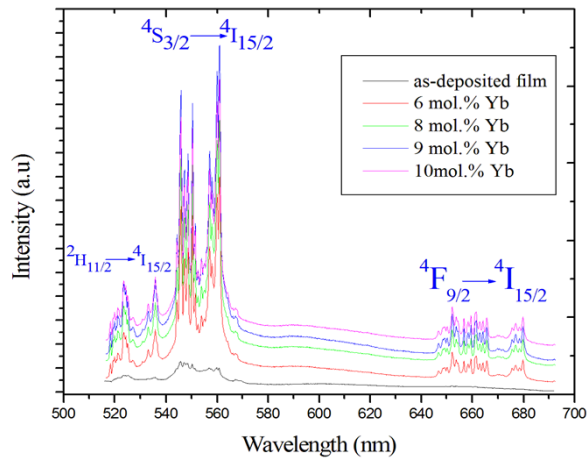
Photoluminescence measurments

Figure S3. Room temperature PL emissions of ZnO:Er,Yb thin films annealed at 1000°C under 488 nm excitation with 11 mW excitation power. Observed PL emissions are attributed to Er^{3+} ions only.

Figure S3 present the room PL emissions of ZnO:Er,Yb thin films annealed at 1000°C under 488 nm excitation with 11 mW excitation power. The observed peak emissions are ascribed to the $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} ions. The luminescence of the Er^{3+} ion in the visible region was observed by a Jobin–Yvon Horiba LabRam spectrometer which is equipped with a multichannel spectrometer (experimental resolution: 2.8 cm^{-1}) associated with a CCD detector (1024). The excitation at 488 generated by an argon laser was used as the pump wavelength. The pump beam at normal incidence, is focused by a microscope objective. The PL setup contains an objective which limits the incident power to 400 mW. This observation technique of luminescence of our layers was invaluable. The equipment used is particularly noticeable effect. Configuration eliminates optical guiding

problems, and therefore the morphology of the deposit and the nature of the substrate. It requires no sample preparation and measurement takes less than a minute.

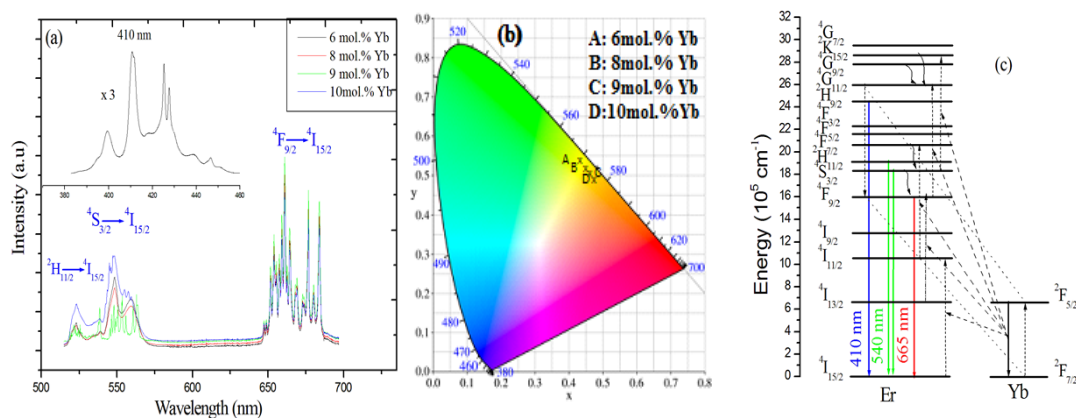**NIR to Visible upconversion measurements**

Figure S4. (a) Room temperature upconversion emissions of ZnO:Er,Yb annealed films under 980 nm excitation. (b) Energy level diagram of Er^{3+}/Yb^{3+} system codoped ZnO thin film showing possible excitation and de-excitation mechanism at 980 nm excitation. (c) Energy level diagrams of Yb^{3+} and Er^{3+}, and their possible UC processes.

Figure S4a shows the room temperature upconversion emissions of the annealed ZnO:Er/Yb films at 1000°C under the direct excitation photon at 980 nm and the UC spectra were recorded in [500-850 nm] with a Jobin-Yvin U1000 spectrometer. It is seen that the observed optical emissions are assigned to the intra 4f transitions of the Er^{3+} ions. The UC emissions spectra exhibit two weak ultraviolet (UV) and green emissions, and also a strong red one. The observed UV 410 nm emission is associated with the $^2H_{9/2} \rightarrow ^4I_{15/2}$ transition. The green bands centered at 525 and 555 nm are assigned to the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions, respectively. The strong red emission band centered at 665 nm is ascribed to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition. It is noted that the strongest red emission intensity is attributed to the film doped with 9 mol.% Yb concentration compared to the other films. The most resolved and strongest

emissions were detected for the film having 9 mol.% Yb content indicating a maximum doping concentration of the Er/Yb incorporated in the matrix. The Yb concentration dependence upconversion emissions of the annealed ZnO:Er,Yb thin films are investigated and it is concluded that, with the increase of Yb^{3+} concentration from 6 to 10 mol.%, the green emission intensity decreases remarkably while the red emission intensity increase. Therefore, it is possible to tune the emission color of the annealed ZnO:Er,Yb thin films by varying the Yb^{3+} concentration. The color chromaticity coordinates of the annealed ZnO:Er,Yb films are estimated using the commission of Internationale del'Eclairage (CIE) 1931 color matching functions, and are represented in Figure S4b. Under 980 nm, the color chromaticity coordinates were calculated and found to be A(x=0.428 y=0.542), B(x=0.446,y=0.527), C(x=0.466,y=0.518) and D(x=0.573 , y=0.486) for Yb concentration of 6, 8, 9 and 10 mol.%, respectively. It is observed that, with increasing Yb^{3+} content, the emission color changes gradually from yellow to orange. To understand the observed upconversion emission originated from the Yb-Er energy transfer under 980 nm excitation, a simple schematic diagram is shown in Figure S4c.

Measurement of quantum yields.

The upconversion quantum yield (QY) is an important parameter to evaluate the efficiency of the emission process in luminescent materials, which is defined as the ratio of the number of emitted photons to the number of absorbed photons per time unit:

$$QY = \frac{number\ of\ emitted\ photons}{number\ of\ absorbed\ photons}$$

Usually, the relative quantum yield of the ZnO:Er,Yb thin film is compared with that of a ZnO film as reference sample. The Er,Yb: ZnO deposited on Si substrate was placed in a quartz dish and then mounted at the focal point of the excitation 980 nm light. The error involved in the UC-QY measurements is 5% relative. QY were measured in the integrating sphere of the spectrofluorometer via synchronous scans of the excitation and emission monochromators. To eliminate any contributions of the host lattice to the scatter and emission spectra, ZnO/Si reference made under the same conditions as the corresponding Er^{3+} and Yb^{3+} doped films were used.

To determine the the pump power dependence of the UC-QY, QY and power density were recorded using various ND filters in the 980 nm excitation beam. The excitation slit width was used to define the area and was kept constant at 20 nm. This ensured that the beam area (square) is same for all the measurements. The beam size was measured using an IR imaging camera (Electrophysics MicronViewer 7290A) and a beam diagnostic software. A total of 238 camera shots were taken and the average beam size was determined as 8×10^{-4} cm^2 with a relative error of 0.05%. The beam power was measured by a calibrated germanium photodiode (Newport 818-IR) positioned at the focus of the excitation spot with a 1 μm resolution XYZ stage. The calibration error of the photodiode detector is ±4%. The combined error of calibration (of the photodetector) and uncertainty associated with the power density (in measured power meter readings and the measured area) measurement is ±4.2%.
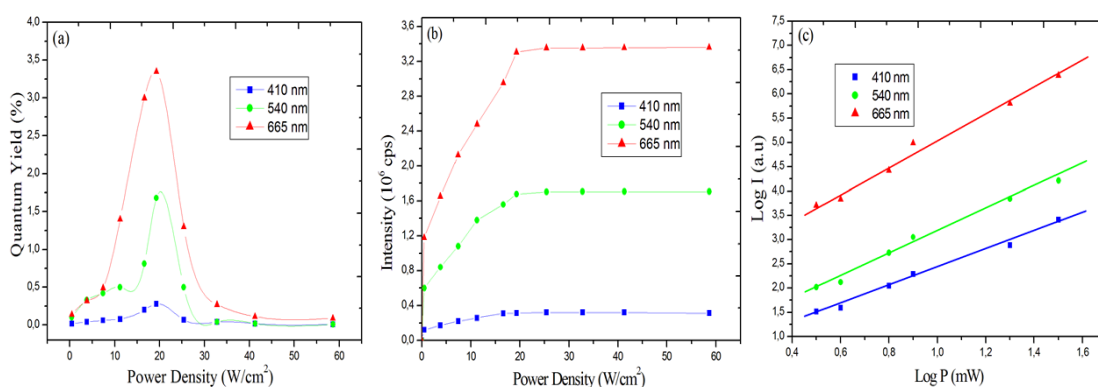
Figure 5. (a) Upconversion QY (%) variation with excitation power density, (b) Upconversion intensity variations with excitation power density and (c) double logarithmic plot of I as a function of power 980 nm laser for ZnO: 3mol.%Er^{3+}, 9mol.%Yb^{3+} upconversion emissions centered at 410, 540 and 665.

It can be seen from the above Figure S5(a) the power density dependence the quantum yield of ZnO: 3mol.%Er^{3+}, 9mol.%Yb^{3+} thin films. These measurements lead to the evaluation of the most efficient doping for the $^4I_{11/2}$ to $^4I_{15/2}$ emission. For this optimized Er/Yb concentration, we get the higher absolute UC-QY for red (3.52±0.12%), green (1.76±0.10%), and UV (0.31±0.03%) emissions with a total UC-QY of 5.59±0.1% at the threshold excitation power density of 19.3±0.3 W/cm^2. As it is shown in Figure S5(b), the power density dependence upconversion emission intensity curve for all four emissions shows that the threshold of the saturation of the emission intensity is at 19.3±0.3 W/cm^2 which is appropriate for Si solar cells applications. Figure S5(c) shows the number of pumping photons n which is evaluated from the slope of the UC intensity versus the laser excitation power in a log–log plot. The n values of the ZnO:3%.mol Er, 9 %.mol Yb thin films are found to be 1.91±0.2, 1.98±0.03 and 2.09±0.03 for the UV, green and red emissions, respectively. These results show that the UC mechanism is mainly happening due to a two-photon process which is mainly responsible for the upconverted emissions.

Ellipsometric measurements

Ellipsometry is an optical characterization and surface analysis technique, based on the polarization state change of the light reflected from a flat surface. In this work, the ellipsometry technique we used to measure the thickness and n thin films. Ellipsometry measures the complex reflectance ρ being the ratio of the amplitudes of R_p parallel and

perpendicular components of the polarized light R_s. It is set by the two ellipsometric angles Ψ and Δ.

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) \exp^{i\Delta}$$

Consider a plane wave arriving at an also flat surface (Figure 2). A portion of the wave is transmitted or absorbed through the surface, the other is reflected by this surface. The electric field E of the incident wave can be decomposed in two components: one parallel to the incidence plane (E //) and the other perpendicular (E$\perp$). Modifying the electric field after reflection on the sample may be described by two complex coefficients each acting on one of the components of the field, and such that:

r// = E//$_r$ / E//$_i$ = r//.exp(iδ//) (together with the perpendicular component)

r// modules and r$\perp$ represent the change in the amplitude of each component, while δ phases and δ$\perp$ // translate the delay introduced by reflection. In practice, the measured quantity r is the ratio of these two coefficients is expressed as follows:

ρ = r// / r⊥ = tanψ. exp(iΔ)

With tanψ = r// / r⊥ et Δ = δ// - δ⊥   is the difference introduced by reflection.

Here the values of the angles Ψ and Δ will judge the validity of the measure if they take no outliers. The experimental process of this thickness measurement requires to know the refractive index of the material and to have an idea of the thickness of the layers (for example with Newton's colors). Indeed the value found by the ellipsometer provides a thickness value of the program related to a phase shift and therefore controlled by modulo. Experimentally, this modulo is a diffraction order. The ellipsometer used a Sentech model at a wavelength of 632.8 nm and an incident angle of 70 °.