SOLSTICE	Name of the PhD: **Abdoul-Razak MOUSSA TANKARI** Title of the PhD thesis: **Study and Optimization of Transparent Conductive Oxides thin films (TCOs) based on doped ZnO nanoparticles for photovoltaic solar Cells**. Dates (start/end): 12.2020 – 12.2023
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Context and objectives

There are many scientific and technological obstacles in the field of nanomaterial synthesis. In fact, at the level of the process, there is a major problem linked to the implementation of a simple technique, environmentally friendly, and reproducible on a large scale. To synthesize doped zinc oxide nanoparticles (NPs), many processes have been designed such as precipitation, decomposition, and supercritical sol-gel, but, unfortunately, many of them involve many steps of synthesis at high pressures and temperatures, which affect the cost, the production capacity, and the perfect control of the different physical and chemical properties of the desired material.
Relying on our expertise in the synthesis on nanostructured thin films, in our previous work, we (PROMES & LaPhyMNE laboratories) set up an original experimental protocol to develop nanostructured thin films by RF sputtering from nanoparticles previously synthesized by supercritical solgel process. Nevertheless, the potentiality of the obtained films is marked by an environmental impact and the complexity linked to the adopted sol-gel route. These limitations are a major handicap for an industrial scale.
In this context, our objective is to implement a new process for the synthesis of doped ZnO nanoparticles. This allows us obtaining an inexpensive and non-polluting aqueous sol-gel procedure in order to develop ultra-thin layers (<300 nm) of TCO nanostructured on rigid or flexible substrates. These ultra-thin layers aim at the design of a high performance optical window, which will be used in the production of solar cells based on CIGS and/or amorphous silicon.

Approach

A purely experimental approach has been adopted for the optimization of the new sol-gel protocol for the synthesis of doped ZnO NPs and the conditions for depositing them in a nanostructured thin film. To achieve this, an innovative experimental protocol is developed by the coupling of two chemical and physical synthesis processes. The first one is a chemical process based on an aqueous Sol-gel by avoiding supercritical conditions (atmospheric pressure, low temperature < 200 °C). The second process is based on the PVD RF sputtering to elaborate nanostructured thin films. Structural, morphological, optical, and electrical characterization of the nanoparticles and thin films will be carried out to determine the optimal conditions for the elaboration of the intended ZnO nanoparticles and ZnO films.

Main results

After several attempts, we have successfully synthesized intrinsic and doped ZnO NPs in aqueous solution and under atmospheric pressure. Thus, the first goal is well achieved since the result is well reproducible either with intrinsic or doped NPs. However, the aluminum-doped ZnO NPs obtained at atmospheric pressure and a temperature below 200°C reveal only secondary phases which do not correspond to the X-ray diffraction patterns (XRD) of zinc oxide, as reported in the literature. This is illustrated in fig. 1a. In addition, we have noticed that after a thermal annealing the XRD pattern reveals the presence of Zinc oxide peaks with additional secondary phases, which are related to the used precursors (fig. 1b). Thus, a filtration step using ethanol was carried out to remove the remaining secondary phases. Fig. 1c illustrates clearly the benefic effect of adopting the filtration step. We notice clearly that after a thermal annealing at 350°C, all XRD peaks related to secondary phases have disappeared, indicating the synthesis of doped ZnO NPs crystallizing under the single hexagonal wurtzite structure. From this protocol, we have succeeded in reproducing the synthesis of the intrinsic and aluminum doped ZnO NPs with different concentrations.
To identify the best ZnO thin films for optoelectronic applications we have varied the Al doping ratio from 1 to 4% and the film thickness from 100 to 300 nm. This enables us to follow the evolution of the electrical and the optical properties of doped ZnO thin films since they are the main parameter of antireflective thin film in optoelectronic devices. The first results related to the different Al doped ZnO thin films are very encouraging. Actually, we investigate the optical properties via studying the evolution of the transmittance spectra. This allows us to follow the evolution of different optical parameters, such as the gap energy, the refractive index and the dielectric constant.

This work was carried out in close collaboration with INSA of Toulouse, L2C laboratory of Montpellier and LaPhyMNE Laboratory University of Gabès, Tunisia.

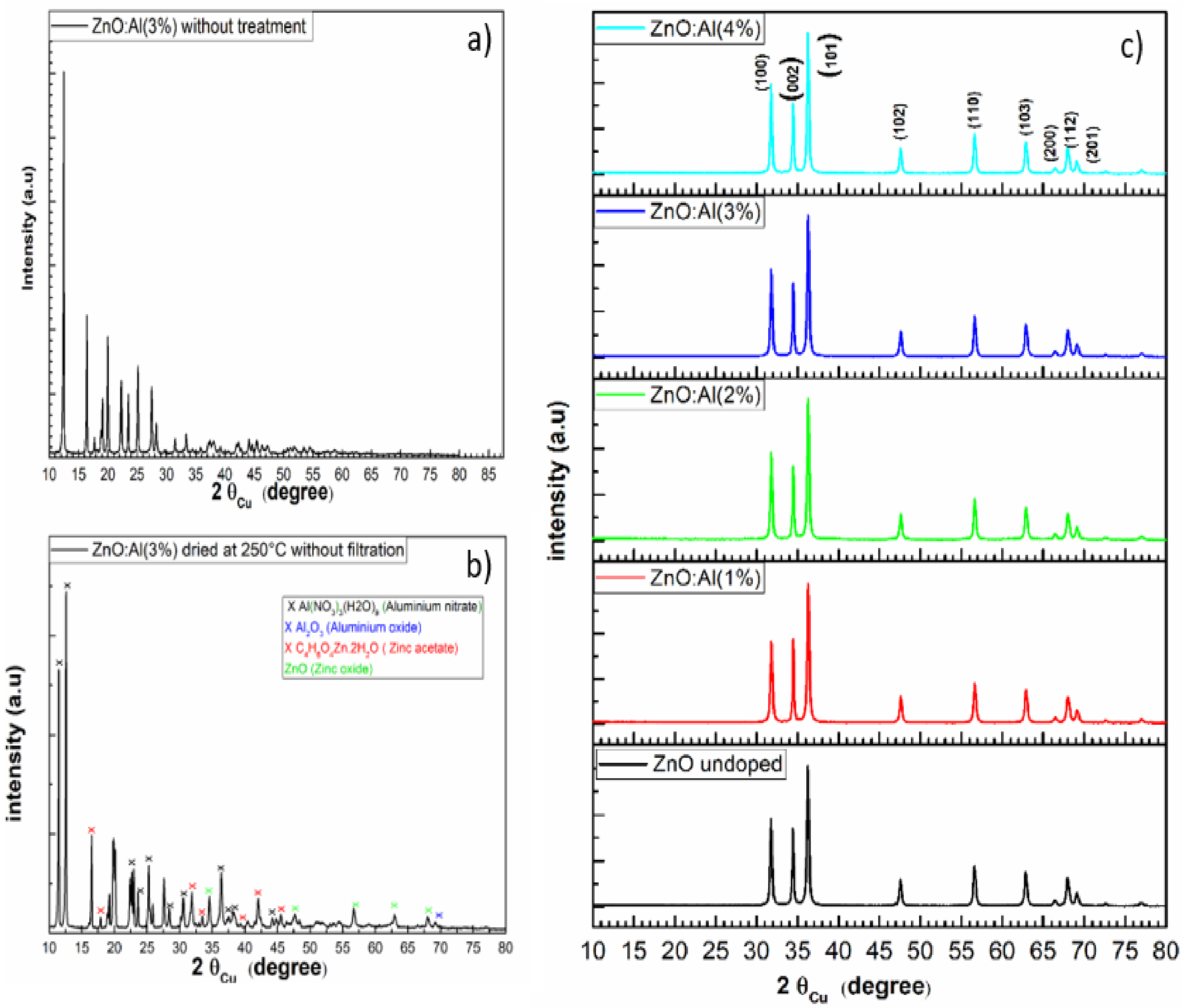

Figure 1: X-ray patterns of doped ZnO NPs, (a) NPs of ZnO:Al (3%) without any treatement, (b) NPs of ZnO:Al (3%) after a thermal annealing, without a filtration step and (c) NPs of ZnO:Al with varied Al doping ratio after a filtration and thermal annealing steps.

Publications in scientific journals and international conferences