Green synthesis and study of Cuprous Oxide nanoparticles

***A. Kerour*, S Boudjadar**

Ceramics laboratory, department of physics, Mentouri University, Constantine
kerour.a@gmail.com

Abstract
Recently, biosynthesis of nanoparticles has attracted more attention due to their different advantages as an eco-friendly, low cost and non toxic alternative approaches. In particular, metal oxide nanoparticles are receiving increasing attention in a large variety of applications. The aim of this work is the synthesis of cuprous oxide (Cu_2O) nanoparticles using green method, we have used sulfate copper and Aloe Vera leafs extract with different concentrations as a precursor and a solvent respectively. The synthesized samples were characterized with X-ray diffraction, Fourier transmission infrared FTIR and electron scanning microscopy SEM. X-ray diffraction confirms the formation and the crystalline nature of cuprous oxide. The average size of the particles ranged from 23 to 67nm, the shape of obtained agglomerated particles is octahedral with an average size varied from 536 nm to 1000 nm.

Keywords: Biosynthesis, Cuprous, Aloe Vera, nanoparticles, green synthesis

Evolution of the structural properties of sol-gel synthetized ZnO with solid phase and solution-based aluminum dopingat different annealing temperatures.

***F. Mahcene**, N. belabed, M. Gouder, S. Kasouit, A. Chari* and A. Chaieb*

Laboratoire de physique chimie des semiconducteurs. Département de Physique, Université Frères Mentouri, Route de Ain El Bey. Constantine.
chabd54@yahoo.fr

Abstract
We report here on the effect of aluminum doping and annealing temperature on the structural properties of ZnO, synthetized using the Sol Gel method. Aluminum doping was performed in two ways, either by adding $AlCl_3$ to the Zn solution or by mixing the obtained gel with Alumina prior to the annealing step. It was found that both methods of doping yield very similar results. Aluminum doping does not affect ZnO crystals dimensions for an annealing temperature of 500°C, while it induces a significant reduction in grain size, as well as the appearance of the $ZnAl_2O_4$ spinel phase for annealing at 700°C and above.These results suggest that no ZnAl bonds are formed in the solution, when doping with $AlCl_3$. Aluminum doping of ZnO yields a heterogeneous material if annealed at 500°C, while diffusion and subsequent alloy formation occur onlyat higher temperatures.

I. Introduction

Zinc oxide is aII-VI semiconductor with very attractive mechanical, chemical, optical and electronic properties allowing it to be used in a wide range of technological applications.In particular, ZnO has a large band gap and hence a low absorption in the visible range. Increase in its electrical conductivity by doping allows it to be used as a window layer in solar cells and an active layer in thin film transistors [1] Aluminum is the most extensively used n type dopant in ZnO. It allows to achieve high electrons concentration but also induces a reduction of crystals size and hence degrades carriers mobility. Despite the extensive research devoted to the subject, the exact mechanism of aluminum incorporation and its atomic environement in the ZnO matrix is still not fully understood.
In order to further understand Aluminum doping mechanism, we studied here the effect of Aluminum introduction on the grain size of SolGel synthetized ZnOnanocrystals. Both the Aluminum source and the annealing temperature were varied in order to shed light onto its microscopic incorporation mechanism.

II. Experiment

NanocrystallineZnO powder was prepared using the SolGelroute. A first mix containing 0.5g of glacial acetic acid dissolved in 120ml of pure ethanol was added to a second solution of 25.05g of zinc acetate dihydrate dispersed in 120ml of distilled water. The two solutions were made to react for 5 hours at

50°C under continuous magnetic stirring. The gel was then heated at 80°C for a sufficient duration until it dried completely.Aluminum doping in the range of 0.5 at.% to 20 at.% was achieved either by adding $AlCl_3$ during magnetic stirring or by mixing the dried gel with nanometric Al_2O_3 powder. Samples were then annealed at temperatures of ranging between 500°C and 900°C for 1 hour. It has been verified that organic phase was completely eliminated at 450°C and that the material reaches steady state in less than one hour.

The samples were characterized using X-ray diffraction in the q-2q configuration. Results were also confirmed using SEM,FTIR and Raman measurements (not shown here for the lack of space, will be presented in the final conference paper).

III. Results and discussion

Figure 1 shows XRD patterns for pure ZnO as well as for samples doped using $AlCl_3$, and annealed at 500°C and 900°C.Spectra from samples with Al_2O_3 doping are very similar.

It could be seen that diffraction peaks are consistent with the wurtzite structure of ZnO.No amorphous ZnO peaks were observed,neither do we observe the characteristic peaks of carbonated impurities in our samples, indicating that our samples are fully crystallized and calcinated at these temperatures. For the samples annealed at 700°C (not shown here) and 900°C, and containing at least 10 at.%, of aluminum, additional XRD peaks are observed, which are ascribed to the $ZnAl_2O_4$ spinel phase. No such peaks are observed for the samples annealed at 500°C.

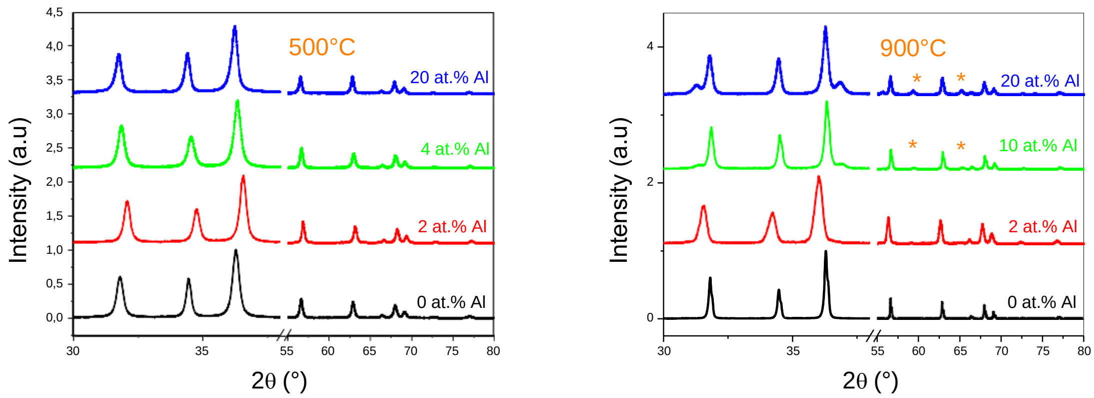

Figure 2 : XRD patterns for ZnO samples doped with AlCl3 and calcinated at 500°C and 900°C. $ZnAl_2O_4$ peaks are highlighted with asterisks.

The grain size of undopedZnOparticles inferred from XRD data (not shown here) is found to increasemonotonically with the annealing temperature, from about 30 nm at 500°C to 50 nm at a temperature of 900°C. SEM images of the samples also confirm that undopedZnO is constituted of nanometric spherical particles, whose size increases monotonically with temperature. This behavior is expected from basic thermodynamic considerations, through defects curing and enhanced mobility at higher temperature. Grain size is also expected to increase above the densification threshold of 600° [2].

Figure 2 shows the evolution of nanoparticles size, normalized to the value of pure ZnO, as a function of doping for various annealing temperatures. One could observe that the two methods of doping, namely solution and solid phase doping, yield strikingly similar trends.No evolution of particles size with doping is observed when annealing at 500°C. On the other hand, particles size decreases sharply at 700°C and 900°C.

The similarity between the trends for the two doping methods suggests that no Zn Al bonds are directly formed in the solution when adding $AlCl_3$. Calcination at 500°C induces the formation of a ZnO/AlO_x biphasic material. Diffusion of metals seems to happen only at 700°C or above.

Aluminum solubility in ZnO is about 3 at.%. Beyond that doping concentration the $ZnAl_2O_4$ spinel phase is commonly observed. The exact atomic environment of atomic Al incorporated in ZnO crystals is still not fully understood, and a homogeneous $(ZnO)_3Al_2O_3$ phase has been proposed for the composite structure[3]. Aluminum doping is however known to reduce crystals size through the increase in defects concentration and the reduction in precursor surface mobility [4]. This mechanism is clearly at play for the samples calcinated at 700°C and 900°C. ZnO crystals are on the other hand aluminum-free at 500°C and hence its size does not depend on the doping level.

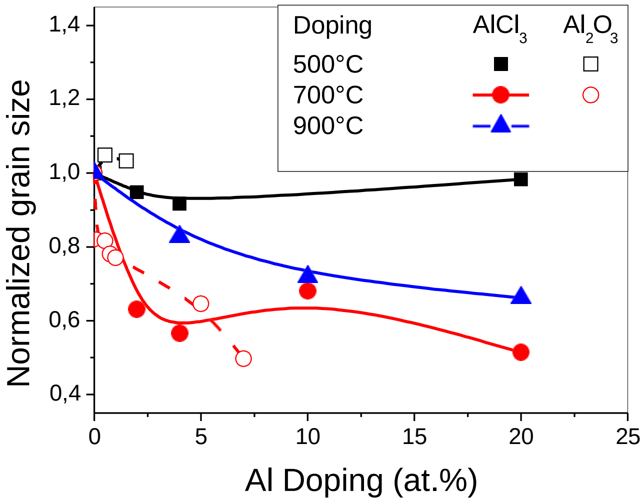

Figure 3 : Normalized grain size of ZnO crystals, for solid phase and solution doping, as a function of dopant concentration and annealing temperature.

IV. Conclusions

We have studied the effect of Aluminum doping using Al_2O_3 incorporation both into the gel and $AlCl_3$- based solution doping. It has been observed that Al doping does not affect ZnO grain size for a calcination temperature of 500°C, while a sharp decrease is seen when annealing at 700°C and 900°C, together with the apparition of the $ZnAl_2O_4$ spinel phase. These results suggest that $AlCl_3$ doping occurs through the oxidation of Aluminum without the formation of ZnAl bonds. No diffusion is induced by annealing at 500°C and a heteroneous material constituted from pure ZnO crystals and Alumina is obtained. On the other hand, exposure to temperatures of 700°C or higher leads to the formation of doped ZnOnanocrystals, whose structural properties are extremely sensitive to the level of doping.

V. Références

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