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Photoluminescence from *c*-axis oriented ZnO films synthesized by sol-gel with diethanolamine as chelating agent

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ABSTRACT

ZnO films were synthesized on SiO_2/Si substrates through the sol-gel technique using diethanolamine as chelating agent and annealed in $Ar+O_2$ atmospheres with different O_2 flow-rates in the 10–100 sccm range. Samples were studied by scanning electron microscopy and X-ray diffraction, evidencing a nanostructured morphology with a preferential orientation along the (0 0 2) direction (*c*-axis orientation), which is uncommon when diethanolamine is used as the chelating agent. The room temperature photoluminescence spectra show strong UV emissions at around 375 and 384 nm from near band-edge transitions and phonon replica, and a broad defect-related band extending from the visible to near infrared (~500–800 nm). The analysis of the defect-related emission band and its various components as a function of the O_2 flow-rate is discussed in terms of contributions from specific luminescent point defect centers established during annealing.

1. Introduction

Zinc oxide is considered an important and promising material. Reasons for this include low-cost, simple and controllable synthesis processes of a wide diversity of nanostructures, such as nanocones [1], nanoparticles [2], nanowires [3], nanostructured films [4]. Furthermore, ZnO is a II–VI semiconductor with interesting optoelectronic properties due to its wide band gap of 3.37 eV and large excitonic binding energy of 60 meV, which is larger than the mean thermal energy at room temperature (RT) [1]. Hence ZnO finds many applications in diverse optoelectronic devices, particularly in light-emitting diodes [5]. Other interesting applications have been proposed for ZnO in catalysis [6], sensors [7], optical waveguides [8] and photodetectors [9].

Nanostructured ZnO can be synthesized through different processes, like vapor transport with and without metallic catalyst [1,3], sol-gel [10,11], pulsed laser deposition [12], electrophoretic deposition [2], hydrothermal synthesis [13] and molecular beam epitaxy [14], among others. The sol-gel synthesis is a powerful and interesting route, as it involves processes at intermediate temperatures with low costs and easy implementation [11]. This technique involves transformations of a molecular precursor onto a stable condensed oxide network through several stages, including hydrolysis and polymerization for the formation of the sol precursor and condensation by dehydration, nucleation and growth (commonly achieved through annealing) [11]. When organometallic salts are used as molecular precursors the solvent used is organic [15]. The aminoalcohols – diethanolamine (DEA) and monoethanolamine (MEA) – are the most common chelating agents when zinc acetate is used as a Zn^{+2} source. The reason for this is that these compounds increase the solubility of organometallic zinc salts, improving stability and homogeneity of sol precursors [4,16,17].

The photoluminescence (PL) of nanostructured ZnO has been studied extensively. Regarding ZnO layers synthesized through the sol-gel technique, most studies have focused mainly on the effects

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of chelating agent/Zn^{+2} ratio [4], pH [17] and annealing temperature [18] on the PL spectrum. However, the effect of oxygen (O_2) flow-rate during annealing/growth processes on the PL of sol-gel synthesized ZnO films has been rarely reported.

In this work, ZnO films were synthesized through the sol-gel technique in combination with the spin-coating deposition method. ZnO samples were deposited on silicon (Si) substrates stored in atmospheric air (therefore, naturally oxidized [19]). The influence of O_2 flow-rate during the annealing process on the PL at room temperature, and also on morphological and structural properties of the ZnO films, was studied. These results contribute to the understanding of the room-temperature PL spectra from ZnO films grown by the sol-gel technique and the role of point defects controlled by annealing in different $Ar+O_2$ atmospheres. Furthermore, they show that it is possible to obtain highly oriented sol-gel synthesized ZnO layers on oxidized Si substrates, using DEA as chelating agent.

2. Experimental details

2.1. ZnO fabrication

To prepare the sol precursor, 2.3 g of zinc acetate dihydrate [Aldrich, $Zn(C_2H_3O_2)_2 \cdot 2H_2O$] was diluted in 30 ml of ethanol at 65 °C to obtain a 0.3 M solution. A volume of 1 ml of DEA (Aldrich, $C_4H_{11}NO_2$) was added to obtain a sol with a 1:1 M ratio of Zn^{+2}/DEA under constant stirring, until the solution went from white to transparent. After stirring at 65 °C during about 2 h the sol precursor was cooled down to RT. The sol was then aged for 24 h and no precipitates were observed.

ZnO layers were deposited onto *p*-type ⟨1 0 0⟩-oriented Si substrates, which were ultrasonically washed first in acetone, then in ethanol and finally air dried to remove organic contaminants. Substrates were not etching with hydrofluoric acid (HF-etched) prior to deposition, so as to leave a passivating thin layer (≈ 2 nm-thick) of native amorphous Si oxide (SiO_2) [19,20].

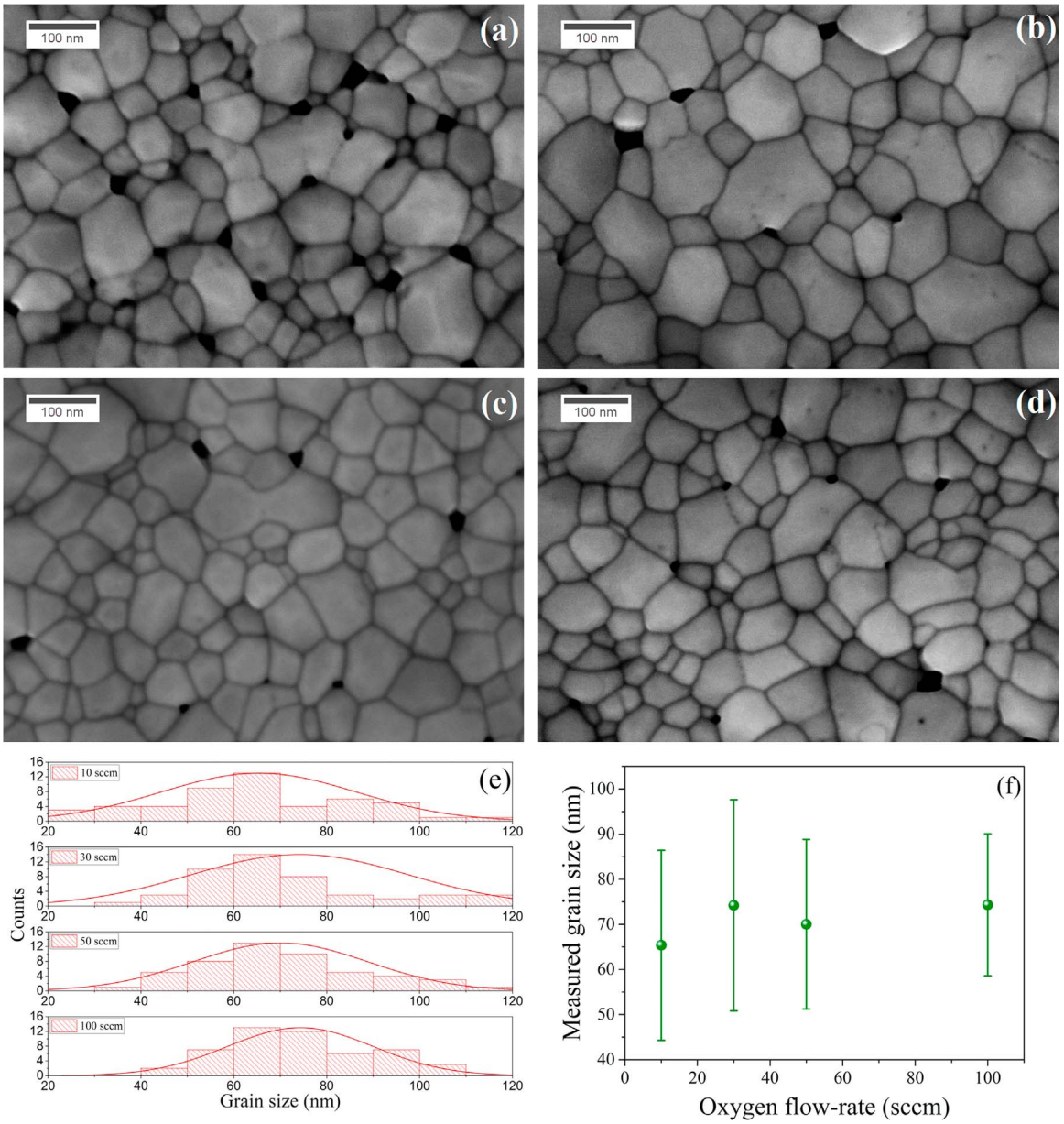

Fig. 1. SEM images of the ZnO films annealed under O_2 flow-rates of (a) 10 sccm, (b) 30 sccm, (c) 50 sccm and (d) 100 sccm, respectively; (e) grain size distributions obtained from SEM images (n=50); (f) measured grain sizes from SEM micrographs.