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Influence of the growth rate on the morphology of electrodeposited zinc oxide

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ABSTRACT

We report on the electrodeposition of ZnO with different surface morphologies. We demonstrate by three different ways that morphology is ruled by the growth rate, and therefore strongly influences the optical properties of the layers. Whereas small size well-connected grains are obtained at high growth rate, the crystals evolve toward large disoriented nanorods since the kinetic of the reaction is hindered. The corresponding RMS roughnesses range from 35 nm to 119 nm, resulting in diffusion of the light from far UV to visible-wavelength. The surface morphology is shown to be directly mastered by electrochemical parameters which enable either a 2D or 3D growth mechanism.

1. Introduction

Zinc oxide is a II–VI semiconductor with a direct wide band gap around 3.3 eV which is commonly n-doped due to its intrinsic defects such as oxygen vacancies and interstitial zinc atoms [1]. Apart from piezoelectric transducers, chemical sensors or light emitting diodes applications [2–4], ZnO is frequently used in photovoltaic devices. It can play different roles as transparent conductive oxide (TCO) contact, textured buffer layer or electron acceptor material depending on the type of photovoltaic structure used, such as hybrid/organic solar cells, $CuInSe_2$ or multijunction amorphous silicon based solar cell [5,6].

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ZnO thin films can be prepared by several ways, including RF sputtering, atomic layer deposition, metal organic chemical vapor deposition, chemical bath deposition, physical vapor deposition, etc. [7]. Among all these deposition techniques, electrodeposition is an inexpensive wet process, due to the little energy required to produce reactions. Electrodeposition is also a powerful technique since changing electrochemical conditions easily leads to the growth of a large variety of nanostructures such as nanorods [8], nanowires [9], nanoflowers [10], nanosheets [11,12], etc. These types of structures are particularly interesting for dye sensitized solar cell (DSSC) applications, in order to elaborate a high quality photoanode with intimate large contact area between the dye and the semiconductor. In opposite, for TCO or buffer layer application in organic devices, surface morphologies have to be compact and smooth to avoid too high roughness and pinholes, which could result in shunt paths and poor electro-optic properties of the devices.

In this study, we propose to investigate how electrochemical parameters influence surface morphology and optical properties of the ZnO thin films deposited.

2. Experiments

The electrochemical growth of ZnO was performed by using a potentiostat in the three-electrode configuration with F-doped SnO_2 (FTO) supplied by SOLEMS, graphite and $Ag/AgCl_{(sat)}$ as working (WE), counter and reference electrode (RE), respectively. The electrolyte was made by dissolving different amount of $Zn(NO_3)_2{\cdot}4H_2O$ in deionized water (18.2 MΩ cm), to reach concentrations from 0.01 M to 0.1 M. The bath was then heated at 80 °C under magnetic stirring and the final pH was around 4.6. Electrodeposition was carried out at a potential ranging between $-0.9\ V_{/RE}$ and $-1.4\ V_{/RE}$ with adjusted deposition time to obtain 350/400 nm-thick layers, in compliance with Faraday's law. Then, the samples were rinsed with deionized water, dried with nitrogen and finally annealed at 200 °C during 30 min at atmospheric pressure.

Optical properties of ZnO thin films were investigated by transmittance using an unpolarized 100 W halogen light source. A HAMAMATSU R928 photomultiplier tube biased at 900 V was used together with a 2400 grooves/mm grating to ensure the detection of wavelengths varying from 3000 to 8000 nm. Surface morphology of thin layers was assessed by Scanning Electronic Microscopy (SEM) in secondary electrons mode and performed by a FEI Quanta 200 FEG SEM equipment operating at an accelerating voltage of 15 keV. Roughness of the samples was probed by Atomic Force Microscopy (AFM) with a SMENA NTMDT system. The measurements were carried out in tapping mode using a silicon cantilever with a typical radius lower than 10 nm. Constant thicknesses of the films were checked by profilometry (Dektak 3 instrument).

3. Results and discussion

3.1. Influence of the applied voltage

Because excellent optical properties are probably one of the most important requirement to use ZnO as window or buffer layer in a solar cell stack [5], we have studied the effect of the applied potential on the transmittance of the electrodeposited layers. The obtained spectra are shown in Fig. 1.

The first striking characteristic of these spectra is the discrepancy of the transmittance before the absorption edge for layers with identical thicknesses. In fact, a closer look at the graph shows that the transmitted signal's intensity reduces with increasing applied potential, and exhibiting an absorption edge less and less pronounced. This later happens around 3.3 eV, which is consistent with the gap of ZnO commonly found in the literature [13], but seems to be also blueshifted with negative biases. This behavior is not so clear in samples D and E, but is more obvious in samples B, C and F. Sample A is an exception because its transmittance is not as weak as in sample B and remains unchanged whatever the wavelength of the light. The absorption edge, which is a fundamental feature of a crystalline material, is no more visible, although the X-ray diffraction pattern of this sample (not shown) demonstrated that our ZnO is well ordered.