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Nanocoral ZnO films fabricated on flexible poly(vinyl chloride) using a carrier substrate

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ABSTRACT

Nanocoral ZnO films on flexible poly(vinyl chloride) (PVC) were fabricated using a three step approach including (1) sputter deposition of a porous Zn film onto a sacrificial Si carrier substrate, (2) formation of the nanocoral ZnO film through annealing in an oxygen flow at temperatures greater than 400 °C and (3) transfer of the film to an adhesive-coated PVC substrate with subsequent removal of the Si carrier. The proposed approach enables the fabrication of porous ZnO films requiring high temperature preparation on flexible polymer-based substrates which would otherwise degrade at high temperatures.

1. Introduction

There is a significant urge to integrate the conventional electronic materials and devices with flexible substrates in order to enable rollable personal electronic devices, wearable electronics or the coverage of complex architectural or automotive surfaces with sensing or photovoltaic devices. As far materials for photovoltaic and sensing applications are concerned, zinc oxide has been receiving considerable attention due to its wide-band-gap-induced transparency in the visible wavelength range, high exciton binding energy of 60 meV (promoting efficient light emission at room temperatures and above) but most importantly due to the plethora of nanostructured ZnO morphologies reported in the literature. Nanorods, nanowires, nanofibers [1–4], nanobelts, nanorings, nanosprings [5], nanoflowers [6] and even hierarchical nanoforests [7] have been presented. These nanocrystallite forms exhibit highly developed surfaces and are therefore regarded as desirable for light and particle absorption applications.

Most of the nanostructured ZnO both on rigid and flexible substrates is produced using solution based methods [8–11], including hydrothermal growth [12], anodization [13] and electrospinning [14]. These techniques are inexpensive to apply and safe for flexible polymer substrates as the used process temperatures are lower than 150 °C–200 °C. However, their scaling for industrial applications is nontrivial with the issues of solution degradation and aging as well as solution composition and purity control. The application of cost-competitive vacuum-based fabrication processes enables to evade these problems while obtaining a high level of material purity and composition control. In particular, magnetron sputter deposition is such a technique widely used in large-area industrial coating applications (e.g. architectural glass coating, photovoltaic cell fabrication).

Until recently there were no reports on the fabrication of nanostructured nanocoral ZnO using magnetron sputtering. In 2012, papers on sputter deposition of porous Zn with subsequent annealing oxidation to ZnO were reported by our group [15] and that of Lambretti et al. [16] using DC and RF magnetron sputtering, respectively. We have chosen the use of DC sputter deposition as more cost-effective compared to RF sputtering due to lower cost of both materials and power supplies needed. Subsequently, we showed the potential of nanocoral ZnO in applications for resistive alcohol sensors and transmission-based gas sensors [17]. However, the direct application of this material on flexible polymer substrates was not possible as the fabrication procedure requires an oxygen annealing step at a temperature of 400 °C or higher while most polymers degrade at temperatures around 200 °C. Therefore, a variation of the method was developed, where a nanocoral ZnO film was fabricated on a rigid carrier substrate through DC magnetron sputter deposition with the post-deposition annealing step modified in a way enabling the detachment of the ZnO film from the carrier substrate. It was subsequently possible to transfer the film onto a selected polymer elastic substrate covered with a thin layer of adhesive.

Similar transfer technologies are often used in the microelectronic industry where it is desirable to combine materials and substrates that

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either have different characteristics or require different technological steps. An example of such transfer technology may be Soitec's Smart Cut™ [18,19] using hydrogen implantation and annealing to break off in a controllable manner a thin layer of a crystalline material from its bulk and to attach it to a carrier substrate. This technology enabled the fabrication of GaN-based microwave HEMT structures on crystalline SiC on poly-SiC (SiCopSiC) substrates reducing the need for thick crystalline SiC wafers and thus cutting costs, while maintaining the high thermal conductivity of SiC [20].

In this report we describe the method of fabricating nanoporous ZnO films on flexible polymer substrates through subsequent steps of sputter deposition onto a carrier substrate, high temperature annealing and transfer onto the polymer.

2. Experimental details

Fig. 1 depicts the schematic of the sample fabrication process. In the first step, porous Zn films were grown on a Si (111) carrier substrate using reactive sputtering of a 3″, 4N-pure Zn target under 80 W DC power in a mixed Ar–O_2 atmosphere. The gas flow rates of Ar and O_2 were 10 sccm and 2 sccm, respectively and the total gas pressure was 1.5 mTorr (0.2 Pa). The deposition was carried out for 1 h. The details of the growth procedure performed in a Surrey NanoSystems Gamma 1000C reactor can be found in our previous report [15], where we showed that the growth of such porous Zn films only takes place under the specific oxygen-poor conditions. If more oxygen is introduced to the sputtering chamber, a dense ZnO film is obtained. Following the deposition, the films were subjected to a 5 minute *in situ* annealing at 600 °C in a 6N oxygen flow of 20 sccm fully transforming the porous Zn into nanocoral ZnO (nc-ZnO) shown in Fig. 2. The resulting material was polycrystalline as evidenced by X-ray diffraction (XRD) studies [15]. The thickness of the fabricated ZnO film was 3.1 μm.

It is crucial to note, that in this configuration a ceramic resistive heater was used which was placed under the sample holder (see Fig. 1c). This heater provided relatively slow temperature changes and its position yielded the propagation of the heat front in the direction from the substrate up. As the oxidation of Zn into ZnO progressed in the same direction, significant stress started to build up in the film. At some point in the transformation the stress was large enough to detach the thin ZnO film from the substrate. As shown later, the step allowed a subsequent transfer of the nc-ZnO film to an adhesive-coated poly(vinyl chloride) (PVC) foil. It is worthwhile to mention that, it was impossible to remove

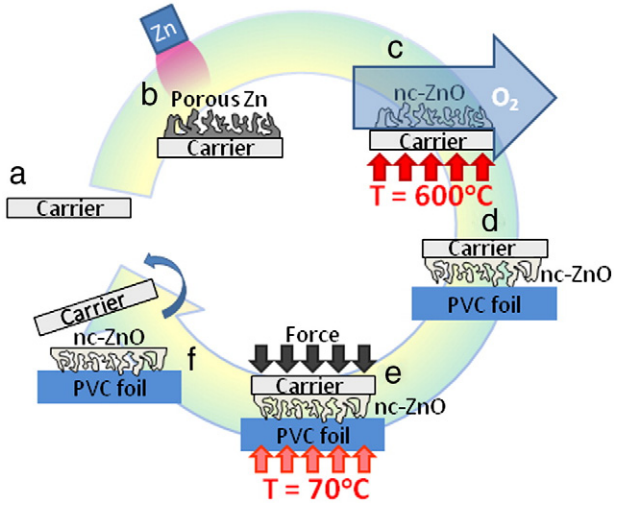

Fig. 1. A schematic presentation of the process flow: (a) free standing carrier substrate, (b) sputter deposition of porous Zn onto the carrier substrate, (c) *in-situ* annealing in oxygen at T = 600 °C to create nanocoral ZnO (nc-ZnO), (d) positioning the sample onto an adhesive-covered PVC foil, (e) heating to 70 °C and pressing, (f) removal of the carrier substrate.

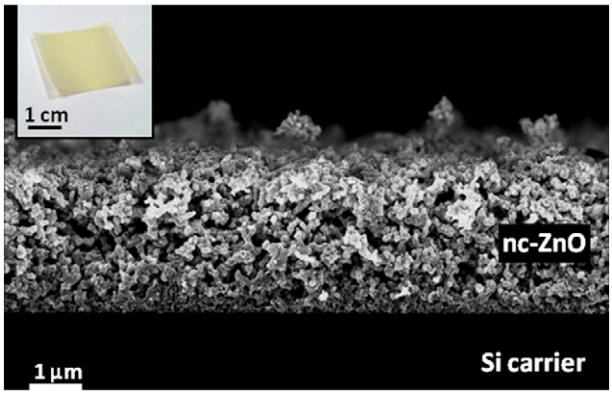

Fig. 2. SEM cross-section image of the nanocoral ZnO film on the Si carrier substrate. The inset is showing the same film on a 200 μm thick soda-lime glass with significant stress-induced bowing.

the film mechanically: using tweezers or by reversing upside down. This relaxation was possible due to the slow propagation of the temperature front in the sample as was shown by comparative studies with porous Zn films on Si substrates annealed in a Rapid Thermal Processing (RTP) furnace. The RTP furnace equipped with quartz lamps delivered the heat rapidly and from the top of the film resulting in a fast oxidation of the film hindering its detachment from the substrate, although the stress in the film remained significant. A scan using a KLA-Tencor D-120 profilometer on a 3 μm-thick nc-ZnO film formed using porous Zn deposition and RTP annealing on a 200 μm thick soda-lime glass substrate yielded 7.5 GPa stress in the total thickness of film. The significant stress-resulted bow of the RTP-annealed nc-ZnO on soda-lime glass sample is shown in the inset in Fig. 2.

The transfer of the nc-ZnO film to the PVC foil was performed using an acrylic adhesive-coated Nitto SWT 10 + 75 μm thick PVC foil. The samples were placed so that the branches of the nc-ZnO contacted the adhesive, heated to 70 °C and pressed together using a roller under a force of around 10 N. After subsequent free cooling down to room temperature, the Si carrier was removed while the nc-ZnO film remained attached to the PVC.

The morphology of the films was analyzed at all steps of the process using scanning electron microscopy (SEM) on a Zeiss Auriga operating at 5 kV. Image processing was applied to extract quantitative information about the pore size and distribution. Electron energy dispersive spectroscopy (EDX) was also performed by means of the QUANTAX 400 Bruker EDX-System (energy resolution of 127 eV) attached to the SEM in order to study any chemical residue on the interfaces after transfer. The measurements were taken for 140 s, under 5 kV high voltage at a working distance of 5 mm and a SEM probe current of 170 pA. The structure of the films was revealed through XRD in ω–2θ geometry using a PANalytical Empyrean equipped with a Cu X-ray lamp and a Johansson monochromator. Finally, photoluminescence (PL) measurements were performed in a closed-cycle Oxford pumped-helium cryostat under the excitation from a He–Cd laser (325 nm wavelength) both before and after the transfer.

3. Results and discussion

From the SEM image presented in Fig. 3a it is evident, that the surface of the nanocoral film reflected the flat interface with the Si carrier, at the same time maintaining the nanoporous structure. The porosity of the film surface was calculated using image processing of a SEM image (see Fig. 3b) using the Otsu method of binarization which chooses a global threshold that minimizes the interclass variance of the two resulting regions [21] with subsequent morphological opening using a disk-shaped structural element of 3 pixel radius for data filtering. The porosity, defined as the ratio of pores to the rest of the image, was