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ZnO Thin Films Deposited on Sapphire by High Vacuum High Temperature Sputtering

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ZnO (0001) layers on sapphire (0001) substrates were fabricated by means of high temperature high vacuum magnetron sputtering. The layers were deposited onto a thin MgO buffer and a low temperature ZnO nucleation layer, which is a technology commonly used in MBE ZnO growth. This paper reports on using this technology in the sputtering regime.

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1. Introduction

Zinc oxide is widely recognised as a material suitable for applications in transparent electronics, photonics, sensors, and high power electronics due to its semiconductor and oxide properties and today is one of the most studied semiconductors worldwide. One of the challenges for ZnO thin film fabrication is obtaining layers of high crystalline quality. Due to high prices of free standing high-quality ZnO substrates, most of the scientific work on ZnO deposition is performed on sapphire substrates, which however has an 18% lattice mismatch to ZnO. To cope with this problem, thin MgO buffer layers are widely used in MBE ZnO growth. The closer fit of the atom positions on [111] MgO and ZnO [0002] surfaces than on sapphire [0001] and ZnO [0001] surfaces leads to less strain and defects in the ZnO layers. Thus MgO layers can promote the correct crystalline growth of the ZnO thin films [1–4]. They can also be used to control the polarity of ZnO films grown on them [5, 6].

Ease of implementation and low costs in comparison to MBE or metal-organic chemical vapor deposition (MOCVD) make sputtering one of the methods of choice for commercial ZnO thin film fabrication. Furthermore, recent improvements in the technology of sputtering systems allow it to perform better than widely expected in the areas of layer purity, homogeneity and physical properties' control, which can lead to obtaining very high quality crystals. These reasons motivated us to undertake the attempt at transferring the MgO buffer layer technology from MBE to sputtering, the results of which are reported herein.

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2. Experimental details

The techniques commonly used for MBE ZnO on MgO deposition are mostly based on the following scheme: deposition of a thin MgO nucleation layer, deposition of a thin ZnO nucleation layer at a low temperature (denoted herein as ZnO_{LT}), *in situ* annealing and deposition of the ZnO layer at a higher temperature (ZnO_{HT}) [1–6]. After reviewing the literature, the following procedure was adapted for the preparation of the samples: Al_2O_3 (0001) substrates were cleaned by boiling in hot organic solvents, rinsed with deionised water and blown dry with N_2 gas. They were then annealed in O_2 flow at 800 °C for 20 min. Subsequently they were introduced into the Surrey NanoSystems Gamma 1000 C UHV sputtering system, which was evacuated to a vacuum of 10^{-8} Torr prior to film deposition. The layers deposited were: 1 or 20 nm thick MgO buffer layer, 6 nm thick ZnO_{LT} nucleation layer followed by *in situ* annealing in vacuum at 750 °C for 5 min and the final 240 nm thick ZnO_{HT} film. The layers were deposited by reactive sputtering in a mixture of Ar and O_2, from 4N pure elemental circular targets of 75 mm diameter. The detailed deposition conditions for each layer are shown in Table. Finally, the samples were RTP annealed in an O_2 flow for 15 min at 800 °C.

The structure of the samples was characterised before and after the RTP annealing by means of X-ray diffraction using a Philips X'Pert with a Cu K_α source, secondary ion mass spectroscopy with a Cameca IMS6F and scanning electron microscopy with a Zeiss Neon 40. The surface morphology and roughness were studied by atomic force microscopy (Veeco Innova) and electric properties of the layers were studied by the Hall measurements in the Van der Pauw geometry. Photoluminescence spectra were also taken at 13 K using a 325 nm He–Cd laser for the excitation.

TABLE

Layer deposition conditions.

	Power and mode*	Ar flow	O_2 flow	Gas pressure	Substrate temperature
MgO	250 W pDC	10 sccm	5 sccm	7.5 mTorr	800 °C
ZnO_{LT}	100 W pDC	10 sccm	5 sccm	10 mTorr	350 °C
ZnO_{HT}	150 W DC	10 sccm	5 sccm	10 mTorr	550 °C

* pDC — pulsed DC mode

3. Results and discussion

We will first describe the properties of thin ZnO films grown directly on the sapphire substrate and then compare them with the ZnO films grown on a MgO buffer layer to discuss the influence of this layer on the properties of the ZnO film. To see whether the thickness of the MgO buffer was relevant to the properties of the films, samples with two thicknesses, 20 nm and 1 nm, of the MgO layer will be discussed.

3.1. ZnO grown directly on sapphire

For the sample grown using the scheme described in Sect. 2, but with the MgO layer omitted, XRD shows that the ZnO film is oriented in the (00.1) direction only, with the lattice constant $c = 5.2132$ Å, and the FWHM of the (00.2) line equal to 1.2°. After annealing, the orientation is conserved, the lattice constant is equal to 5.2036 Å and the FWHM diminishes to 0.4°. The lattice constant is very close to the bulk value of 5.2062 Å [7]. In the SEM images, a columnar structure of the film was observed before and after annealing (see Fig. 1a). The surface roughness decreased from 6.4 nm rms to 4.1 nm rms after annealing. The Hall measurements reported an electron concentration of the order of 10^{14} cm^{-3}, in which case we have to describe the layers as highly resistive. Secondary ion mass spectroscopy profiling showed that the Zn:O ratio in the films was constant and that the H_2 concentration drops after annealing from 10^{21} to 10^{19} atoms/cm^3. The photoluminescence measurements revealed no features in the spectra.

3.2. Influence of the MgO buffer layer

The film grown on the 20 nm thick MgO layer exhibited poor crystalline quality with the (00.2) orientation being the only one visible in X-ray diffraction (XRD), but the FWHM was reliably immeasurable and scanning electron microscopy (SEM) images revealed very large, noncolumnar grains (see Fig. 1b). This situation did not improve after RTP annealing.

On the other hand, the film grown on a 1 nm thick MgO layer showed excellent crystalline quality, where again the (00.2) orientation was the only one present, the lattice constant c was equal to 5.2236 Å and the FWHM was 1.4°. After annealing the lattice constant changed to 5.2036 Å and the FWHM to 0.7°. However no grains nor columns could be seen in the SEM images. The only patterns visible on the ZnO film are the lines

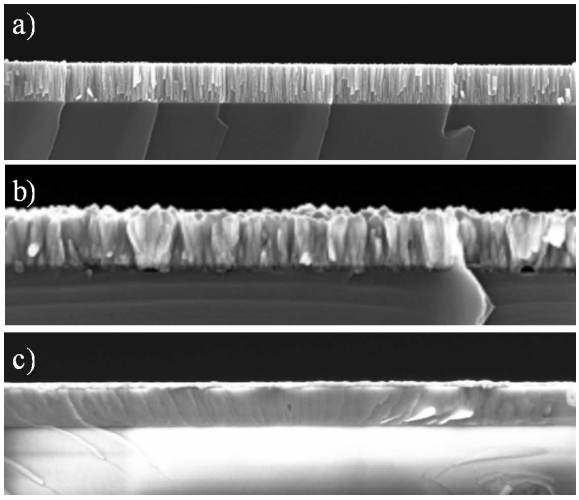

Fig. 1. SEM images of the films grown directly on sapphire (a) and on a 20 nm (b) and 1 nm (c) thick MgO buffer layer. The magnifications and voltages are 8×10^4 and 5 kV, 1×10^5 and 6 kV, 8×10^4 and 3 kV for (a), (b) and (c), respectively.

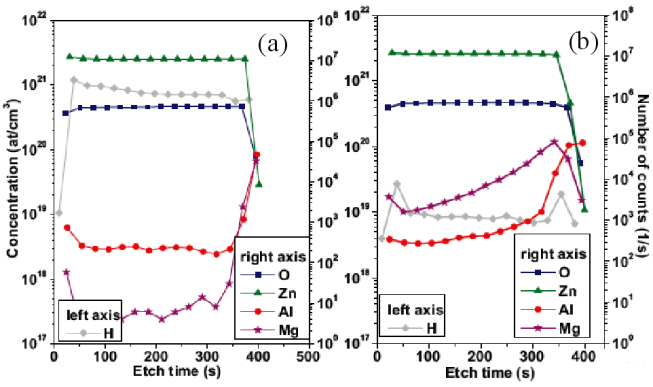

Fig. 2. SIMS depth profiles for the sample grown on 1 nm thick MgO layer before (a) and after (b) annealing.

related to the breaking of the sapphire substrate during the preparation of the sample for SEM imaging. The surface roughness of these layers is equal to 1.8 nm rms before and 2.2 nm rms after annealing and the layers are highly resistive. SIMS profiling again shows a constant Zn:O ratio and the lowering of H_2 concentration by two orders of magnitude in the consequence of annealing. There is however significant outdiffusion of Mg into the

ZnO layer (see Fig. 2). The photoluminescence spectrum showed only two peaks, a distinct one at 3.365 eV, that can be attributed to donor-bound excitons [8] and a less pronounced one, at 3.337 eV that yet remains unidentified.

4. Conclusions

We have demonstrated an adaptation of the MBE method of high crystalline quality ZnO growth involving the deposition of a thin MgO buffer layer to the sputtering technology. The introduction of the MgO buffer layer allowed us to improve the crystalline quality of the sputter deposited films through a transition from a clearly polycrystalline columnar structure to a structure where no columns could be resolved in SEM images. In the result, we obtained (00.1) oriented 240 nm thick films with the lattice parameter $c = 5.2036$ Å and the FWHM of 0.7° for the (00.2) line.

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