SIMS CHARACTERISATION OF ZnO LAYER PREPARED BY PULSED LASER DEPOSITION

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Summary New material development requires new technologies to create and prepare basic materials for semiconductor industry and device applications. Materials have given properties, which exhibit particularly small tolerances. One of the most important and promising material is recently ZnO. ZnO has specific properties for near UV emission and absorption optical devices. The pulsed laser deposition (PLD) is one of the methods to prepare this type of material. The aim of this paper is to compare properties of ZnO layers deposited from pure Zn target in oxygen atmosphere and those deposited from sintered ZnO target. In this paper we will present the results of the preparation of ZnO layers and the analysis of their surface properties by secondary ion mass spectroscopy (SIMS), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

1. INTRODUCTION

The new material technology for preparation of ZnO thin films is represented by pulsed laser deposition. Among many other methods suitable for ZnO thin film preparation like MBE [1], MOCVD[2], RF sputtering [3] the PLD has some advantages [4-6]. To produce defect free material from synthesizing from laser ablation the main features of pulsed laser deposition are the chemical purity, lower substrate temperatures and the possibility to introduce reactive or other type of atmosphere. PLD allows to prepare ZnO layers by two different ways, either by sputtering Zn target in O_2 atmosphere or by sputtering ZnO target onto a sapphire substrate with a high power pulsed laser.

ZnO has a very good combination of large values of band gap energy (3.37 eV), cohesion and exciton stability. The very large exciton binding energy (60 meV) gives a very large potential for room temperature light emission [7]. New applications in optoelectronics are stimulated (exciton lasing) with the research on materials for shorter wavelengths. Since the ZnO is a very attractive material, its use is predicted and realised in a form of micropillars in nanotechnology [8].

SIMS is based on energetic ion bombardment of the sample surface. SIMS measurements are very useful tool to determine the doping and impurity concentrations of the layers. The investigated surface is sputtered by bombardment of the primary ions, from which about 5% secondary ions are ionised particles. The positive or negative secondary ions are subsequently detected according to their mass/charge ratio in a mass spectrometer. The sensitivity is in the range of ppm or even ppb under favourable conditions. Three basic outputs from SIMS analyse are available, corresponding to mass spectra, ion image and depth profile. All three outputs can help in the surface analysis of the ZnO layers.

2. EXPERIMENTAL

The PLD has some advantages in comparison to other technologies in preparing of compound oxide films. One of them is the ability to keep different temperatures between the target material and substrate at different temperatures within relatively wide range. This feature is important in presented experiments because the melting point for the metallic Zn is relatively low (T_m= 420° C) and very close to the deposition temperature.

ZnO films were deposited on 10x10 mm^2 sapphire substrates. Pure metallic Zn target (99.99 % purity) and sintered ceramic ZnO pellet (99.999 %) were used as the target materials.

All investigated samples were deposited in vacuum chamber at 400° C in pure O_2 background atmosphere with subsequent annealing at 400° C for 10 min.

The pressure during the deposition was kept at 5 Pa. The targets were placed on a rotating holder inside the vacuum chamber which was evacuated by a turbomolecular pump down to 5.10^{-4} Pa before deposition. Ablation of the target materials were performed by the focused beam of third harmonic generated frequency (wavelength of 355 nm) of Nd:YAG laser (Quanta Ray Pro 1550 - Spectra Physics). The fluence of 2.2 $J.cm^{-2}$ (with FWHM = 15 ns and repetition rate 10 Hz) was the same for all experimental samples. The main technological parameter – number of pulses of target ablation were varied in the range from 3000 to 12000 pulses. The laser beam was led to the chamber trough a quartz window on the target surface with incident angle of 45° while target - substrate distance was 45 mm.

In this study we employed a time of flight based SIMS instrument (Ion-TOF, SIMS IV) with high energy Au^+ primary source. Standard spectra were taken from each sample before the surface analysis. The negative ions were detected, since they were more sensitive for the analysis. For the

depth profiling of the structure the high energy pulsed primary gun is combined with a low energy sputter gun (Cs^+) because of low erosion rate. The sputtering ion beam is rastered over the area of 300x300 μm while the primary beam is rastered within the 90x90 μm area in the center of sputtered area. The high resolution TOF detection system is performed by a single particle counting using microchannel plate detector, which has parallel mass detection in range up to 10.000 amu [9].

The AFM measurements were performed with NT-MDT Solver P47 AFM measurement system in semi contact (tapping) with resolution in the range of 0.1 nm. The qualitative analysis was employed for investigated surfaces via characteristic surface roughness R_a and standard deviation for Z direction on the sample surface R_q parameters. These parameters are in accordance to R_a – DIN 4768 and R_q – ISO 4287/1 evaluation [10]. The measured results from the investigated samples are shown in the figure insets. The surface morphology was observed with a LEO SEM 1550 microscope.

3. RESULTS

Characterization of produced films was performed by secondary ion mass spectroscopy (SIMS) in order to investigate the composition and the impurity content of the atomic layers. Atomic force microscopy (AFM) was used to reveal the layer thickness and roughness. The surface morphology investigations were performed by scanning electron microscopy (SEM).

Typical mass spectra from ZnO layer is shown in the Fig. 1. In this negative secondary ion spectrum we can identify C, O and the isotopes of ZnO. Fig. 2a represents the SIMS depth profile of the ZnO layer on sapphire deposited from pure Zn target. The ZnO layer deposited from the sintered ZnO target prepared by PLD is shown in Fig. 2b. The interface between the sapphire and ZnO layer is possible to identify due to ^{64}Zn peak height increase and by the changing ^{16}O peak height. The sapphire substrate shows less oxygen incorporated. The layer thickness differs a little from the 150 nm measured with AFM.

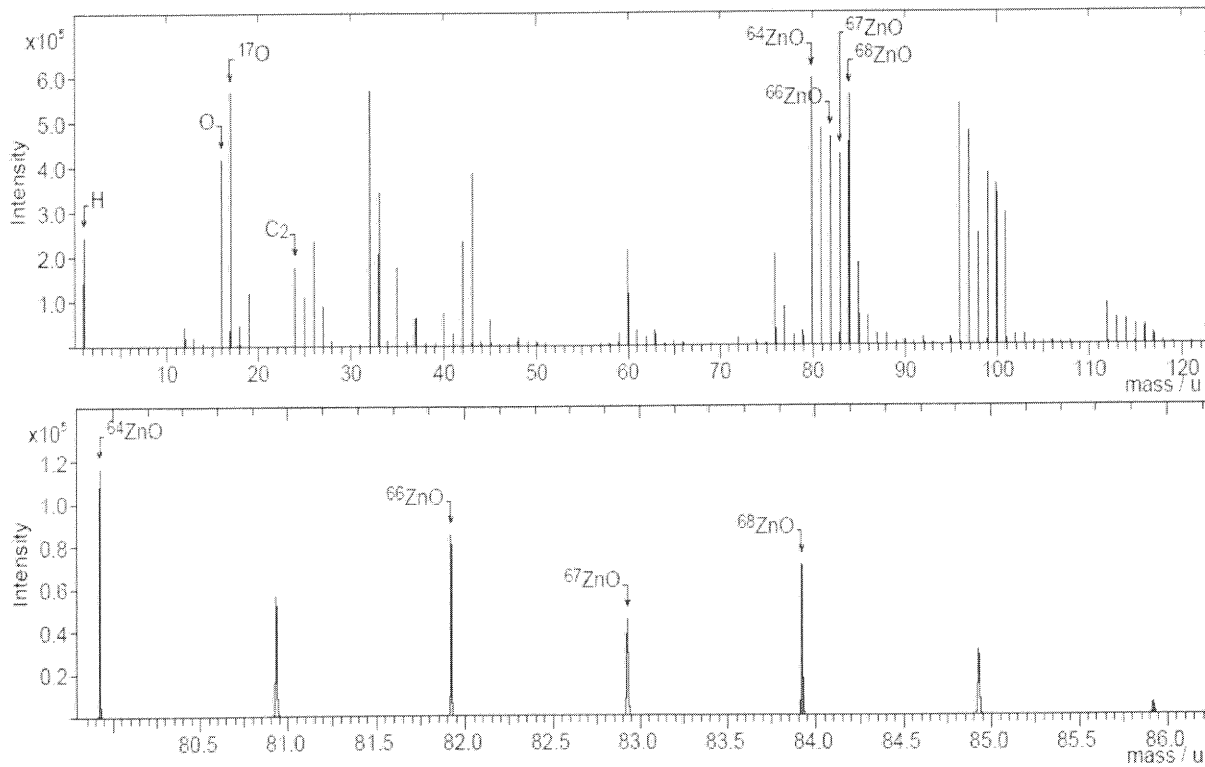

Fig.1. Mass spectra of the deposited ZnO layer

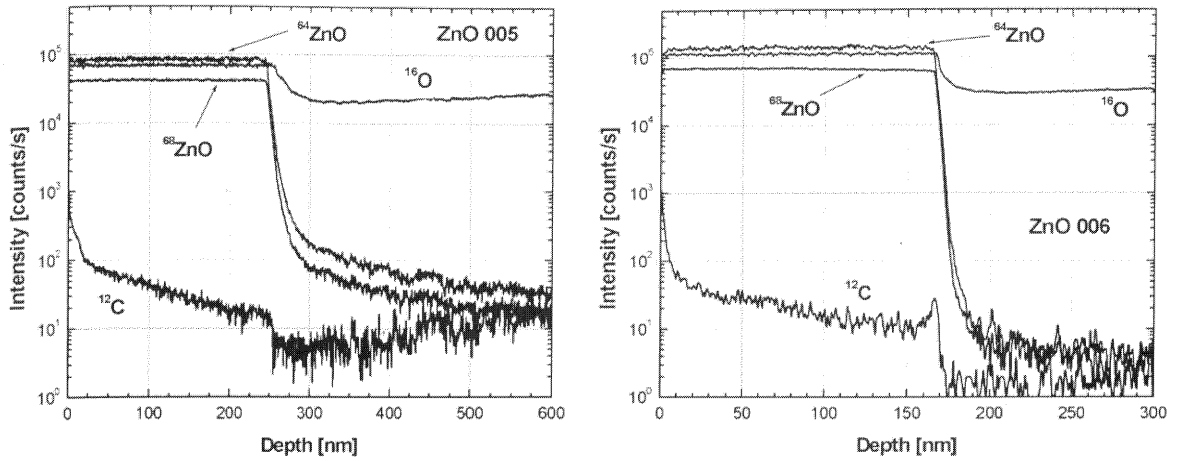

Fig. 2. SIMS depth profiles for both samples on sapphire substrate. Both of them show the characteristic layer thicknesses, which are in agreement with AFM results

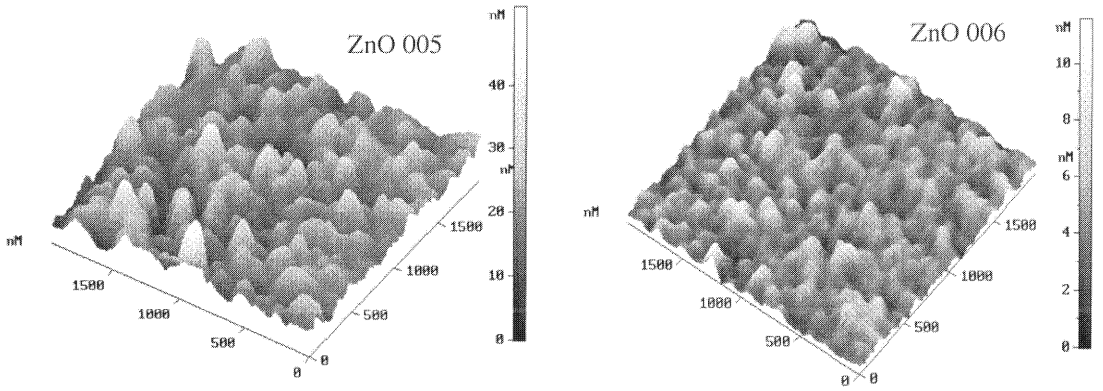

Fig. 3. AFM picture of typical surface morphology of the film deposited from the Zn and ZnO target

Tab.1. Characteristic surface roughness R_a and standard deviation for Z direction on the sample surface R_q parameters for investigated samples

Sample	Target	Thickness	Rq	Ra	No. of pulses
ZnO 005	Zn	240	8.337	6.439	12000
ZnO 006	ZnO	150	2.643	2.142	3000

The AFM micrographs of ZnO films are shown in Fig. 3. The grain size depends on the number of the applied pulses and on the temperature of the substrate. The qualitative analysis results via characteristic surface roughness R_a and standard deviation for Z direction on the sample surface R_q parameters are shown in Tab.1.

Fig. 4 represents a specimen of ZnO deposited on sapphire. The surface is polycrystalline with typical grain size of 50 nm approximately. Other specimens under different deposition parameters were prepared. The number of laser pulses was the parameter to be varied (from 1000 to 4000 pulses). From the analysis we can conclude that typical grain structure was the same with equal grain dimensions despite different thickness of prepared films.

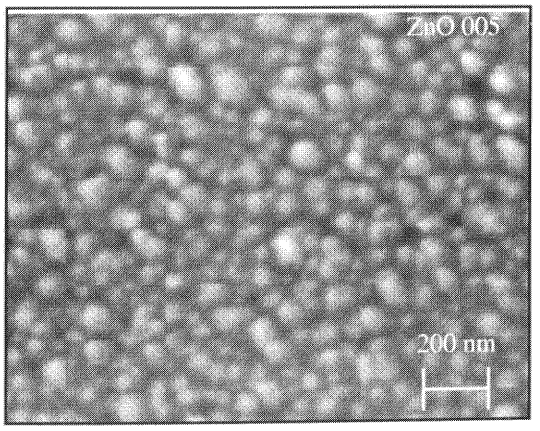

Fig. 4a. SEM picture from the surface of the ZnO sample ZnO 005

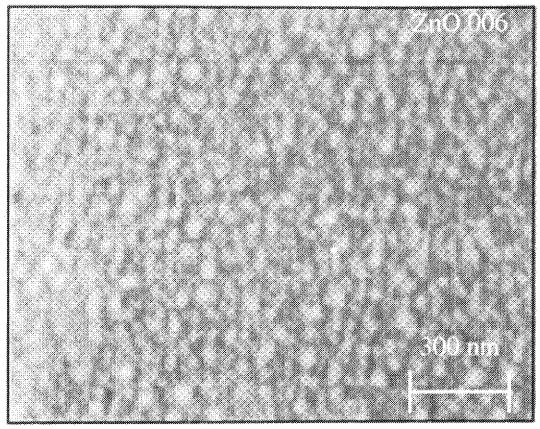

Fig. 4b. SEM picture from the surface of the ZnO sample ZnO 006

4. CONCLUSION

This contribution is devoted to ZnO material technology using PLD from Zn target and from sintered ZnO target in O_2 atmosphere onto a sapphire substrate and its subsequent characterisation.

The compared results show differences between these two differently deposited targets. From the AFM and SEM measurements we can conclude that the layers are homogenous, the growth deposition rate in the dependence on the pulse number is well defined. The SIMS depth profile analysis shows the interfaces between the deposited layer and substrate with a slightly higher ^{64}Zn peak. For future it will be suitable to analyse the sputtering targets and to make the whole impurity map analysis for the ZnO layers.

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