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Aluminium-Substituted Zinc Oxide Thin Films: Thermoelectric Properties and Structural Characterisation

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***Abstract*— Thin films of polycrystalline 2% Al-substituted ZnO were synthesised by RF magnetron sputtering. In this work the characterisation and the measurement of the thermoelectric properties of the thin films is described. The grains show columnar morphology with preferential orientation of the c-axis perpendicular to the substrate. The electrical conductivity and the Seebeck coefficient of the thin film were measured as a function of the temperature. The thin film is changed at a temperature above 640 K leading to an increase in the electrical resistivity and the Seebeck coefficient absolute values. The influence of the morphology and the composition on the thermoelectric properties is discussed.**

***Keywords*— Al-substituted ZnO, thin film, thermoelectric properties, TEM, XRD**

I. Introduction

Thermoelectricity (TE) allows the direct transformation of heat into electricity. The heat source can either be IR radiation from the sunlight, geothermal or excess heat from combustion processes. In TE modules, there is no need for mechanical parts that cause noise and abrasion and there are neither emissions nor waste products. Suitable TE materials are those with a high figure of merit $ZT = S^2T / \rho\kappa$ (with the temperature T, the Seebeck coefficient S, the resistivity ρ and the thermal conductivity κ). State-of-the-art Bi_2Te_3 materials display good TE properties in a low temperature range, however they are toxic and unstable at high temperatures. Materials with a high thermal stability open the field to high temperature applications (high conversion efficiency with large temperature gradients).

Zinc oxide is one of these materials with a high stability in air at temperatures even higher than 800 K. It has already been pointed out to be a promising TE material by Tsubota et al in 1997 [1] due to its high Seebeck coefficient, low-cost production and non-toxicity. But zinc oxide exhibits high electrical resistivity and high thermal conductivity. Substituting 2 at% zinc by aluminium improves the thermoelectrical properties [1]. The electrical resistivity decreases without showing a strong effect on the Seebeck coefficient. However, the high thermal conductivity is still a drawback of both substituted and non-substituted zinc oxide in comparison to the state-of-the-art TE materials. One way to reduce the thermal conductivity is structuring the morphology on the nano-scale range. The increase of boundary scattering for phonons could be highly beneficial to lower the lattice thermal conductivity in oxides without deteriorating the electron mobility.

The aim of this work was to analyse the nano structure, crystal structure and thermal stability of aluminium-substituted zinc oxide thin film synthesised by radio-frequency magnetron sputtering. The structure was evaluated by transmission electron microscopy and X-ray diffraction. The thermoelectrical properties were defined by the analysis of thermal conductivity and Seebeck coefficient.

II. Experimental

Radio-frequency (RF) magnetron sputtering was used to synthesise polycrystalline thin films of 2 % Al-substituted ZnO [2]. The target used was 2 wt% Al_2O_3-doped ZnO with a purity of 99.995 % (Williams Advanced Materials). The sputtering was done at a pressure of 10^{-3} mbar with a gas mixture of Ar and Ar with 3 % O_2 on soda-lime glass substrates. After 16 minutes of sputtering with a plasma power of 200 W, the film thickness for the Al:ZnO sample was 470 nm. The substrate was not heated during sputtering, but due to the process it reached a temperature of around 350 K.

Phase purity of the films and orientation of the grains was investigated by X-Ray Diffraction (XRD) with a PANanalytical X'pert diffractometer using Cu-Kα radiation. A grazing angle configuration was used to measure the films with a pure soda-lime glass substrate as a reference. The nano structure of the samples was studied by Transmission Electron Microscopy (TEM) using a Philips CM30 and a Jeol JEM 2000FS TEM/STEM.

The electrical conductivity and Seebeck coefficient were measured in air simultaneously as a function of temperature from 323 K to 823 K using the film configuration of the RZ2001i measurement system from Ozawa Science, Japan. A piece of substrate and film of around 10 x 15 mm was used for the measurement. The electrical conductivity was determined using a four-point probe method. Four electrical Pt contacts were directly pushed against the film for measurement.

III. Results and Discussion

Thin films of polycrystalline 2% Al-substituted ZnO were successfully deposited by RF magnetron sputtering. The thin film was investigated by grazing angle XRD. Fig. 1 shows the XRD pattern of the Al-substituted ZnO. The diffractogram shows preferred orientation in c-direction with the 002 plane. It reveals that some of the crystallites have a slight mis-orientation in a- and b-direction (planes 102, 103 and 112).

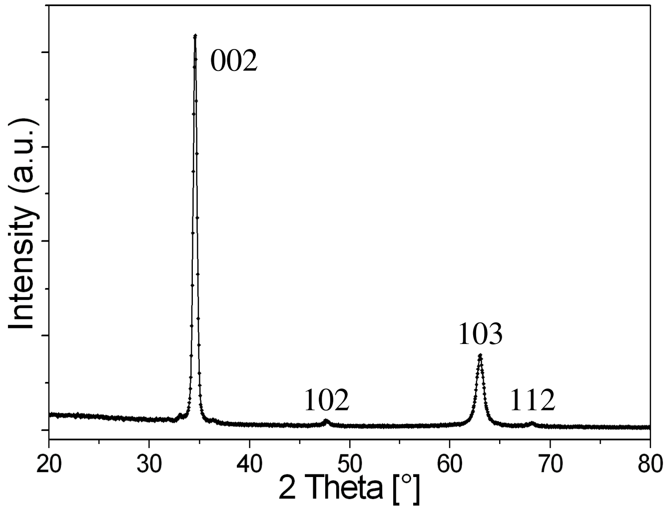

Fig. 1: XRD pattern of the Al-substituted ZnO thin film.

The c-orientation of the grain structure can be confirmed by TEM. Fig. 2 a) and b) show bright field and dark field images of the Al-substituted thin film. The grains have columnar shape perpendicular to the substrate surface. They are 15 to 35 nm wide and up to 200 nm long.

Electrical resistivity and Seebeck coefficient were measured as a function of the temperature up to 800 K in air atmosphere. At temperatures up to around 640 K the thin film grown in Ar atmosphere shows very low electrical resistivity values of less than 10^{-3} Ωcm. Above this temperature the electrical resistivity increases abruptly to 3 Ωcm at 800 K. During cooling down to 350 K the value reaches 10 Ωcm. The heating and the cooling curve of the electrical resistivity is shown in Fig. 3. The Seebeck coefficient is coupled to the resistivity and shows a reciprocal behaviour, which is shown in Fig. 4. The Seebeck coefficient values are relatively small with -30 to -60 µV/K for the heating cycle up to around 640 K and increase with temperature to reach -650 µV/K at 800 K. In the cooling cycle the Seebeck coefficient decreases to reach -500 µV/K at 350 K.

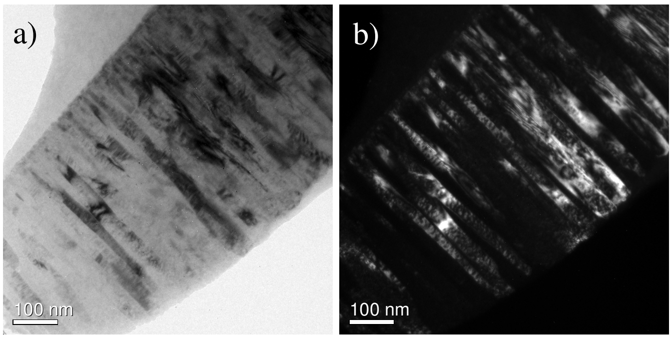

Fig. 2: TEM images of the Al-substituted ZnO thin film, a) bright field, b) dark field.

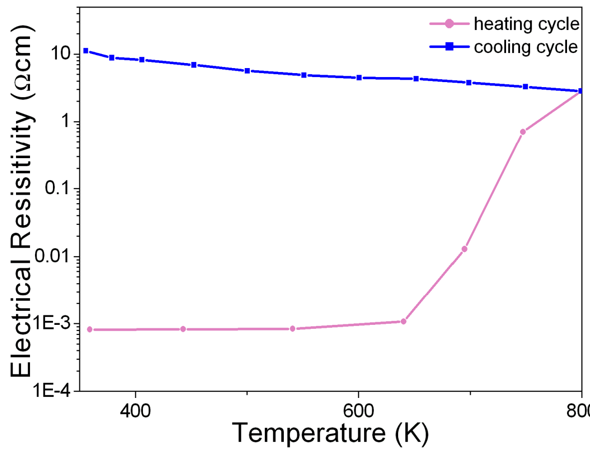

Fig. 3: Electrical resistivity as a function of the temperature for the Al-substituted ZnO thin film.

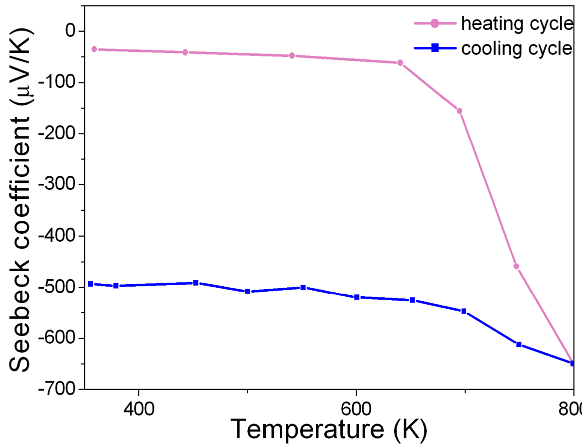

Fig. 4: Seebeck coefficient as a function of the temperature for the Al-substituted ZnO thin film.

For the figure of merit ZT of the 2 % Al-substituted ZnO thin film, an estimation was done with the thermal conductivity values of a bulk sample synthesised by solid state reaction. The highest ZT value of 0.019 is reached at 640 K.

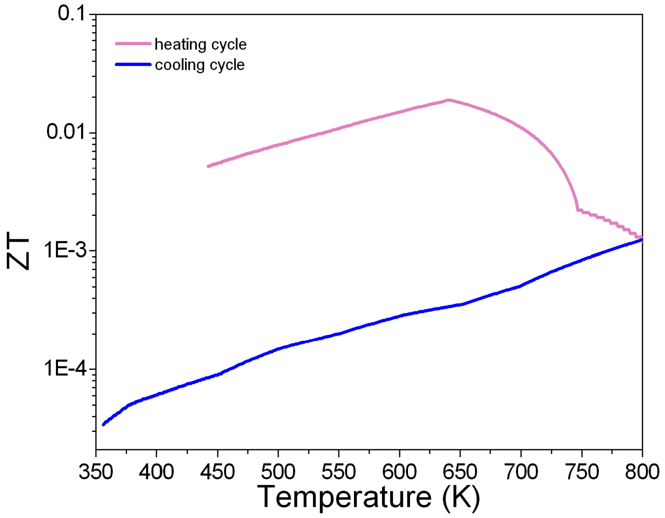

Fig. 5: Estimated ZT values as a function of the temperature calculated from the electrical resistivity and Seebeck coefficient from the thin film and an approximation of the thermal conductivity of a bulk sample from solid state reaction.

The thin film after thermoelectric property measurements up to 800 K was analysed by TEM to search for possible changes in the microstructure. In Fig. 6 TEM images of the samples with and without heat treatment are compared. The analysis by TEM reveals the same columnar grain morphology as for the as grown sample.

XRD measurements were performed of an as grown sample and after thermal treatment air atmosphere at temperatures of 623 and 723 K. The forth measurement was done with the sample after the evaluation of the thermoelectric properties in air up to 800 K. Fig. 7 shows the XRD patterns of the described measurements.

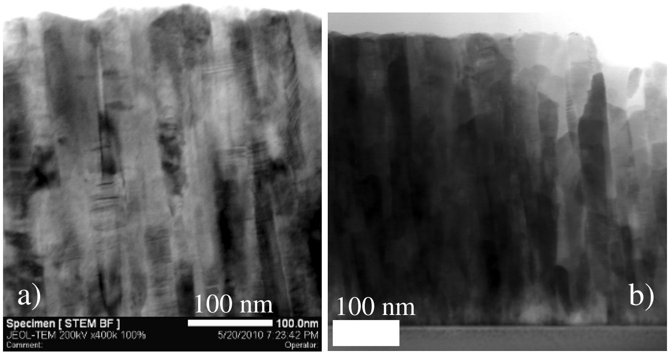

Fig. 6: TEM images of the Al-substituted ZnO thin film a) without heat treatment and b) after heating up to 800 K.

There is a change in the ratio for the intensities of the 002 and the 103 diffraction poles with temperature. With increasing temperature, more grains show 103 compared to 002 planes in XRD. This means that the amount of grains with a contribution of the a-axis perpendicular to the substrate increases.

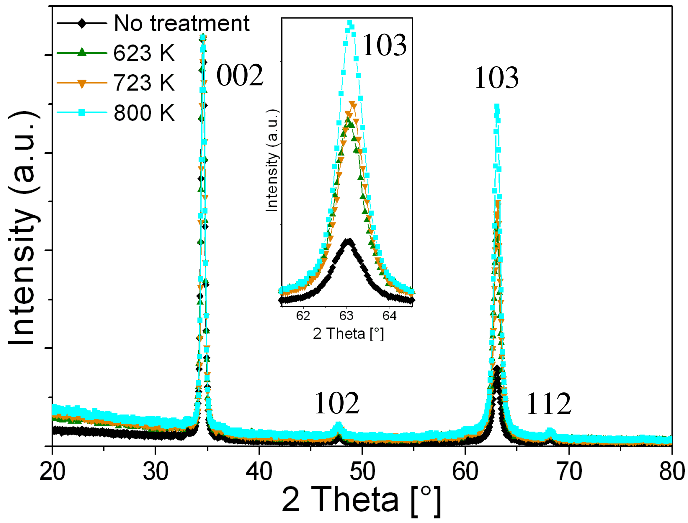

Fig. 7: XRD patterns of Al-substituted ZnO samples measured after treatment at different temperatures.

This change in orientation could have an influence on the electrical resistivity since there is anisotropy of this property respect to the different orientation in the hexagonal structure of Al-substituted ZnO. Kaga et al. [3] discussed the influence of the texture orientation on the electrical resistivity. They found that the resistivity values perpendicular to the c-axis are only half of the ones parallel to it. On the other side Kaga et al. [3] described that the Seebeck coefficient is not influenced by the orientation of the grains. The Seebeck coefficient values in this work are changed with temperature in the range of one order of magnitude.

However, the change of electrical resistivity in this work is around four orders of magnitude comparing before and after annealing, and it cannot only be due to the change in texture orientation. A more reasonable factor for the change in electrical resistivity and Seebeck coefficient with temperature is a change in the oxygen content. The thin film was grown in an Ar atmosphere resulting in oxygen deficiencies during deposition. Oxygen deficiencies decrease the resistivity of the material. During heating up to 800 K in air atmosphere, the oxygen deficiency is eliminated resulting in an increase of the resistivity. Kim et al. described the effect of Ar and N_2 atmosphere on the oxygen concentration resulting in oxygen deficiency and lower electrical resistivity compared to annealing in air [4]. Further investigation needs to be done on the effect of the oxygen content on the thermoelectric properties.

IV. Conclusions

Magnetron sputtering is an appropriate method to synthesise ZnO thin films with 2 % Al-substitution. The films show columnar grains with a preferred orientation of the c-axis perpendicular to the substrate. The resistivity of the thin film changes when heated in air. Seebeck coefficient and electrical resistivity show an evolution with temperature with a maximum effect above 640 K. The ZT value calculated with thermal conductivities of the bulk 2 % Al-substituted ZnO sample reaches a maximum of 0.019 at 640 K. The change in the thermoelectric properties with temperature could be due to the anisotropic character of the sample with hexagonal structure. But more probable is a change in the oxygen content with heating the sample in air atmosphere. More investigation by TEM and X-ray photoelectron spectroscopy (XPS) will be done to study the two effects.

Acknowledgment

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