Investigations on the energy balance of the substrate during ZnO magnetron sputtering

S. Bornholdt[1], K. Kuwahara[2], N. Itagaki[2], H. Wulff[3], M. Shiratani[2], H. Kersten[1]
[1]*Institute of Experimental and Applied Physics, University of Kiel, Kiel, Germany*
[2]*Institute of Electrical Engineering, Kyushu University, Fukuoka, Japan*
[3]*Institute of Physics, University Greifswald, Greifswald, Germany*

Introduction

ZnO is a wide-band gap semiconductor which has gained vast attention over the past ten years because it has a wide range of applications such as light emitting diodes (LED), piezoelectric devices and transparent conductors [1,2]. Owing to its material abundance and environmentally friendly composition, ZnO is a potential alternative to tin-doped indium oxide (ITO) [3] for transparent conducting oxide (TCO). However, there is a major drawback in making ZnO based TCO competitive because its resistivity is still considerably higher than that of ITO and increase with decreasing the thickness below 10nm [4]. Hence, improvement of the crystal structure of zinc oxide thin films deposited by Physical Vapor Deposition (PVD) is a key issue for industrial manufacturing of display panels and solar cells [5].

Experimental determination of the particle and energy fluxes and their influence on the energy balance at the substrate surface as well as for the films deposited by PVD is of essential interest. For this purpose, calorimetric measurements [6,7] at substrate position were performed in a triple rf-magnetron sputter deposition system with ceramic ZnO targets using different gas mixtures (Ar/N_2 and Ar/H_2) and a correlation between the energy influx from plasma to substrate during sputter deposition and the resulting film properties is presented.

For example, by variation of the probe bias the different contributions originating from the kinetic energy of charge carriers, their recombination at the surface as well as the contributions due to the impact of sputtered neutral particles and subsequent film growth have been determined. Radial scans in the substrate plane were recorded in order to monitor inhomogeneities in the total energy influx.

Experimental

The energy flux measurements and deposition experiments were carried out in a deposition chamber equipped with three rf-magnetrons using ZnO targets (2 inch in diameter) which are usually operated at 100W each. The calorimetric probe [7] used for energy flux measurements consists of a brass plate (diameter = 10mm) inserted into a ceramic shielding. The probe was mounted 50mm above the center of the targets at typical substrate position (Fig.1). The temperature of the probe (substrate dummy) is recorded by a thermocouple which is welded to the backside of the plate. An additional wire connected to the backside allows control of substrate potential and measurements of electric currents to the probe. By using a vacuum feedthrough radial profiles of the energy flux across the targets can be obtained. A detailed description of the thermal probe diagnostic method and examples for applications can be found elsewhere [8,9].

The gas flow rates of argon and admixtures of nitrogen (and hydrogen) were controlled via mass flow controllers. Typical gas pressure for magnetron operation during ZnO thin film deposition was 0.3 Pa.

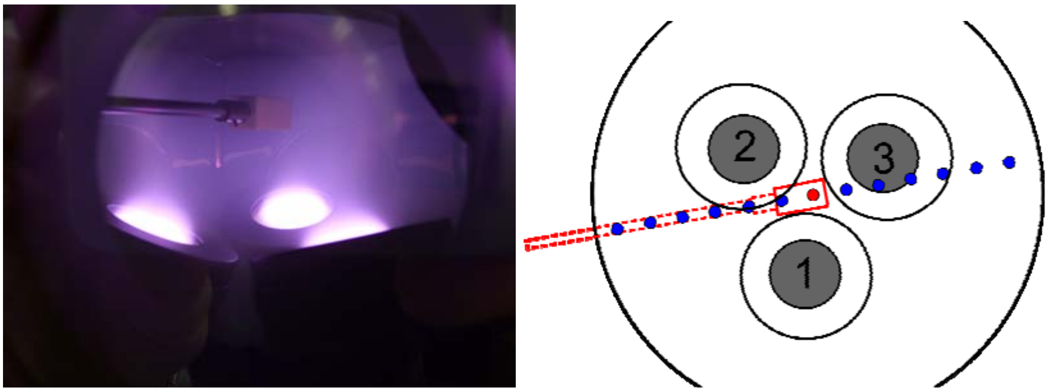

Fig.1: Calorimetric probe mounted 5 cm above the center of the targets (left). Right: Top view into the chamber with indicated positions of the radial scan (dots). Usually, the measurements are carried out in the center.

Results and Discussion

In general, the total energy influx J_{in} to the probe is the sum of fluxes due to electrons (J_e), ions (J_i), and radiation (J_{rad}). The electrons and ions hitting a substrate transfer their kinetic energy and, moreover, recombination energy is released when a positive ion and an electron recombine at the surface. Furthermore, gas atoms can associate into molecules at the surface (J_{ass}) or they may react with the surface (J_{react}). Additional energetic contributions are due to the sputtered neutral particles (J_n) and to condensation of the particles contributing to film growth (J_{cond}). The several contributions can be estimated by taking into account the related plasma parameters [6,9]. For the experimental conditions during ZnO deposition by sputtering in a pure Ar atmosphere these contributions have been calculated and their sum is compared with measurements of the total energy influx showing a quite good agreement, see Fig.2.

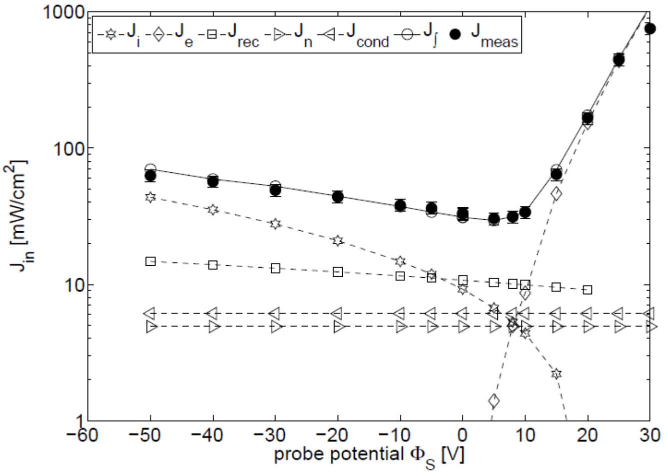

Fig.2: Comparison of the calculated (open symbols) and measured energy influx (filled circles) in dependence on the probe voltage Φ_S for pure argon at 0.3 Pa with three magnetrons operated at 100 W each.

If nitrogen is added in order to mediate a better crystallization of the ZnO films [10] the energy influx is about 10% smaller than for pure argon, since the contributions by the ions and their recombination decreases due to the lower electron temperature.

However, by admixture of hydrogen the energy influx increases remarkably (Fig.3). This effect can be employed for local heating of the growing film [11]. For the measurements the total Ar pressure was kept constant at ~16 sccm resulting in a pressure of 0.2 Pa and then different H_2 fluxes were added resulting in different total pressures. For better comparison also the energy fluxes for pure Ar plasma were determined. The steep increase of the energy influx by hydrogen admixture can be attributed to the formation of H_2 molecules from atomic hydrogen at the surface and the subsequent release of molecule binding energy (J_{ass}).

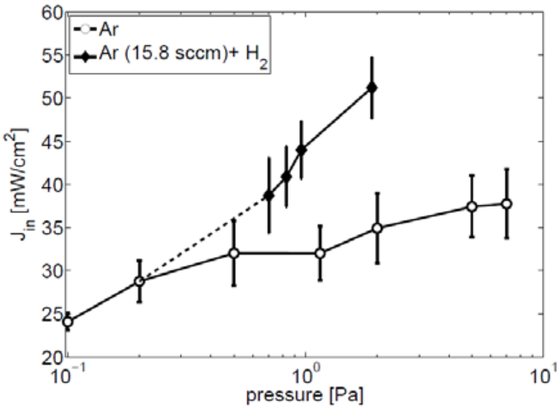

Fig.3: Influence of H_2 addition, resulting in different total pressures, on the total energy influx.

Finally, radial scans were performed for various discharge configurations: all 3 magnetrons (1,2,3) and only 2 magnetrons (1,3) were operated. From the difference of both the values for one magnetron (2) were calculated. The results of these measurements are shown in Fig.4.

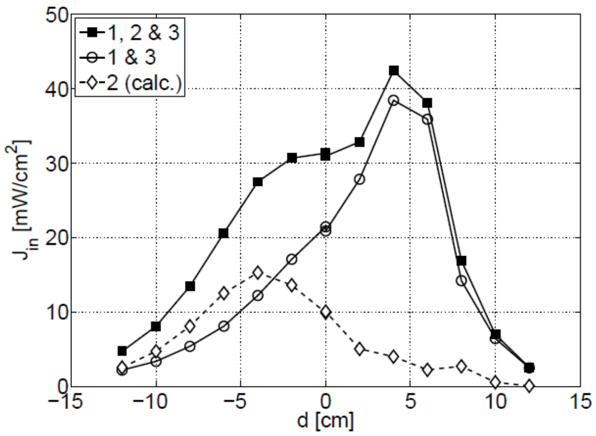

Fig.4: Radial distribution of the energy flux for various numbers of magnetrons in operation.

One can clearly observe the effect of each magnetron which results by superposition in a rather homogeneous profile of the energy influx and deposition rate. Since for industrial applications a homogeneous quality (e.g. film thickness, crystal structure, transparency, resistivity) across a wide substrate area is required these results are important for the optimization of ZnO deposition by sputter PVD.

Conclusion

Calorimetric measurements were performed in a triple magnetron sputter system for deposition of ZnO films. Variation of the Ar/N_2 ratio shows only a small influence on the resulting energy influx, while the effect of the Ar/H_2 ratio is much more pronounced. Local heating by hydrogen admixture seems to be a promising method for future improvement of crystal structure of ZnO thin films. Radial scans of the energy flux were performed to check the reasonable film homogeneity in the substrate plane.

References

[1] J. Combrero, A. Elmanouni, B. Hartiti, M. Mollar, and B. Mari, Thin Solid Films 451-452, 198 (2004)
[2] T. Xu, G. Wu, G. Zhang, and Y. Hao, Sensor Actuat. A - Phys. 104, 61 (2003)
[3] T. Yamamoto, Thin Solid Films 420-421, 100 (2002)
[4] T. Yamada, A. Miyake, S. Kishimoto, H. Makino and N.Yamamoto, Appl.Phys.Lett. 91, 051915 (2007)
[5] B. Rech, O. Kluth, T. Repen, T. Roschek, J. Springer, J. Muller, F. Finger, H. Stiebig and H. Wagner, Solar Energy Materials and Solar Cells 74, 439 (2002)
[6] H. Kersten, H. Deutsch, H. Steffen, G.M.W. Kroesen and R. Hippler, Vacuum 63, 385 (2001)
[7] M. Stahl, T. Trottenberg and H. Kersten, Rev. Sci. Instrum. 81, 023504 (2010)
[8] H. Kersten, D. Rohde, H. Steffen, H. Deutsch, R. Hippler, G. Swinkels, and G.M.W. Kroesen, Appl. Phys. A, Mat. Sci. Proc 72, 531 (2001)
[9] S. Bornholdt, T. Peter, T. Strunskus, V. Zaporojtchenko, F. Faupel, and H. Kersten, Surf. Coat. Technol. 205, 388 (2011)
[10] K. Kuwahara, N. Itagaki, K. Nakahara, D. Yamashita, G. Uchida, K. Kamataki, K. Koga, and M. Shiratani, Thin Solid Films 520, 4674 (2012)
[11] M. Wolter, I. Levchenko, H. Kersten, and K. Ostrikov, Appl. Phys. Lett. 96, 133105 (2010)