Reactive Sputtering of doped ZnO: Steps towards an atomistic understanding of structure formation

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Introduction

Zinc oxide (ZnO) continues to receive significant attention mainly due to its use as a transparent conducting oxide [1]. Therefore many studies on ZnO thin films, in which different deposition methods such as spray pyrolysis, pulsed laser deposition, metal organic chemical vapor deposition, reactive evaporation, and several sputtering techniques [2,3] are utilized, have been published. Notably RF magnetron sputtering is the most commonly used technique, since highly oriented films with low resistance and high transparency are synthesized [4]. Nonetheless, for large area coatings, such as architectural glass, reactive DC sputtering is preferable, since the process can be scaled more easily.

Therefore, we have applied the latter technique to study the influence of the process parameters on the film properties. Usually films with strong orientation of the crystallites are desirable for good electrical conductivity or piezoelectric response [5]. At the same time, the residual stresses often found in sputter-deposited films should be minimized. Finally, these film properties must not be achieved at the expense of a low deposition rate. In this report, we focus on the influence of the total gas pressure during deposition on these properties. We will show that the relationship between pressure and different film properties can be explained by a single mechanism. This knowledge enables the tailoring of films with desired characteristics.

Results and discussion

In Fig.1, the dependence of the deposition rate on the total pressure is depicted. At low pressures, the rate increases with total pressure until 1.5 Pa, where a maximum is reached. For higher pressure, the rate r decreases with pressure. The latter behavior can be explained by the Keller-Simmons relation [6]:

$$r = r_0\left(1-\frac{(pd)_0}{pd}\exp\left\{\frac{-pd}{(pd)_0}\right\}\right),$$

where p is the total pressure, d is the distance between target and substrate, r_0 is the deposition rate without scattering losses, and $(pd)_0$ is a characteristic pressure-distance product. This formula accounts for the scattering of sputtered particles by gas atoms and molecules between the target and the substrate. After these collisions, the sputtered particles are thermalized and only contribute to the film growth by omnidirectional diffusive transport. In our case, values of $(pd)_0 = 160 \pm 12$ Pa mm and $r_0 = 1.75 \pm 0.05$ nm/s were found. From this, the average number of collisions for the sputtered particles can be estimated for each pressure.

In this model, the deposition rate can only decrease with pressure, whereas an increase of the deposition rate was observed at low pressures. A possible explanation is resputtering (i.e., the growing film is sputter-etched by energetic particles, which would be more prevalent at lower pressures).

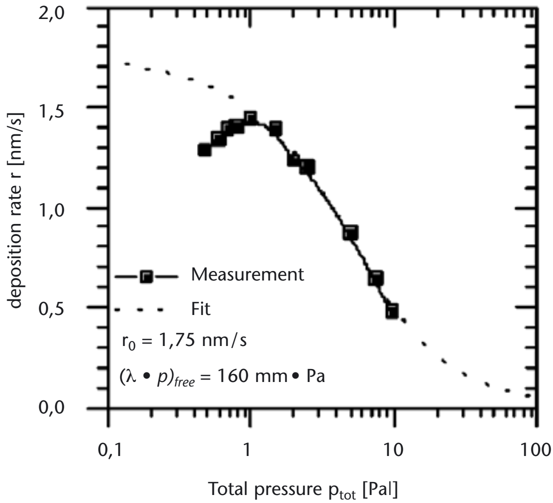

Figure 1
Dependence of deposition rate on total pressure. The decrease in deposition rate below and above 1.5 Pa is due to resputtering and gas phase collisions, respectively. The dotted curve denotes the Keller-Simmons fit for total pressures >1.5 Pa.

To verify this concept, samples were prepared on silicon substrates facing away from the target, so that it was not possible for the zinc atoms sputtered from the target to reach these substrates directly, but only by diffusion. By placing microscope slides facing the target and the silicon substrate, an additional zinc source is introduced. From the film growing on the microscope slides, material can be resputtered and contributes to the growth of the film on the silicon substrate. If resputtering plays a major role, the growth rate on the silicon substrates should depend significantly on the presence of this additional source of zinc.

The results are shown in *Fig. 2* as a function of the average number of collisions obtained from the fitting procedure described above. The direct deposition rate *(Fig. 2a)* shows a maximum at around 0.5 collisions. As a new target had been used for this series, the deposition rate is slightly higher than in *Fig. 1*. Below 0.5 collisions, the deposition rate increases with increasing number of collisions. In this range, the indirect deposition rate is significantly higher for the samples with the microscope slides as for those without *(Fig. 2b)*. Thus, we can conclude that there is significant material transport from the microscope slide to the silicon substrate, which is a strong indication for resputtering from the film growing on the microscope slide by energetic particles. These could be fast negative oxygen ions sputtered from the oxide-covered area of the target, which impinge on the growing film after being accelerated by the full cathode potential [7]. Indeed we have recently observed that structure formation in transition metal oxides deposited by reactive magnetron sputtering is controlled by the influence of fast oxygen ions [8].

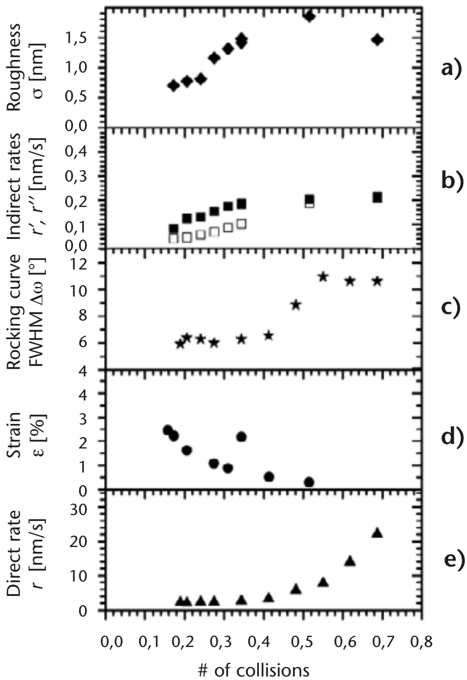

Figure 2
Variation of direct and indirect deposition rates r and r (with microscope slides: solid symbols; without: open symbols), film strain e, surface roughness r and texture (FWHM Dx of rocking curve) against the number of relevant collisions. The films used for strain, texture, and roughness analysis were of approximately 100 nm thickness. The analysis was carried out on samples prepared in four different runs: resputtering setup for (a)+(b) with = 0.32 and = 0.32; conventional deposition for samples (c)+(e) (one run) and (d).

Increasing the number of collisions (i.e., total pressure) should lead to a decreasing flux of fast particles. Therefore, sputter etching of the directly deposited film should decrease as well, and hence an increase of the deposition rate is observed. The increased thermalization of the sputtered particles can be seen directly from the increase of the indirect deposition rate without backing microscope slides. In this case, the zinc atoms can reach the substrate by diffusion only, so that with increasing scattering, the deposition rate also increases. For sufficiently high collision numbers, the flux of energetic particles, and therefore sputtering of the growing film facing the target, should become negligible. Hence, the difference in the deposition rates between the indirectly deposited films (i.e., with and without the microscope slides acting as additional zinc oxide source) should also vanish. This is observed for more than 0.5 collisions and, consequently, with no resputtering occurring, the direct deposition rate drops according to the Keller-Simmons law.

The impact of energetic particles does not only lead to changes in the deposition rates, but also has a pronounced influence on the properties of the directly deposited films. The film texture, as represented by the full width at half maximum in the XRD rocking curve of the most prominent (0002) peak *(Fig. 2c)*, deteriorates significantly for more than 0.5 collisions. This can be explained by assuming that resputtering is selective, and c-axis-oriented grains are less rapidly etched than slightly tilted grains. Therefore, misaligned grains would only be deposited if their deposition rate is higher than the etch rate. At this rate, a step-like behavior is evident as shown in *Fig. 2c*.

Furthermore, bombardment of growing films with ions can lead to significant stress levels, which is also observed here for low numbers of collisions [9]. Instead of stress σ, the strain ε, which is proportional to the stress ε is shown *(Fig. 2d)*, since this value can be determined directly by XRD. While above 0.5 collisions the films are almost stress free, for lower values, the stress increases smoothly with the flux of energetic particles, corresponding to low numbers of collisions. The importance of fast particles for the development of stress can also be seen from the films grown on the silicon substrates. As they were facing away from the target, they could not be reached by energetic particles. As a consequence, by XRD measurements, no stress was observed in any of these samples, no matter what the pressure was during deposition.

In addition to stress and grain orientation, the film roughness of the directly deposited samples is strongly influenced by the number of collisions. For low values, smooth films are produced. Increasing the collision number above 0.5 leads to increasingly rough films *(Fig. 2e)*. The roughness varies smoothly with the collision number, as does the stress. The texture on contrast shows a step-like dependence. This different behavior can be exploited to produce films with tailor-made properties. In particular, close to the transition around 0.5 collisions, a variation in the film texture only leads to marginal changes in stress and roughness.

Acknowledgement

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