Preferred Orientation and Anisotropic Growth in Polycrystalline ZnO:Al Films Prepared by Magnetron Sputtering

Frank FENSKE, Burkhardt SELLE and Mario BIRKHOLZ[1,*]

Hahn-Meitner-Institut, Silizium Photovoltaik, Kekuléstr. 5, 12489 Berlin, Germany
[1]*Fraunhofer Institut für Schicht- und Oberflächentechnik, Bienroder Weg 54 E, 38108 Braunschweig, Germany*

A thorough growth study of thin polycrystalline ZnO:Al samples prepared by DC magnetron sputtering is presented. The atomic areal density as a function of deposition time t was determined by Rutherford backscattering (RBS), from which a growth rate $G(t)$ can be defined. It was found, that in the initial stages of film growth $G(t)$ increases with increasing deposition time up to a thickness of about 300 nm, although the process conditions were kept constant. In addition, the preferred orientation of each sample, as characterized by a $\langle 00.l \rangle$ fiber texture, was quantified by evaluating the texture index J for each sample. The course of $J(t)$ was identified to concomitantly increase with $G(t)$. The variation of both, growth rate and preferred orientation, with deposition time is interpreted to be caused by an anisotropic growth velocity of ZnO grains. It seems that such a close correlation between growth rate and texture has not been observed so far. [DOI: 10.1143/JJAP.44.L662]

Thin films of doped and undoped ZnO are currently under intense investigation and development for optoelectronic and energy conversion applications. For instance, the low electrical resistivity in combination with its optical transparency makes ZnO:Al a highly attractive material for thin-film transistors in future liquid-crystal displays as well as for solar cells. The growth of polycrystalline ZnO and ZnO:Al films was found for a large variety of deposition techniques to be associated with the evolution of preferred orientation of crystallites[1–9] which is also called texture (both notions will be used interchangeably in the following). In most studies a pronounced $\langle 00.l \rangle$ fiber texture could be revealed with the majority of crystallites having their crystallographic c axis directed normal to the substrate plane. Moreover, the effect turned out to be highly relevant to film functionality, since it was shown that the increase of preferred orientation is accompanied by an improvement of electronic properties as indicated by a decrease in resistivity, for a recent study see ref. 9. Rather low resistivity values of only a factor of about 200 distinct from metallic copper were realized for thin ZnO:Al films with a nearly perfect alignment of individual crystals.[8] Therefore, a thorough understanding of the crystallographic film growth and the texture evolution is a highly relevant issue for the processing of thin ZnO:Al films with optimized optoelectronic properties. It will be shown in this letter that in the initial stages the increase of texture in thin magnetron-sputtered ZnO:Al films is accompanied by an increase in growth rate. To our knowledge, this is the first time that such an effect is reported and we interpret it as being caused by an anisotropic growth rate.

Fiber textures are a typical phenomenon observed in the growth of polycrystalline thin films, not only for ZnO but also for a variety of materials, *e.g.*, thin Si films for semiconductor applications[10,11] or nitride compounds for wear protection and diffusion barriers.[12–14] Processes, which dominate the texture evolution are precursor sticking probability, adatom surface diffusion, interaction of energetic particles with the surface of the growing film (creation of damage, re-sputtering) and grain growth. Theoretical models to account for it rely on (i) anisotropic surface diffusion and surface energy,[15,16] (ii) re-crystallization effects in the bulk of the film and residual stresses associated with a volume-proportional elastic energy and (iii) ion impact effects. A recent synchrotron-radiation-based study on thin TiN films revealed the evolution of the $\langle 111 \rangle$ texture as a re-crystallization texture.[14] The ion-impact-related models are focussed on the influence of plasma or ion beams on the growing film that may cause texturing due to a selection of grain orientations by easy-channeling directions,[17,18] on differential damage and subsequent re-crystallization,[19] on preferential etching,[11] or on plastic deformation.[20] Texture also plays an important role in the structure zone model,[21,22] especially in growth zone T, which is restricted to deposition temperatures between 20 and 40% of the melting temperature.[23] In this zone the film morphology is characterized by an increase of grain size and texture with increasing film thickness. It should be emphasized that the texture evolution in various materials systems is still controversially discussed and for many of them no final consensus has been achieved yet. The status of the discussion has recently been reviewed by Kajikawa *et al.* for the case of reactively sputter-deposited nitrides.[24]

The thin ZnO:Al films presented in this study were prepared by reactive dc magnetron sputtering from a metallic alloy target containing 2 wt% Al[9] without intentionally heating the substrate. An average growth rate was estimated in a preliminary deposition experiment by measuring the film thickness d with a profilometer. A series of eight samples was prepared by setting the appropriate deposition time to obtain ZnO:Al films of an intended thickness between $d_1 \approx 25$ and $d_8 \approx 500$ nm. No significant heating of the substrates was observed during the deposition runs. Rutherford backscattering (RBS) spectra were recorded at the Tandetron accelerator JULIA of the University Jena using 1.4 MeV ^{4}He ions. From these measurements the atomic areal density N_A (with the units atoms/cm^2) of the ZnO films was determined, which is the total number of Zn and O atoms per unit area in the deposited layer.

In order to characterize the growth of thin films it is

*Present address: ihp-microelectronics, Im Technologiepark 25, D-15236 Frankfurt (Oder), Germany.

intriguing to compare the total atomic areal density N_A measured by RBS with a usual profilometer measurement of the film thickness d. The first gives the real quantity of the deposited material. The latter represents a pure geometrical quantity. The relation between both values is given by $N_A = N \times d$, where N represents the atomic volume density. The usage of N_A instead of a thickness d has the advantage that no assumptions on the microstructure of the polycrystalline films have to be made. It is well known that thin films typically exhibit networks of voids and microcavities causing a deviation of the film density N from the value of the bulk material. It is thus more appropriate to define the growing film by a growth rate, which corresponds to the real number of deposited atoms.

$$G(t) = dN_A/dt = N \times dd/dt + d \times dN/dt \qquad (1)$$

Usually the growth rate is defined by purely geometric data as dd/dt neglecting changes of film density N during the growth. A second advantage of using N_A is the high precision that can be obtained by RBS-analysis. Even for very thin films the error can be reduced to less than 1% by improving the counting statistics. Such a high precision cannot be obtained by mechanical profilometers, measuring the absolute film thickness. Apart from that profilometry may give erroneous results due to surface and interface roughness. It is concluded that all misleading morphological features are avoided by simply measuring N_A.

In our experiments we obtained the growth rates by this procedure. They are plotted in Fig. 1. It can be deduced from the plot that the growth rate increases with time and saturates after the film has reached a thickness of a few hundred nm. The increase amounts to about 36% from the lowest to the final value. It is concluded that the prepared ZnO:Al films exhibit a non-linear increase of growth rate G versus deposition time.

The structural properties of the samples were investigated by X-ray diffraction procedures. All thin films showed the Bragg reflections of wurtzite-structure ZnO (ICDD card

number 36-1451) when investigated in the symmetric $\theta/2\theta$ scanning mode. The texture analysis was performed with a highly sensitive area detector which enables to determine complete pole figures with only three ψ tilts of the sample.[9] Furthermore, even for the thinnest sample a data collection with sufficient signal-to-noise ratio was possible in a short time of only a few minutes due to the high degree of parallel counting of scattering events from many different crystallites. Experimental pole figures were analyzed in the framework of Bunge's texture formalism.[25] The samples were all found to exhibit a pronounced $\langle 00.l \rangle$ fiber texture that increased with increasing film thickness. The analysis yielded a set of C_l^μ coefficients to describe the orientation distribution function (ODF) of the ZnO grains, for further details see ref. 9. From the C_l^μ coefficients the texture index J was derived according to $J = (4\pi)^{-1} \Sigma_{l,\mu} (C_l^\mu)^2$, which is a measure of the texture sharpness.

The values of J for each sample have also been included in Fig. 1. The texture index $J(t)$ as a function of deposition time can be seen to increase similarly to the growth rate $G(t)$. We conclude that both the degree of texture and growth rate have concomitantly increased. The small deviations in the course of $G(t)$ and $J(t)$ in Fig. 1 do not contradict such an approach, but may be understood from the fact that the information stems from the different sample regions: whereas the growth rate G is governed by the surfaces of the topmost layer, the texture index J monitors the bulk of the sample, since ZnO grains from all depths contribute to the evaluated Bragg reflections.

The variation of the film's growth rate during the process appeared an unexpected result, because the deposition conditions were kept constant varying only the deposition time. We therefore checked very carefully the experimental conditions to exclude instrumental effects possibly responsible for it. Our reactive sputter system was especially designed to realize a stable pressure over the whole range of reactive gas flows. The well-known hysteresis effect of reactive gas partial pressure was overcome by choosing an appropriate high vacuum pumping speed as was already outlined in ref. 26. The usage of the voltage mode of the plasma generator served as a further stabilizing factor. This mode makes use of a positive feedback mechanism and prevents target poisoning.[27] Because of the measures taken we are convinced that the obtained growth rate change with deposition time is a significant effect of the growth process.

It shall finally be discussed the possible interpretations of this interesting result. We will interpret the experimental data by assuming that the increase in film growth rate G and in preferred grain orientation are correlated. This approach is corroborated by investigations of ZnO single crystals that were prepared by the hydrothermal synthesis technique.[28,29] In these works the growth rates were found to take maximum values along the $\langle 00.l \rangle$ direction, associated with a prismatic growth habit of ZnO crystallites. Of course, one must not transfer the results of these experiments directly to the magnetron sputtering process, because the reaction conditions in both preparation procedures differ substantially. The decisive point, however, is the pronounced anisotropic growth rate, i.e., the difference in growth rate between c axis direction and those in the basal plane. This may be caused by the energetics of the hexagonal crystallo-
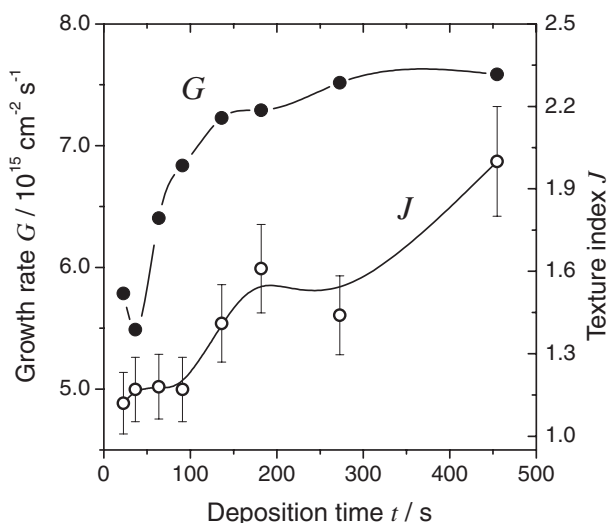

Fig. 1. Growth rate G derived from atomic areal density measurements (left ordinate) and texture index J (right ordinate) for a set of ZnO:Al samples as a function of deposition time t. Growth rate G and texture index J are seen to increase concomitantly.

graphic structure of ZnO, which is an intrinsic property. We interpret the concomitant increase in G and J as corroboration that anisotropic growth rates also occur by ZnO grains in thin film growth. We observed that the concentration of preferentially oriented crystallites at the surface will increase with deposition time. Consequently, the growth rate increases. We emphasize that the known mechanism for texture evolution might also be active during the growth of thin ZnO:Al films—independent of the above considerations.

In conclusion, we have presented experimental results on the textured growth of magnetron-sputtered ZnO:Al films. Characterizing the film growth rate by the highly accurate atomic areal density from RBS-measurements and evaluating X-ray diffraction pole figures we observed a concomitant increase of $\langle 00.l \rangle$ preferred orientation and growth rate. These results are interpreted in the framework of an anisotropic ZnO grain growth, which predicts the density of $\langle 00.l \rangle$ crystallites on the surface of the growing film to increase with increasing thickness. This new experimental result should be helpful in the optimization of fully fiber-textured ZnO:Al films.

1) N. Fujimura, T. Nishihara, S. Goto, J. Xu and T. Ito: J. Cryst. Growth **130** (1993) 269.
2) K. Ellmer: J. Phys. D **33** (2000) R17.
3) S. V. Prasad, S. D. Walck and J. S. Zabinski: Thin Solid Films **360** (2000) 107.
4) J. H. Choi, H. Tabata and T. Kawai: J. Cryst. Growth **226** (2001) 493.
5) X. Wang, S. Yang, X. Yang, D. Liu, Y. Zhang, J. Wang, J. Yin, D. Liu, H. C. Ong and G. Du: J. Cryst. Growth **243** (2002) 13.
6) K. T. R. Reddy, T. B. S. Reddy, I. Forbes and R. W. Miles: Surf. Coat. Technol. **151–152** (2002) 110.
7) B. J. Lokhande, P. S. Patil and M. D. Uplane: Mater. Lett. **57** (2002) 573.
8) X. Jiang, C. L. Jia and B. Szyska: Appl. Phys. Lett. **80** (2002) 3090.
9) M. Birkholz, B. Selle, F. Fenske and W. Fuhs: Phys. Rev. B **68** (2003) 205414.
10) R. Bisaro, J. Maraino, N. Proust and K. Zellama: J. Appl. Phys. **59** (1986) 1167.
11) M. Birkholz, E. Conrad and W. Fuhs: Jpn. J. Appl. Phys. **40** (2001) 4176.
12) F. Adibi, I. Petrov, J. E. Greene, L. Hultman and J.-E. Sundgren: J. Appl. Phys. **73** (1993) 8580.
13) C.-S. Shin, D. Gall, Y.-W. Kim, N. Hellgren, I. Petrov and E. Greene: J. Appl. Phys. **92** (2002) 5084.
14) N. Schell, J. Bottiger, W. Matz and J. Chevallier: Nucl. Instrum. Methods Phys. Res. B **199** (2003) 133.
15) A. van der Drift: Philips Res. Rep. **22** (1967) 267.
16) G. Knuyt, C. Quaeyhaegens, J. D'Haen and L. M. Stals: Phys. Status Solidi B **195** (1996) 179.
17) R. M. Bradley, J. M. E. Harper and D. A. Smith: J. Appl. Phys. **60** (1986) 4160.
18) B. Rauschenbach and K. Helming: Nucl. Instrum. Methods Phys. Res. B **42** (1989) 216.
19) L. Dong and D. J. Srolovitz: Appl. Phys. Lett. **75** (1999) 584.
20) M. Birkholz, C. Genzel and T. Jung: to be published in J. Appl. Phys. **96** (2004).
21) B. A. Movchan and A. V. Demchishin: Phys. Met. Metallogr. **28** (1969) 83.
22) J. A. Thornton: Annu. Rev. Mater. Sci. **7** (1977) 239.
23) P. B. Barna and M. Adamik: Thin Solid Films **317** (1998) 27.
24) Y. Kajikawa, S. Noda and H. Komiyama: J. Vac. Sci. Technol. A **21** (2003) 1943.
25) H.-J. Bunge: *Texture Analysis in Materials Science* (Butterworth, London, 1982).
26) S. Kadlec, J. Musil and J. Vyskocil: Vacuum **37** (1987) 729.
27) J. Affinito and R. R. Parsons: J. Vac. Sci. Technol. A **2** (1984) 1275.
28) R. A. Laudise and A. A. Ballman: J. Phys. Chem. **64** (1960) 688.
29) W.-J. Li, E.-W. Shi, W.-Z. Zhong and Z.-W. Yin: J. Cryst. Growth **203** (1999) 186.