Modified Thornton model for magnetron sputtered zinc oxide: film structure and etching behaviour

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Abstract

ZnO:Al films were prepared on glass substrates with different sputter techniques from ceramic ZnO:Al_2O_3 target as well as metallic Zn:Al targets using a wide range of deposition parameters. Independent of the sputter technique, sputter pressure and substrate temperature were found to have a major influence on the electrical and structural properties of the ZnO:Al films. With increasing deposition pressure we observed a strong decrease in carrier mobility and also an increase of the etching rate. The surface morphology obtained after etching of RF sputtered ZnO:Al systematically changes from crater-like to hill-like surface appearance with increasing pressure. The correlation of sputter parameters, film growth and structural properties is discussed in terms of a modified Thornton model.

1. Introduction

Magnetron sputtered ZnO films are applied in a variety of thin film devices. For example ZnO films are the standard front TCO contact in CIS thin film solar cells [1] and are investigated as an alternative TCO material for silicon thin film solar cells [2,3]. However, for the latter application a textured TCO surface is required to provide an effective light trapping. Such an adapted surface texture can be realised for sputtered ZnO:Al films by the combination of optimised sputter process conditions and a post deposition wet chemical etching step in diluted acids or bases. The applied sputter process parameters and sputter techniques control the ZnO film structure. Depending on the structural film properties different surface textures with respect to the root mean square roughness as well as the feature size and shape develop during the etching process. Besides the technical application of the etching technique for the preparation of TCO coated glass substrates for silicon thin film solar cells a study of the etching behaviour gives valuable information about the structural properties of sputtered ZnO films in general.

This paper addresses the relationship between sputter deposition parameters, film growth and film structure and the surface structure, which develops after wet chemical etching in dilute hydrochloric acid (HCl). The first part briefly reviews the relationship between the process parameters deposition pressure as well as substrate temperature and the electrical film properties for different deposition techniques. Systematic High Resolution Scanning Electron Microscopy (HRSEM) and Atomic Force Microscopy (AFM) studies were performed to characterise the surface textures obtained after etching. These results are shown for RF sputtered ZnO films on glass. Finally, we suggest a modified Thornton model for these ZnO:Al films to describe the presented experimental results.

2. Experimental

ZnO:Al films were prepared on glass substrates with different sputter techniques (RF, DC and MF, i.e. mid frequency) from ceramic ZnO:Al_2O_3 targets as well as metallic Zn:Al targets using a wide range of deposition parameters. The RF and DC films were deposited in static mode from 6” circular magnetron cathodes. In the case of reactive DC sputtering the O_2-flux was manually adjusted. The MF films were deposited in an inline sputter system (VISS 300, supplied by Ardenne Anlagentechnik) with linear double magnetron cathodes using Zn:Al metallic targets. These depositions were made in dynamic mode. Process stabilization was done using plasma emission monitoring. The electrical properties were obtained by Hall measurements. To determine differences in film structure, HRSEM on cross-sections and AFM-characterisation of the surface morphology obtained after wet chemical etching was performed.

3. Results

3.1 Sputtering of highly conductive and transparent ZnO:Al

In previous work, we reported that the sputter parameters deposition pressure and substrate temperature T_S were found to have a major influence on the ZnO:Al material properties of RF and reactively DC sputtered films [4-7]. This study is now extended to ZnO:Al films deposited with DC from ceramic targets as well as to MF sputtering from metallic targets in dynamic mode (see [8] for more details). Fig. 1 shows the pressure dependence of the resistivity of these sputtered ZnO:Al films prepared with different techniques at substrate temperatures T_S of 150 °C and 270 °C. Resistivities below $5x10^{-4}$ Ωcm were achieved with all sputter techniques at low sputter pressures. A strong increase in resistivity is observed if a certain sputter pressure is exceeded. For RF sputtered ZnO films the range of deposition pressure yielding highly conductive films is rather small at low substrate temperatures and improves with increasing T_S. For DC sputtered films, the transition from low-ohmic to high-ohmic films occurs at higher pressures compared to the RF case,

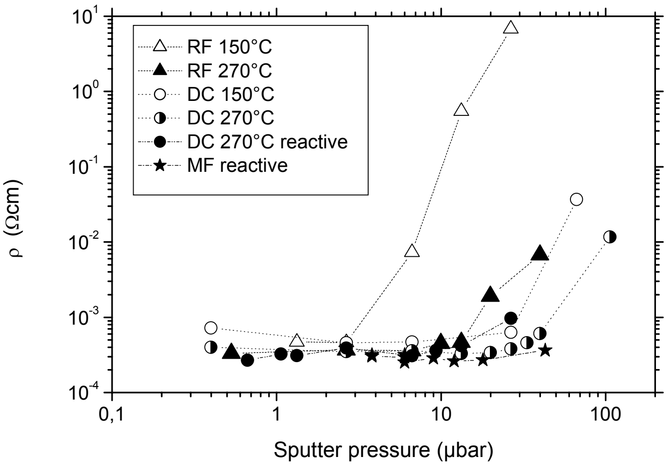

Fig. 1. Pressure dependence of the resistivity for RF and DC ZnO:Al films, sputtered at T_S = 150 °C and 270 °C. All RF and DC sputtered films are deposited in static mode from ceramic $ZnO:Al_2O_3$ targets or metallic Zn:Al target adding O_2. For comparison data of MF films reactively sputtered in dynamic mode from Zn:Al targets have been included.

yields highly conductive films even at deposition pressures up to 45 µbar. A detailed study of the electrical properties is presented in a related paper [8]. One should note that the increase in resistivity results from a strong decrease in carrier mobility if a certain deposition pressure is exceeded. Moreover, all films, which show low resistivity, exhibit similar high transparency. However, in spite of their similar opto-electrical properties the etching behaviour is quite different. This will be discussed in more detail in the next sections.

3.2 Sputter deposition parameters and surface morphology

First information about the different structural material properties of sputtered ZnO:Al films can be gained from measuring the etching rate. This was done using a Dektak surface profiler. Since the films develop surface roughnesses in the range of 10 to 150 nm some measurement errors have to be taken into account. The etching rates for DC and RF sputtered films are shown in Fig. 2 as a function of deposition pressure. Below 10 µbar the etching rate is almost constant and suddenly increases for deposition pressures above 10 µbar. The films are more easily attacked by the etching fluid (0.5 % HCl). This increase roughly correlates with a decrease in carrier mobility.

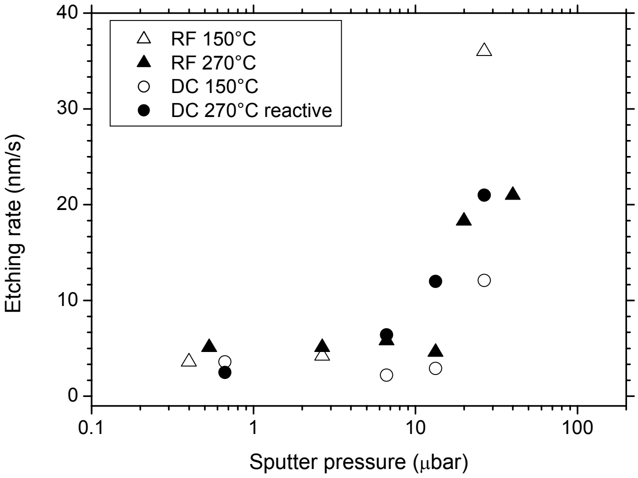

Fig. 2. Pressure dependence of the etching rate of RF and DC ZnO:Al films sputtered at T_S = 150 °C and 270 °C.

HRSEM- and AFM measurements reveal systematic correlations between the deposition parameters and the etching behaviour. In the following we focus on the results obtained for the ZnO:Al films which have been RF sputtered at T_S = 270 °C. Fig. 3 shows the influence of the sputter pressure on the surface morphology obtained after 15 s of etching in 0.5 % HCl. This series is also included in Figs. 1 and 2. For a quantitative analysis surface plots, cross-section profiles and depth distributions have been generated from AFM measurements. The depth distribution is calculated from the deviation of surface points with respect to the "mean surface level". Negative values are defined as height and positive values as depth. Depending on the deposition conditions and the resulting film structure of the initial film, a characteristic change of the surface morphology is observed if a sputter pressure of 13 µbar is exceeded. For sputter pressures below 13 µbar, statistical spread craters of irregular lateral size and depth arise at the surface upon etching. Exceeding the transition pressure leads to a regular hill-like surface structure with significantly smaller feature size. The rough surface appearance of this film is not created by craters but by the convex shape of grains remaining on the surface after the etching step. The regular surface structure leads to an almost Gaussian depth distribution with slightly higher contribution on the height side (negative values).

In contrast, the craterlike structure obtained for films sputtered at low pressures leads to an unsymmetrical depth distribution with emphasis on the depth side (positive values). Note that although the films deposited in the low pressure regime exhibit similar electrical and optical properties as well as comparable low etching rates (see Fig. 2), differences in the

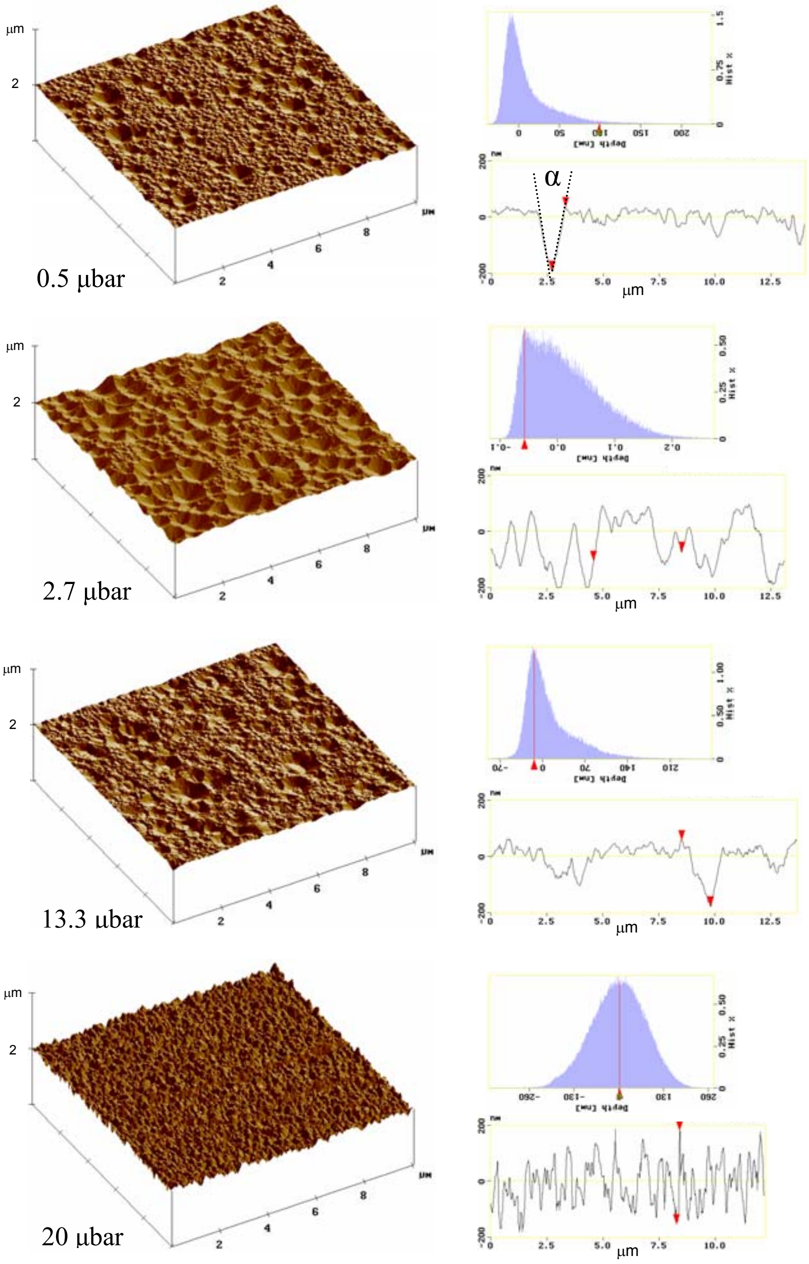

Fig. 3. Surface morphology, cross-section profiles and depth distribution of RF sputtered ZnO:Al films (T_S = 270 °C) on glass obtained after 15 s of etching in 0.5 % HCl. The data were generated from the AFM measurements.

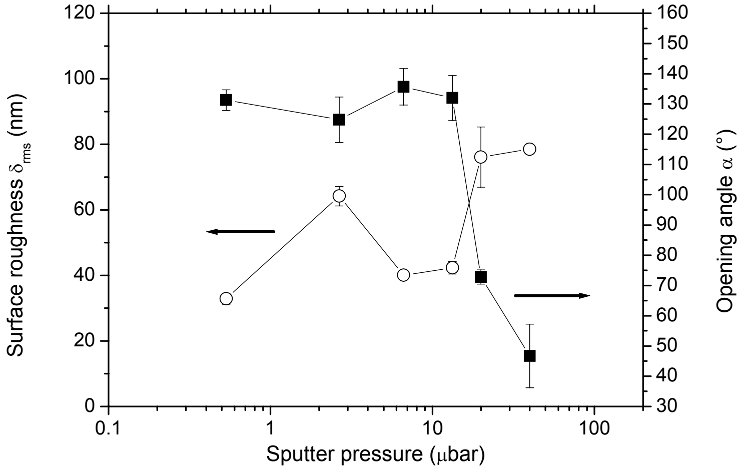

Fig. 4. Surface features (opening angle and root mean square roughness calculated from AFM data, see text) of RF sputtered ZnO:Al films (T_S = 270 °C) shown in Fig. 3.

the surface morphology after etching are clearly shown by the depth distributions and AFM profiles.

The transition in surface morphology with increasing sputter pressure of the initial film is also reflected in the results from a quantitative AFM analysis of the surface features. Fig. 4 shows the root mean square roughness and the opening angles. The latter have been derived from the AFM cross-section plots as indicated in Fig. 3. While the surface roughness shows some scattering, the opening angles are characteristic for the different surface morphologies observed. Opening angles of 135° are typical for the crater structures obtained at low pressures while the hill like surfaces show opening angles of ~70° down to 47°.

Similar results were obtained for reactively DC sputtered films [6] and also for films prepared on Ag coated glass substrates [7]. For static sputtering conditions we observe similar trends for a variation of the deposition pressure. However, the transition between different structures depends on the deposition temperature, substrate type, sputtering technique or even position on the substrate. For dynamic sputtering techniques additional effects have to be considered. HRSEM studies of MF sputtered and texture-etched ZnO films are reported in [9].

4. Structural properties and surface morphology – modified Thornton model

For the further discussion we first briefly summarise the main experimental findings for RF sputtered ZnO:Al films. With increasing deposition pressure we observed a strong decrease in carrier mobility and also an increase of the etching rate. The surface morphology obtained after etching systematically changes from crater-like to hill-like surface appearance with increasing pressure. This is reflected by a decrease of the opening angle from an almost constant value of 135° down to ~47° for craters and hills, respectively. In general the initial film structure, which depends on the sputter process parameters controls the surface texture obtained after etching. This correlation of sputter parameters, film growth and structural properties will be discussed in terms of a modified Thornton model which is shown in Fig. 5.

Originally, the Thornton model was developed to describe the growth of sputtered metals in dependence of two parameters, substrate temperature and sputter pressure [10,11]. In literature, this model is very often applied to describe the growth of sputtered films from different materials (e.g. [12,13]). Since there are some fundamental differences between TCO material and metals, we suggest some modifications of the original Thornton model to make it applicable to RF sputtered ZnO:Al films on glass substrates. First, we have to take into account that ZnO exhibits a distinctly higher melting point (1975 °C) than typical metals. Therefore, the ratio of substrate temperature T_S and melting temperature T_M considered in the Thornton model becomes very small for the typical range of T_S (80-400 °C) applied during sputtering of ZnO:Al. Thus, in the modified Thornton model the substrate temperature is taken into account instead of the normalised value T_S/T_M. Furthermore, our experimental results underline that for sputtered ZnO:Al, the substrate temperature plays a less important role than the sputter pressure. Therefore, the pressure axis has been exchanged with the substrate temperature axis. Note that due to the high melting point of ZnO, Zone 3 of the original Thornton model is not present in the applied temperature range. Recrystallisation, which is typical for Zone 3, appears at much higher substrate temperatures. The general statement of the original Thornton model is maintained: increasing the substrate temperature and reducing the sputter pressure leads to a more compact and dense film structure.

The bandwidth of variations in bulk and surface structure is demonstrated by the example of three representative ZnO:Al samples, which have been deposited in three different deposition regimes characterised by typical sputter pressure and substrate temperature. Sample A was deposited with high sputter pressure of 40 μbar and without intentional heating, while sample B was deposited at medium pressure of 2.7 μbar and 150 °C substrate temperature. Sample C was sputtered with the lowest pressure of 0.4 μbar and $T_S = 270$ °C. To obtain information about the bulk structure and the surface morphology, HRSEM was performed on the cross-sections of the films. Fig. 5 shows the micrographs of Type A, B and C before and after etching. For Type A ZnO, the grains extend from the substrate to the top of the film.

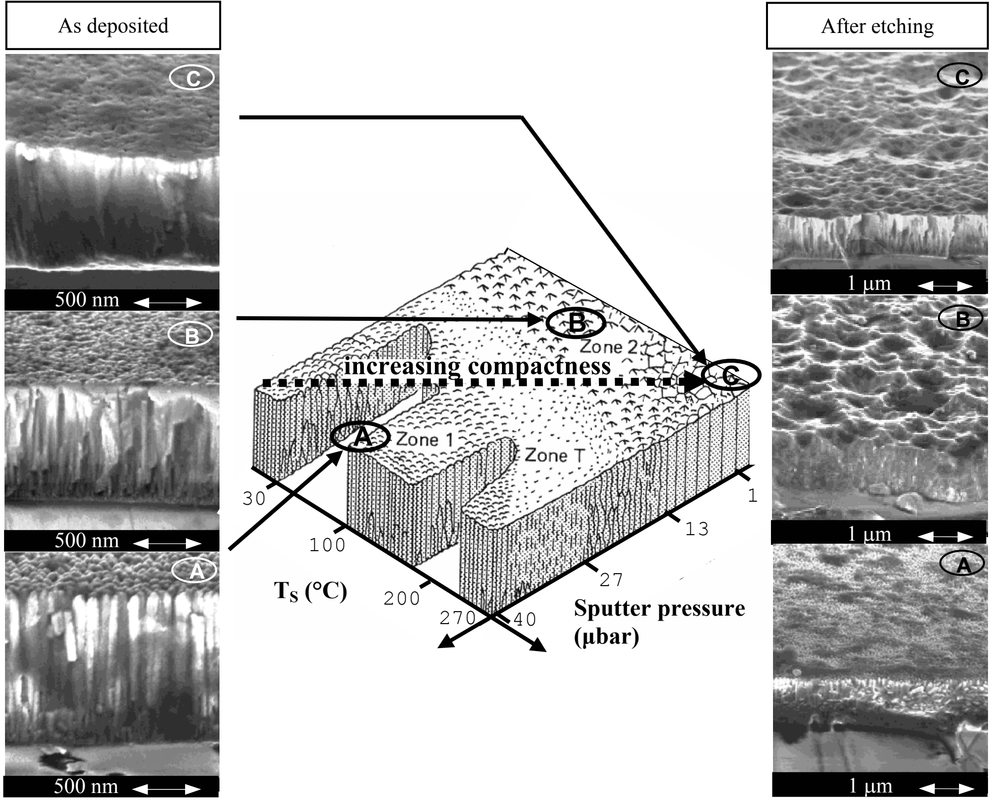

Fig. 5. The modified Thornton model describes the correlation between sputter parameters (sputter pressure and substrate temperature), structural film properties and etching behaviour of RF sputtered ZnO:Al films on glass substrates. The pressure series at T_S = 270 °C shows the systematic influence of the sputter pressure on the surface morphology after etching (see text).

Their c-axis is predominantly oriented parallel to the substrate normal and a fibre texture could be established by additional XRD measurements [6]. Crystallites of Type B and C material are also highly oriented, but their c-axis exhibits a small inclination with respect to the substrate normal**.** Single crystallites can be easily distinguished in Type A ZnO by the HRSEM cross-sections, however, this is more difficult for Type B and C films indicating an increasingly compact and denser structure for the transition from Type A to Type C material.

After 20 seconds etching in diluted HCl structural differences between the three samples are more obvious (see Fig. 5 right side). At the first glance entirely different surface morphologies can be observed. Since Type A material is homogeneously etched with high rate, chemical etching has no impact on the surface morphology but only reduces the film thickness. Type B and C ZnO are anisotropically etched leading to a crater-like surface structure. The regular, rough morphology of the Type B film indicates a homogeneous attack of the complete initial surface by the etchant. Due to its extremely compact film structure Type C material is only partly etched leading to a few randomly spread big craters on the film surface.

Sample A can be identified as a Zone 1 film with typical low compactness. The more compact film structure of sample B and the highly dense film structure of sample C can be found in the middle and at the edge of Zone 2, respectively. The presented modified Thornton model correlates the deposition parameters (sputter pressure and substrate temperature) of RF sputtered ZnO:Al on glass with the compactness of the film structure. Highly compact polycrystalline ZnO:Al films exhibit to an increasing extent the properties of single crystalline ZnO. This is reflected in increased hall mobility due to an improved film structure with less structural defects [14-16] and by a higher mechanical and chemical stability for example during tempering in oxygen atmosphere [17]. The highly dense film structure reduces the physisorption of oxygen at grain boundaries. A compact film structure also prohibits the penetration of fluid etchants. Consequently, the highly oriented ZnO:Al films are only attacked by the etchant from one crystallite site. This leads to an anisotropic etching process, which produces the observed crater structure. While the films prepared in Zone 1 show inferior electrical properties and only small features, ZnO:Al films of Zone 2 with high and medium compactness provide both, high conductivity and larger surface features after etching. Especially Type B films shown in Fig. 5 exhibit a regular crater structure with opening angles of 120° and feature sizes up to 1μm. Such surface structures are an example for a morphology, which leads to an effective light trapping in silicon thin film solar cells.

6. Conclusions

A comprehensive material study on sputtered ZnO:Al films was performed focusing on the relationship between sputter process parameters, structural properties and the surface morphology obtained after etching in diluted HCl. Irrespective of the sputter technique, the deposition pressure and substrate temperature were found to have the major influence on the ZnO:Al material properties. With increasing deposition pressure we observed a strong decrease in carrier mobility and an increase of the etching rate for differently sputtered films. The influence of film structure on the surface morphology obtained after wet chemical etching was systematically studied by HRSEM and AFM for ZnO:Al films which were RF sputtered at T_S = 270 °C. With increasing sputter pressure a transition from a crater-like surface structure with a characteristic opening angle $\alpha = 135°$ to a hill-like surface structure with α as low as 47° is observed. Films prepared at low T_S and high deposition pressure are homogeneously etched without any surface texturing effect due to their low compactness. Based on these results a modified Thornton model was developed which correlates the deposition parameters sputter pressure and substrate temperature of RF sputtered ZnO:Al on glass with the compactness of the films.

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