ABSTRACT: Doped Zinc Oxide thin films were grown by ion beam assisted sputter deposition (IBAD) technique at room temperature. Our new sputtering chamber allows us to operate with a 2wt.% Ga doped ZnO-target and an inverse ion beam etching tool, simultaneously. Several films were grown by varying the ion gun power of the ion beam etcher. With increasing the ion source power the resistivity increased from $11 \times 10^{-4}$ $\Omega$cm to $33 \times 10^{-4}$ $\Omega$cm. However, x-ray analysis revealed that the crystalline quality of the grown ZnO:Ga thin films could be improved if the power of the ion source was set to 50W. The c-lattice parameter increased with increasing ion gun power, indicating compressive stress in the films. In parallel, a similar tool was used to prepare IBAD ZnO buffer layers and then thicken the films by reactive DC sputtering. These films are known to behave similar even without ion bombardment during bulk material deposition. After etching in diluted HCl (0.5%) for 30 s the ZnO films revealed a textured surface. The standardly sputtered, unbuffered films etch quite fast and reveal very small features, whereas the IBAD ZnO:Ga or buffered ZnO:Al developed large craters indicating highly compact films. A certain compactness is required to develop large craters for effective light scattering. By this method, such highly compact ZnO films can be grown even at room temperature.

Keywords: doped zinc oxide, ion beam assisted deposition, etching
Figure 1 shows the resistivity measured by four-point probe method as function of the applied ion source power. Each data point is labelled by the corresponding film thickness. The unbombarded sample (0 W) shows a resistivity of 1.1 mΩcm., but with the addition of ion bombardment resistivity increases quite linearly to 3.3 mΩcm at a maximal ion source power of 200 W.

The ZnO:Ga films exhibited mainly the (002) peak at around 34.4° and the (101) peak at 36.2° in XRD measurements in Bragg-Brentano geometry. Figure 2 shows the corresponding XRD patterns of the ZnO:Ga films grown at different ion source power. We only evaluate the (002) peak here, but the (101) peak follows similar trends. The sample without ion bombardment (black line) shows a maximum at about 34.3°. With the addition of ion bombardment at 50 W (green curve) the intensity of the diffraction signal shows a significant increase and a remarkable shift to smaller angles. Further increase of the ion power to 100 W (red line) results in a decrease of the signal intensity but it is still higher than the diffraction curve of the reference sample. At more than 100 W the intensity of the (002) reflection diminishes. The increase in the signal is an indication of improved crystalline quality compared to the unbombarded sample. The very low intensity and the broad width indicate ion damage to the crystal structure.

Figure 1: Resistivity as function of the ion source power. The numbers above the measuring points denote the ZnO:Ga thicknesses.

Now we evaluate the peak shift in more detail. Figure 3 exhibits the exact peak position (a) and calculated length of the c-axis (b) as function of ion source power. The peak position decreases linearly with increasing ion source power by more than 1°, illustrating strong compressive stress. Therefore, the c-lattice parameter increases with increasing ion gun power from 5.2 Å to 5.4 Å, which means a change in the lattice parameter of about 3.8%. In addition, at this strong ion bombardment the diffraction peak shows a shoulder on the left hand side. This is explained by splitting in two separate peaks showing that some crystallites relax to the unstrained ZnO lattice while other crystallites exhibit an even more strained lattice. The peak splitting at high ion source power is indicated by additional data (red line in Figure 3).

The unbombarded sample as well as the sample with the best crystalline structure after IBAD were etched in diluted HCl (0.5 %) for 30s. The surface structures after etching of ZnO:Ga are shown in Figure 4. The unbombarded sample in Figure 4a) (left side) shows quite small features with an RMS roughness of 45.7 nm. The etch rate of this film is 11.2 nm/s. The small, sharp-edged features and the high etch rate are typical for type I ZnO of the modified Thornton model [8, 9]. On the other hand, the surface of the IBAD grown ZnO film in Figure 4a) (right side) reveals some large craters with a lateral size of up to 1 µm surrounded by smaller ones. The etch rate of 5.8 nm/s is half as large as that of the film without additional ion bombardment. RMS roughness of the IBAD sample is 58.9 nm. However, the roughness is still limited due to the wide area that is only covered with small craters and thus quite smooth. These properties were found to be typical for type III films in the previously mentioned model [10, 11].

Further, in Figure 4b) we also demonstrate the IBAD results by AFM images of Aluminum doped ZnO thin films after etching in diluted HCl for 20 s. The different oxygen flow rates given in the graph indicate different operation points during the reactive sputtering process.

The images on the left side show standard ZnO:Al films grown at room temperature on glass substrate without additional ion bombardment while the films on the right hand side were bombarded during the initial stage of the deposition. All unbombarded films show slightly rough surfaces with small features as already seen in Figure 4a) for the ZnO:Ga films. The ion beam assisted films reveal at least partially large craters with a diameter of up to 3 µm, especially for an O₂ flow rate above 11 sccm.

Figure 2: XRD patterns for ZnO:Ga films with different ion gun bombardment power as referred to by the horizontal numbers. The vertical lines label the crystal orientations of the unstrained ZnO lattice.

Figure 3: a) Peak position of the (002) x-ray diffraction peak and b) c-axis parameter for different ion source power.

If we compare the AFM images in Figure 4 we see that surfaces with the smallest oxygen flow rate of 10.5
sccm are similar to our Ga doped surfaces in Figure 4a). These oxygen flow rates represent the least oxidic modes that are still able to grow transparent films. More oxidic conditions seem to strengthen the effect of ion bombardment during deposition.

3 DISCUSSION

The results presented above show that IBAD technique leads to significant structural and accordingly morphological changes of the ZnO films. From structural point of view one might expect a decrease in the resistivity since the improvement in crystalline structure was reported to improve electrical properties of ZnO:Al films [10]. However, in our case the resistivity increases from 1.1 mΩcm to 1.7 mΩcm. This increase in resistivity might be caused by the increase of stress in the ZnO films as indicated in figure 3.

Figure 4: AFM images of a) ZnO:Ga and b) ZnO:Al films after etching in diluted HCl (0.5%). On the left: Standard ZnO grown at room temperature. On the right: ZnO grown by ion beam assisted deposition. The numbers between the images denote the flow rate of oxygen during deposition.

Köhl et al [Fehler! Textmarke nicht definiert.] also noticed an expanding in the c-lattice parameter for the growth of IBAD ZnO:Al films accompanied by an improvement in the crystalline structure. This was attributed to atomic peening i.e. implantation of atoms by the ion bombardment.

Crater sizes with a diameter of up to 3 µm surrounded by a relatively flat surface as seen in Figure 4b) for the ZnO:Al films indicate that these types of surfaces belong to the type III material of the modified Thornton model [10,11]. These types of films are normally achieved at high substrate temperatures, proving that the additional ion bombardment during film growth leads to a similar effect as the increase in substrate temperature.

The formation of big craters after etching is an indication of increased film compactness compared to the standard ZnO:Ga sample, since the acid can only affect at crystal defects. Due to the decreased amount of attack points for the IBAD films the etching rate decreases and the films are etched anisotropically. This might be overcome by a new texturization process to regularly create large craters [12].

4 SUMMARY

Doped ZnO films were grown on glass substrates by ion beam assisted magnetron sputtering. The addition of an ion beam resulted in an improved crystalline structure as the ion source power was set to 50 W. On the other hand the resistivity increased from 1.1 mΩcm to 1.7 mΩcm at this ion source power. This effect was attributed to the strong compressive stress in the bombarded ZnO:Ga films.

AFM images of the etched samples revealed a transition to highly compact ZnO films by additional ion bombardment that is usually expected at high substrate temperatures. Compared to the standard ZnO films the etching rate for the IBAD films decreased by a factor of two illustrating an increase in compactness by ion bombardment, even if the ion bombardment was only present in the initial growth stage.

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6 REFERENCES