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The effect of perpendicular electric fields on the orientation of zinc oxide crystals during the oxidation of zinc thin films

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The effect of direct current (d.c.) electric fields on the crystal orientation of zinc oxide thin films was investigated. Evaporated zinc thin films were oxidized in air under the application of perpendicular electric fields (detached electrodes) at different temperatures. The application of positive fields at 550 °C improved the *c*-axis orientations up to 1000 V cm^{-1}. Further increase in field strength caused the *c*-axis orientations to decline to their original values (no applied field). The application of negative normal fields at 550 °C deteriorated the *c*-axis orientations up to 800 V cm^{-1}. The *c*-axis orientations improved to their original values by increasing the field strength to greater than 800 V cm^{-1}. The crystal size remained unchanged, but the surface morphology was affected by the application of the electric fields at temperatures above the melting point of zinc. No significant change in optical properties was detected for samples that were subjected to electric fields. Whenever the *c*-axis orientation improved, crystals on the film surface became rounded and a more ordered microstructure was observed. On the other hand, the deterioration of *c*-axis orientation was manifested by the increase in the number of whisker-shaped crystal needles on the surface of the ZnO thin films.

1. Introduction

The effects of an electric field (detached electrodes) on nucleation, growth and orientation of metal oxides are controversial. The complexity of taking into account all parameters influenced by an external field, such as the movements of charged cation and anion interstitials and vacancies, electrons, holes, dipoles, pair vacancy–interstitial dipoles, internal dipole interactions, induced charge, surface charge, space charge, polarization, ionic transport, diffusion, etc., during the oxidation process has made it impossible to devise any model describing the whole event. Most of the works on nucleation, growth and orientation were done experimentally on metallic deposits subjected to electric fields (attached electrodes). The results have been contradictory. Some researchers have found no relation between the growth parameters and the applied field [1–3], while others have reported some effects [4–10]. The relation between electric field (attached electrodes) and oxidation rate was first investigated by Jorgensen [11]. He found that the rate of oxidation increases with the application of an accelerating field (metal–oxide interface is positive with respect to oxide–gas interface) and decreases with the application of a retarding field. It was argued that an external or net current must flow in the oxide in order to modify the potential distribution in the oxide layer. Later [12] an opposite effect was observed experimentally. Anderson and Ritchie [13] showed that at temperatures of 390 °C and below, an applied field (attached electrode) of about 10^3 V cm^{-1} did not have an appreciable influence on the oxidation rate of zinc.

2. Experimental procedure

Substrates play an important role on the orientation of the resultant zinc oxide films. Even different types of amorphous glass substrates may produce films with different crystallographic orientations. All substrates used in this study were Pyrex glass (Corning 7059). The vacuum chamber was pumped down by means of a cryopump in conjunction with a mechanical pump. A molecular sieve trap was used to prevent mechanical pump oil backstreaming, causing organic contamination in the chamber. The vacuum system was equipped with a resistive heating evaporation source (tantalum boat). The source jacket was water cooled for long evaporation experiments. The substrate was mounted on a ceramic block (Dow Corning machinable glass–ceramic) on the end of a cantilevered stainless steel tube. Producing a homogeneous zinc layer is difficult because of the formation of islands. Further problems result from the adherence on quartz, etc. [14]. Experimentally, it was found that better and more uniform zinc films were deposited onto substrates that were sputter-cleaned by an argon glow discharge. Therefore, the sputter cleaning was routinely performed before the deposition process. Due to the

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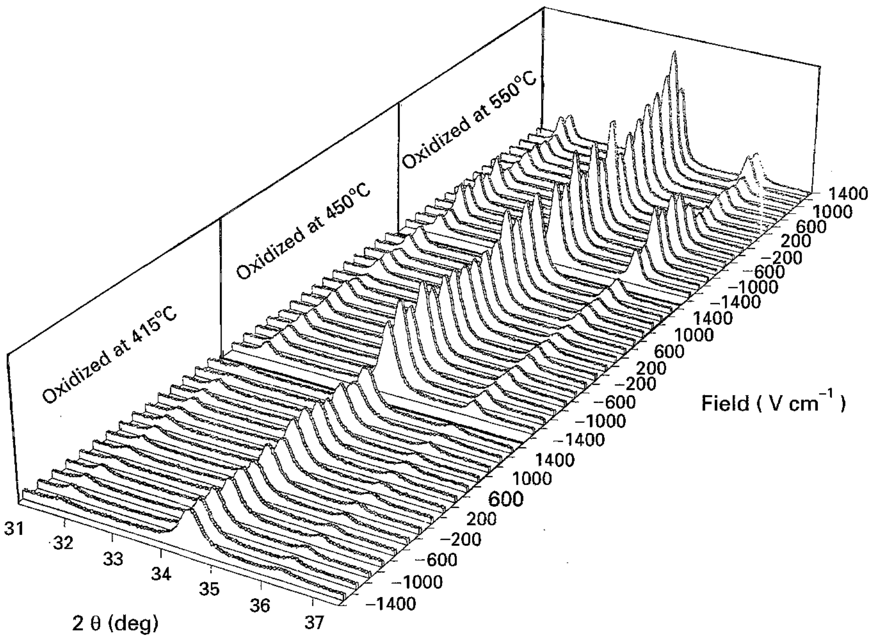

Figure 1 The X-ray spectra of samples subjected to different field strengths, oxidized at different temperatures.

fact that zinc sublimes and evaporates at the same time, control of the evaporation rate becomes very difficult. In order to minimize these undulations, a few grams of gallium was added to the charge [15]. The role of gallium is to melt (30 °C) and transfer the heat uniformly to zinc to improve the evaporation uniformity. Due to gallium's low vapour pressure it will not evaporate at the evaporation temperature of zinc. When the chamber pressure reached below 6.7×10^{-4} Pa, the zinc source was heated moderately (with a double shutter system closed, zinc vapour decimates readily) for 2 min for source outgassing and desorbsion of contaminants. The deposition rate was set to $0.5\ \mathrm{nm\,s^{-1}}$ for all samples and the entire deposition cycle process was controlled by a programmable deposition controller. To avoid oxidation of the source, the vacuum chamber was brought up to atmospheric pressure after a cool down period. Immediately after sample removal from the deposition chamber, the sample was stored in a vacuum vessel to avoid any potential surface oxidation. Subsequent oxidation of zinc was carried out in air during the application of a d.c. electric field (detached electrodes). Perpendicular fields were applied at different oxidation temperatures. Field strengths of up to $1400\ \mathrm{V\,cm^{-1}}$ in $200\ \mathrm{V\,cm^{-1}}$ increments were applied at 415, 450, and 550 °C. The field plates were a little larger than the area of the sample to avoid the field fringe effect generated at the plate edges and corners. A floated power supply provided the necessary potential difference between the field plates. A positive field is defined when the sample is positive (anode) and a negative field is defined conversely.

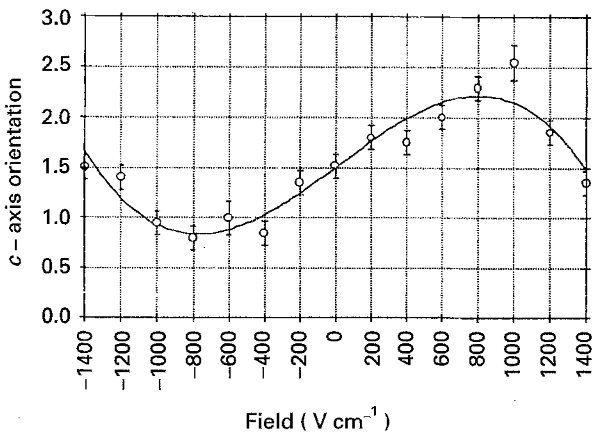

Figure 2 The c-axis orientation of samples subjected to different field strengths, oxidized at 550 °C.

3. Results

3.1. Determination of preferred orientation

Evaporated zinc samples show a very strong preferred orientation. Zinc crystallizes in a hexagonal close-packed structure. An evaporated zinc sample has a natural tendency to grow with its c-axis perpendicular to the substrate surface, i.e. crystal platelets orientate themselves parallel to the substrate surface. Oxidized zinc (ZnO) crystals also show a preferred orientation (not as strong as its zinc counterpart). Preferred orientation is determined by X-ray diffraction (XRD) data. Here, one defines the c-axis orientation as the XRD intensity ratio of the $(0\,0\,0\,2)$ diffraction peak to the sum of the $(1\,0\,\bar{1}\,1)$ and $(1\,0\,\bar{1}\,0)$ peak intensities, assuming the intensity of the strongest peak is 100 units.

3.1.1. Oxidation at 550 °C

The X-ray spectra of samples subjected to electric fields are presented in Fig. 1. The field effect on c-axis orientation is shown in Fig. 2. It can be seen that in the case of a positive field, c-axis orientation improves up to the field strength of $1000\ \mathrm{V\,cm^{-1}}$ and then it declines to its reference value. In the case of a negative field, the preferred orientation deteriorates up to 800 V cm^{-1} and then increases as the field approaches 1400 V cm^{-1}. The scanning electron microscope (SEM) micrographs of ZnO thin films for reference, + 1000 and − 600 V cm^{-1} samples are shown in Figs 3–5, respectively. It can be seen that the reference ZnO sample (no field applied) shows Redwood leaf-shaped surface morphology. The SEM micrograph of the ZnO sample produced under − 600 V cm^{-1} shows more dendrite-shaped interwoven texture with respect to the reference sample and it seems that the overall surface features are more pronounced. On the other hand, the surface morphology changes drastically when + 1000 V cm^{-1} is applied during oxidation. Here, the crystals are bigger and have rounded peripheries when compared to the reference sample.

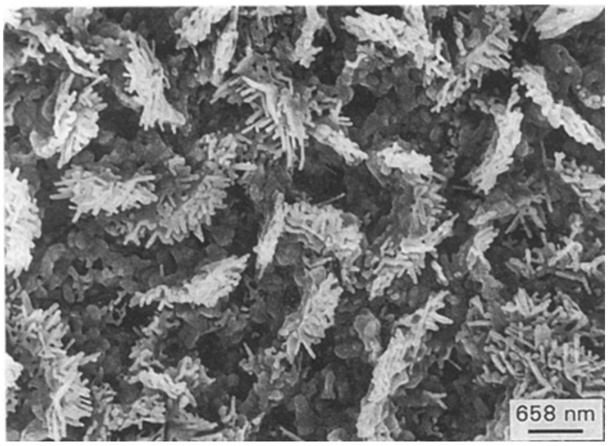

Figure 3 SEM micrograph of the sample subjected to no applied electric field, oxidized at 550 °C.

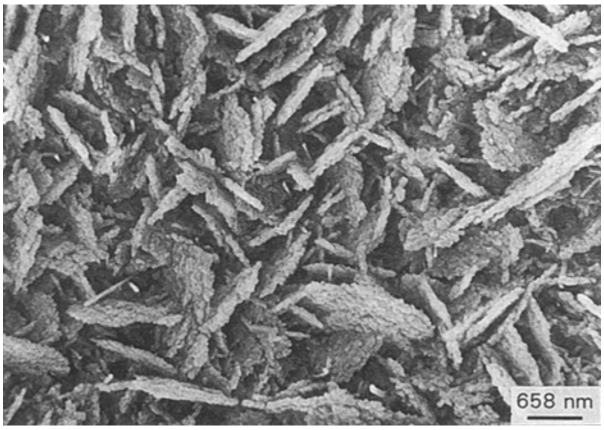

Figure 4 SEM micrograph of the sample subjected to + 1000 V cm^{-1} applied electric field, oxidized at 550 °C.

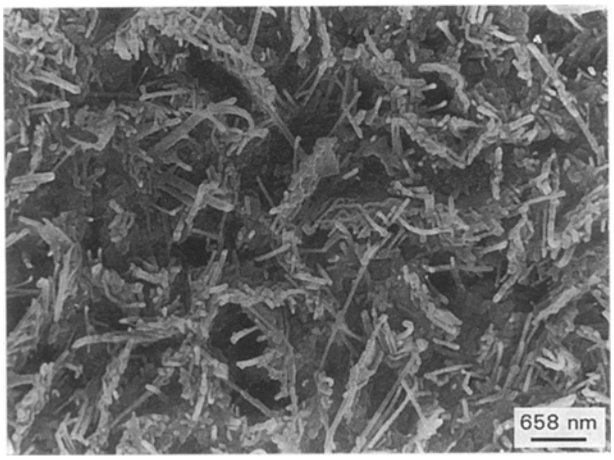

Figure 5 SEM micrograph of the sample subjected to − 600 V cm^{-1} applied electric field, oxidized at 550 °C.

3.1.2. Oxidation at 450 °C

From the X-ray spectra (Fig. 1) it can be deduced that application of negative fields does not have a significant effect on the orientation of the samples, while application of positive fields improves slightly the orientation up to 600 V cm^{-1} and then *c*-axis orientation descends to its original value. The surface feature of the ZnO sample is composed of very fine crystals (~ 70 nm). No significant differences exist between the surface morphology of ZnO samples subjected to fields and samples which were not.

3.1.3. Oxidation at 415 °C

The X-ray spectra of samples subjected to electric fields were presented in Fig. 1. It is seen that *c*-axis orientation is not affected by the application of the electric field for either polarity. Typical transmittance spectra for four applied fields and photoluminescence spectra for two excitation wavelengths of 365 and 337 nm for reference (no field applied) ZnO samples are shown in Figs 6 and 7, respectively. Product films show more than 80% transparency at wavelengths greater than 550 nm. Also, the optical band gap could be evaluated, at the wavelength where transparency approaches zero ($\lambda = \sim 380$ nm; band gap energy $E_g = 3.26$ eV). Photoluminescence spectrum for 337 nm excitation wavelength shows two emission bands, ultra violet band (peaks at 400 nm), and blue band (peaks at 470 nm). The photoluminescence spectrum for a 365 nm excitation wavelength shows a green emission (peaks at 570 nm). The surface texture of the ZnO sample is composed of very fine crystals (~ 50 nm). There appears to be no difference between the surface morphology of ZnO samples subjected to electric fields and samples which were not.

4. Discussion

It was shown that at a temperature of 415 °C, an electric field had almost no effect on the orientation of ZnO cyrstals. By increasing the oxidation temperature to 450 °C, the applied field started to show some effect. With the application of positive fields, *c*-axis orientation was enhanced, while the application of a negative field had almost no effect on crystal orientation. Increasing the oxidation temperature further to 550 °C and examining the field effect showed that the positive field improved the orientation up to 1000 V cm^{-1}, while applying a negative field deteriorated the orientation up to 800 V cm^{-1}. The same results of field effect on preferred orientations for an oxidation temperature of 550 °C were obtained at 650 °C for positive

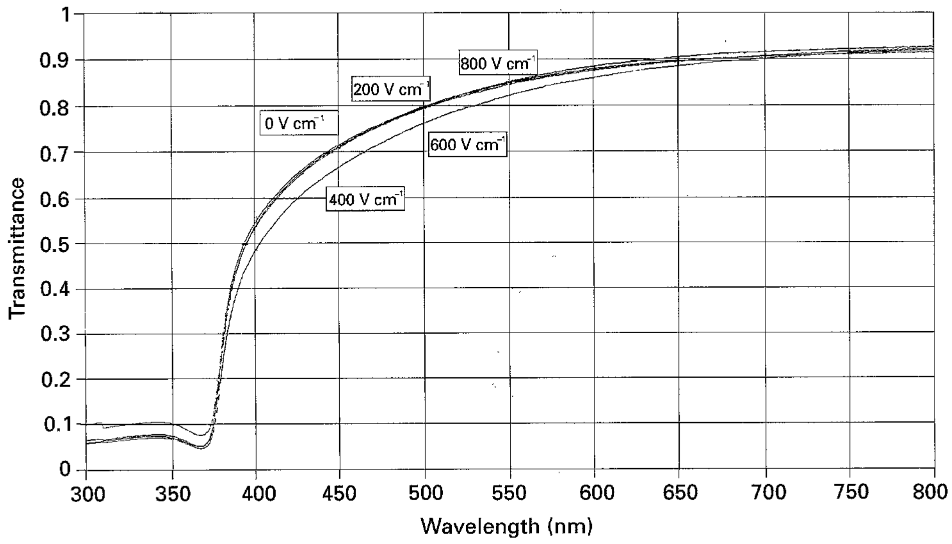

Figure 6 The transmittance spectra of samples subjected to different positive fields, oxidized at 415 °C.

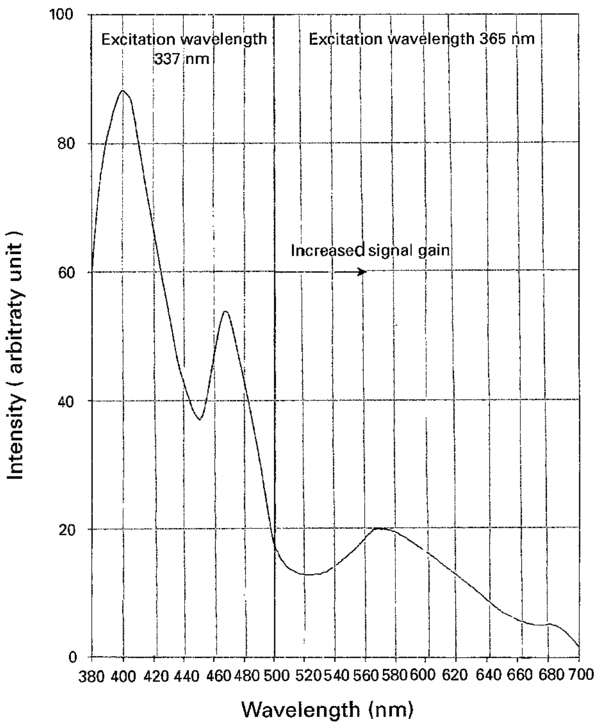

Figure 7 The photoluminescence spectrum of the reference sample (no applied field), oxidized at 415 °C.

fields and 500 °C for negative fields. Here, all the production and characterization of samples were performed with respect to the same imaginary direction. There are a few factors that influence the orientation and must be taken into consideration in order to avoid misinterpretation of data.

4.1. The effect of film thickness

A study of varying film thickness on *c*-axis orientation for samples oxidized at 500 °C showed that increasing the film thickness increases the *c*-axis orientation of the ZnO crystals. Even though the surface morphology of the oxidized zinc is different from the sputtered zinc oxide, the bulk of the oxidized film could resemble the sputtered film. It can be envisaged that according to the sputtered model [16] axial texture improves by increasing the crystal length in the normal direction. Therefore, statistically, in thicker films more planes could contribute to the basal plane reflection during X-ray diffraction increasing the (0 0 0 2) reflection intensity and consequently improving the *c*-axis orientation.

4.2. The effect of substrate temperature

As one knows, substrate temperature influences the crystal properties of deposited films, such as orientation and crystal size. In order to study the field effect on ZnO, the conditions for evaporating zinc must be the same. If not, the field's effect on oxidation cannot be singled out from the other effects introduced by previous treatment of the zinc thin films. Here, the deposition temperature was kept at room temperature. Heating the substrate during evaporation of zinc produced low quality films, which is probably due to the re-evaporation of zinc and a decrease in the sticking coefficient of the evaporant.

4.3. The effect of oxidation period

The oxidation period is estimated from the following experimental relationship, obtained by Cope [17].

$$K = 2.2 \times 10^{-5} \exp^{-25500\,(\mathrm{Cal})/RT}$$

in the temperature range of 440–700 °C. Here, K is the oxidation rate constant (cm^2 s^{-1}) and R is the gas constant. The data on oxidation rates of zinc have much scatter, and have not been worked out for zinc thin films. The oxidation period is related to the scale thickness as:

$$X^2 = 2Kt$$

where X is the oxide thickness (cm) and t is the oxidation period (s). Another estimation is made for the K value below the melting point of zinc as a result of work by Hauffe [18]. The K value would be

8.4×10^{-14} ($cm^2 s^{-1}$) at 390 °C in air. The values obtained from Cope's and Hauffe's results are taken to be the minimum oxidation time. It is very important in these experiments to oxidize completely the zinc samples. To find out if the duration of oxidation, after a zinc sample was fully oxidized, has any effect on the c-axis orientation, a zinc sample was oxidized at 550 °C without any applied electric field. Then the sample was X-rayed and placed in the furnace again and remained there for the same time period (no field applied). Then the sample was X-rayed and the cycle repeated for twice the usual oxidation interval. The result proved that once the sample is fully oxidized, the c-axis orientation remains unchanged regardless of the oxidation period.

It is important to recognize three electric fields participating in the process. First is the electric field that exists between the capacitor plates, E_0; second, is the electric field induced in the dielectric film due to the external field, E_i; and the third one is the field produced in the ZnO film during the oxidation process, E'. The third field exists because of the fact that chemisorbed oxygen has a large electron affinity. Consequently, electrons are withdrawn from the oxide with the simultaneous formation of oxygen ions. By applying a positive field, E_0, an induced field, E_i, is developed across the oxide layer in the opposite direction to the original field. The surface charge field, E', produced across the ZnO layer due to the oxidation process, has the same direction as that of the induced field in the film. It can be rationalized that application of a positive field facilitates the transport of electrons to the surface of the oxide, which in turn increases oxygen ionization (O^{-1}, O^{-2}) and eventually increases the oxidation rate. The increase in chemisorption of oxygen on the ZnO surface by application of a positive field was confirmed by Hoenig and Lane [19] by monitoring film conductivity. On the other hand, application of a negative field retards the oxidation rate by reducing the number of electrons available on the surface of the zinc oxide film. In the presence of an external electric field one can rewrite the linear diffusion equation [20, 21], due to the effects of electrochemical and electrostatic energies, as follows

$$J = -D\frac{dC}{dx} + \frac{ZeDC}{kT}(E' + E_i)$$

where E' is the electric field developed in the oxide film due to the oxidation process, D is the diffusion coefficient, C is the concentration, Z is the valence, T is the temperature, e is the electron charge, and k is the Boltzmann constant. It can be seen that by applying a positive field, the induced field is in the same direction as the oxidation field, therefore, the flux of electrons to the oxygen–oxide interface is increased by the application of a positive external field. The reverse is true when a negative field is applied. There, the induced field is in the opposite direction with respect to the oxide field and retards the migration of the electron to the surface of the oxide film, which in turn decreases the oxidation rate. Considering the experimental results, it seems that there is a direct relationship between crystal orientation and oxidation rate. In general, the application of a positive field improves the c-axis orientation. Also, the oxidation rate will increase by employing a positive electric field. The reverse is true when the field is retarding (negative field), which degrades the c-axis orientation.

An increase in the oxidation rate yields an increase in the number of zinc interstitials. The increased number of zinc interstitials leads to an increase in the strain in the lattice. The strain normal to the substrate is proportional to $(c_0 - c)/c_0$; where c is the lattice constant obtained from the (0 0 0 2) reflection and c_0 is the corresponding value for bulk ZnO (0.5205 nm). Maniv *et al.* [22] computed the stress, σ, in the plane of the sputtered thin film as

$$\sigma = 4.5 \times 10^{11} (c_0 - c)/c_0 N m^{-2}$$

Fig. 8 shows the relative strain $(c_0 - c)/c_0$ in the samples oxidized at 550 °C under the influence of positive electric fields. It is seen that this graph has the same characteristic features as that of the c-axis orientation graph corresponding to the same oxidation temperature. Here, with improvement of c-axis orientation one notices a corresponding lattice strain increase and vice versa. If the concentration of interstitial zinc increases, one would expect a decrease in the concentration of electrons. This fact becomes clear by considering the following equations

$$Zn(gas) = Zn_i^{+1} + e^- \text{ and } K = [Zn_i^{+1}][e^-]/P_{Zn(gas)}$$

Because K is a constant, by increasing $[Zn_i^{+1}]$, $[e^-]$ decreases.

When $[e^-]$ declines, the conductivity drops. One does not expect a great increase in the film resistance, because of the fact that ZnO films are fully oxidized. The resistance of ZnO samples oxidized at 550 °C for applied positive fields is presented in Fig. 9. It can be seen that in general resistance increases by applying a positive electric field.

Originally it was thought that the increase in the population of singly charged zinc interstitials situated 0.5 eV below the bottom of the conduction band would probably influence the transmittance spectra of the ZnO samples. No significant or detectable change regarding the change in the number of interstitial zinc

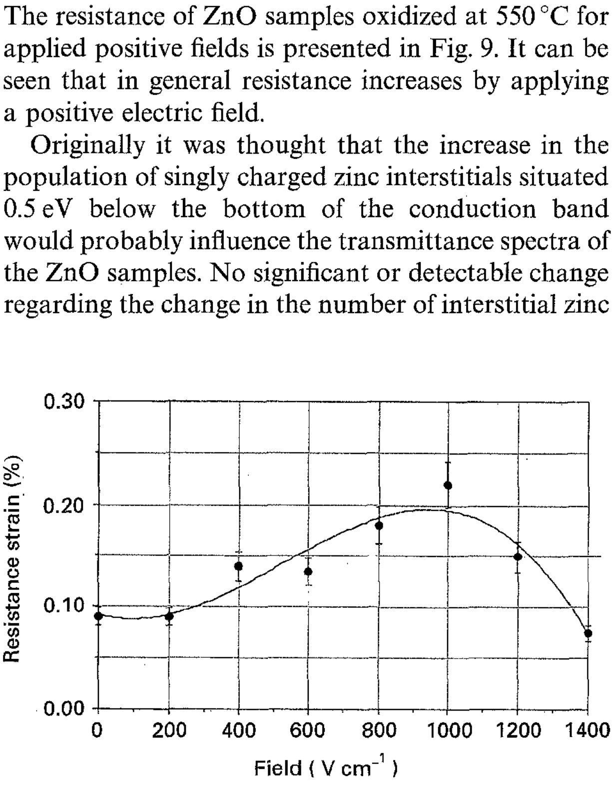

Figure 8 The relative strains in the samples subjected to different positive applied fields, oxidized at 550 °C.

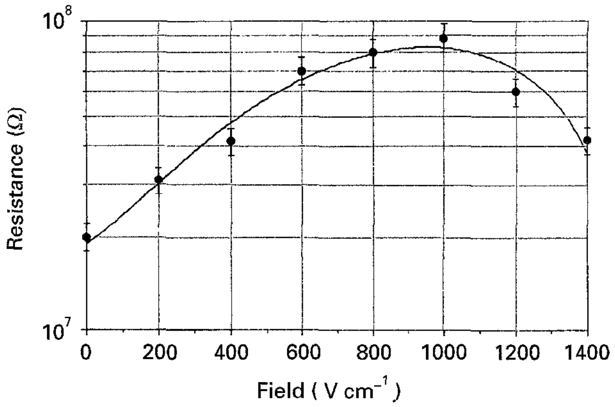

Figure 9 The resistance of the samples subjected to different positive applied fields, oxidized at 550 °C.

ions has been found. The general characteristics of the samples' spectra remain the same within the instrumentational and experimental error ranges. However, all the samples exhibit the same optical band gap of 3.2 eV regardless of the oxidation temperatures.

The effect of electric field on the crystal size for a given temperature which is related to full width at half maximum (FWHM) of the (0 0 0 2) reflection peak was calculated from the Scherrer formula

$$B = \frac{0.94\lambda}{d\cos\theta}$$

where B is the broadening of the diffraction line measured at half its maximum intensity (rad), d is the crystal size, θ is the reflection angle and λ is the incident X-ray wavelength. It was concluded that crystal size does not change significantly in any given temperature under the influence of the electric fields. The effect of oxidation temperature on the preferred orientation is pronounced. By increasing the oxidation temperature, *c*-axis orientation weakens. This could be related to the original orientation of zinc thin films that is deteriorated by increasing the temperature.

The most important factor influencing *c*-axis orientation, is the melting of zinc (~ 420 °C). Experimentally it was shown that the electric field stimulates the *c*-axis orientation when the oxidation temperature is higher than the melting point of zinc. It can be postulated that in the early stages of oxidation, the zinc oxide crystallites created on the molten zinc possess more degrees of freedom to align themselves in the direction of the field. Once the first layer becomes orientated in relation to the field direction, the growth direction would follow up. When the zinc film is not melted, the rearrangement of atoms becomes difficult due to strong covalent–ionic bonding of ZnO molecules and influential interaction between solid atoms.

The influence of the electric field on the surface morphology of the ZnO thin films is pronounced. Each oxidation temperature yields a particular surface morphology characteristic of that temperature. As indicated earlier, zinc crystals are much more orientated in the *c*-direction than zinc oxide crystals. Below the melting point of zinc, zinc oxide preserves the strong *c*-axis orientation of the zinc, to a certain extent, and exhibits the strongest *c*-axis orientation in the series. The surface texture study of the reference sample oxidized at 415 °C shows a relatively smooth surface with most of the crystals orientated normal to the substrate surface. The application of an electric field seems to have no significant effect on the surface morphology of the samples at this temperature. By increasing the temperature to 450 °C, it seems that complete melting has not occurred yet, probably due to the temperature gradient on the sample surface, or at least the very first layer is oxidized before the whole sample is completely melted. The surface morphology for the reference sample oxidized at 450 °C resembles the reference sample which was oxidized at 415 °C, but the surface is not as smooth as the sample produced at 415 °C. Here, some interwoven crystals (small leaf-like) appear on the surface of the samples. These crystallites do not contribute to the normal *c*-axis orientation. Therefore, the *c*-axis orientation is not as strong as the samples obtained at 415 °C. By increasing the oxidation temperature to 550 °C, the surface morphology changes again. Referring back to the SEM micrograph for the reference sample oxidized at 550 °C without application of the electric field, one sees Redwood leaf-shaped crystallites on the surface. The sample subjected to a $+1000\ \mathrm{V\,cm^{-1}}$ field shows more rounded crystals with better orientation when compared to the reference sample oxidized at the same temperature. On the other hand, the sample exposed to the $-600\ \mathrm{V\,cm^{-1}}$ field exhibits crystals with sharper edges resembling dendrite growth. This sample shows worse orientation than that of the reference sample oxidized at the same temperature.

As discussed earlier, the application of a positive field promotes the migration of electrons to the surface of the oxide, which enhances the oxidation rate and promotes the *c*-axis orientation of ZnO films. On the other hand, application of a positive field retards the migration of the zinc interstitials to the oxide surface. It was shown that by applying a positive field the *c*-axis orientation improves up to about $1000\ \mathrm{V\,cm^{-1}}$. This is attributed to the availability of electrons for the oxidation process on the oxide surface. It can be postulated that by the application of the higher fields ($> 1000\ \mathrm{V\,cm^{-1}}$) not readily available zinc interstitials retard the oxidation rate and lessens the *c*-axis orientation. The reverse is true in the case of negative fields.

In general, the orientation deteriorates when the surface morphology changes from rounded crystals to dendritic growth type (Redwood leaf-like) to needle-whisker type growth. The *c*-axis orientation ratios obtained from X-ray diffraction spectra perfectly conform to the above surface morphology criterion.

5. Conclusions

The effect of an electric field on the orientation of polycrystalline zinc oxide thin films was investigated. It was found that the application of an electric field stimulated the ZnO *c*-axis orientation. By applying positive normal fields at 550 and 650 °C, the *c*-axis orientations improved for fields up to $1000\ \mathrm{V\,cm^{-1}}$ and then declined to their reference values. On the other hand, the application of negative normal fields at 500 and 550 °C deteriorated the *c*-axis orientations up to about 800 V cm^{-1}. Further increase in field strengths caused the *c*-axis orientations to increase to their reference values. There was no significant difference in the optical properties, i.e. transmittance, luminescence, of samples that were subjected to electric fields at any given temperature. In general, the resistance of samples increased due to the application of positive electric fields (more zinc interstitials); however, the average crystal size remained unchanged (a pronounced function of the temperature). Another important finding was the fact that applied electric fields affect the *c*-axis orientation only when the zinc is melted. No change in crystal orientation was detected when samples were oxidized below the melting point of zinc. Also, the surface morphology of ZnO samples was altered by the application of the field. It was found that the surface texture has a direct relationship to the crystal orientation. The more rounded crystals represented a better orientation. The more whisker-shaped needle crystals represented the deterioration of *c*-axis orientation. The effect of an electric field with respect to the effect of the temperature on *c*-axis orientation is negligible. Increasing the oxidation temperature worsens the crystal orientations and enlarges the crystallites dimensions. The thicker zinc oxide films are also associated with the better *c*-axis orientations. It was found that once the zinc sample is fully oxidized, the extension of oxidation period will not influence the crystal orientation at all.

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