# Effects of substrate material and annealing temperature on morphology of zinc oxide films

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A two stage chemical deposition (TSCD) technique is used to produce ZnO films on quartz glass (QG), soda lime glass (SLG) and high purity alumina (HPA) from an aqueous solution of zinc complex. The effects of the substrate material on the chemical composition and morphology of the deposited layer are investigated. The effects of different annealing temperatures (180, 300, 500 and 800°C) on the morphology and orientation of the ZnO crystallites are also determined. X-ray diffraction diffractograms show that above 300°C, the intensity of (002) peak considerably decreases with increasing temperature. Results indicate that changing the substrate from QG to SLG does not significantly influence the chemical composition of the deposited layer. These variations can be attributed to different factors including (a) physorption of cold complex solution, (b) growth behaviour of the nuclei forming on the substrate and (c) the surface energy of the substrate. Owing to the existence of the morphological differences bound to the molecular nature of the substrate, properties of the coatings are found not to be the same. HPA substrate causes clustering of the ZnO crystallites, while QG and SLG substrates do not distinguishably show this effect. Observations show that clustering is intensified by annealing at temperatures >180°C.

**Keywords:** Zinc oxide, Soda lime, Quartz, Alumina, Substrate, Microstructure, Annealing

## Introduction

Zinc oxide coatings have numerous applications. Highly oriented low conductivity films serve, for example, as ultrahigh frequency electroacoustic transducers benefited by their desirable piezoelectric properties.[1,2] High conductivity ZnO films with a high visible spectrum transparency coefficient can be used as a transparent electrode in the field of optoelectronic display and in the field of photovoltaic solar energy conversion.[3,4] Bulky ZnO is, however, rather expensive and generally unavailable as large wafers. ZnO film is therefore a desirable choice for substitution.

ZnO films can be produced by numerous methods, e.g. sputtering, electron beam evaporation,[5] spray pyrolysis,[6] metal organic chemical vapour deposition,[7] electroless bath deposition,[8] pulsed laser deposition[9] and chemical deposition.[10] Chemical deposition is an advantageous technique for formation of a largely surfaced thin film. Deposition of ZnO films with controllable thickness and conductivity is made possible using this method. Deposition is performed onto any substrate inactive with the chemicals used for deposition.

Although an overwhelming volume of literature is confined to the deposition of ZnO, very little attention has been paid to two stage ZnO chemical deposition. No studies have been conducted on the role of the substrate material on characteristics of chemically deposited ZnO films. It is interesting to know how the microstructure of the chemically deposited coatings changes with the substrate materials. Therefore, the purpose of the present paper is to present results of such studies for chemical deposited ZnO films.

Two stage chemical deposition (TSCD) is used here to produce ZnO films. The substrate was first immersed into a cold aqueous solution containing a complex compound consisting of $Zn^{2+}$ ions. The substrate was first covered with a layer of the complex. It was then dipped into a distilled boiling water bath to facilitate the decomposition of the complex into the desirable ZnO layer.

## Experimental procedures

### Deposition

Quartz glass (QG), soda lime glass (SLG) and high purity alumina (HPA) plates with dimensions of $25 \times 15 \times 1$ mm were used as the solid substrate for film growth. After degreasing, the plates were washed with deionised water and dried in a steam of hot air. The final solution composition and the bath conditions used in the present work are shown in Table 1. The zinc complex solution having the composition shown in Table 1 was prepared by mixing concentrated $NH_4OH$ with 0·5M $ZnCl_2$ until white $Zn(OH)_2$ was precipitated. Further addition of $NH_4OH$ resulted in dissolving of the

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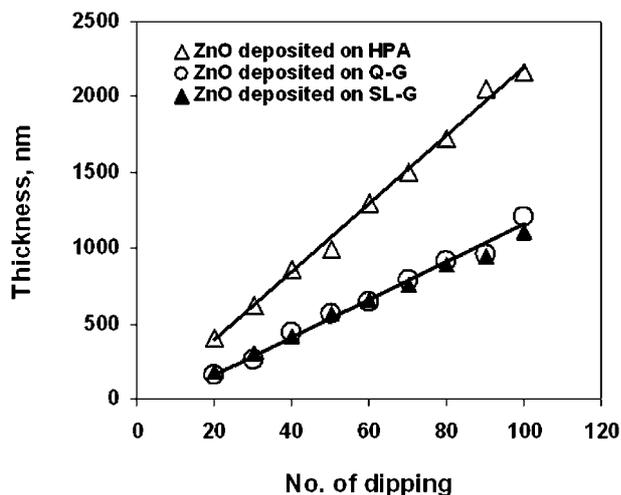
1 Variation of film thickness *v.* number of times dipped

precipitate. The solution was diluted up to appropriate concentration of $Zn^{2+}$ complexes. This was found to be the most convenient concentration for production of a good quality film on the substrate. Cleaned substrates were first immersed into a cold complex containing solution and then in hot water for 2 s. After a required number of repetitions of dipping, the substrate with the deposited ZnO film was annealed at various temperatures in a tube furnace for 1 h.

## Deposit characterisation

ZnO films produced in the present work were characterised for their surface morphology, chemical composition, phase present and preferred orientation. The surface morphology was studied by scanning electron microscopy (SEM) using a Philips model MV2300 operated at 25 kV. The chemical composition of the deposits was determined using the Kevex model energy dispersive X-ray spectroscopy (EDAX) system attached to the SEM. All chemical composition values are quoted in wt-% and represent the average of at least five measurements. In order to verify the accuracy of the EDAX analysis, one deposit was also analysed by wet chemistry using atomic absorption spectroscopy (AAS).

X-ray diffraction (XRD) was used to determine the phase present and preferred orientation of the deposits. A Philips Xpert-Pro X-ray diffractometer with a Cu $K_{\alpha}$ radiation ($\lambda=1\cdot5418$ Å) was employed to obtain XRD spectra using standard $\theta$–$2\theta$ geometry. A computer based search and match was used for phase identification.

## Results and discussion

The study of the role of the substrate type in influencing the chemical deposition and deposit characteristics of ZnO

Table 1 Bath conditions and chemical deposition parameters with their various ranges for ZnO deposition

| ZnCl$_2$, g L$^{-1}$ | NH$_3$, mL | Additive (tiron)* | pH | Temperature of complex solution, °C | Temperature of hot water, °C |
|---|---|---|---|---|---|
| 20–100 | 10–50 | 1 drop L$^{-1}$ | 8–11 | 10–20 | 90–105 |

*A compound based on the benzene molecule.
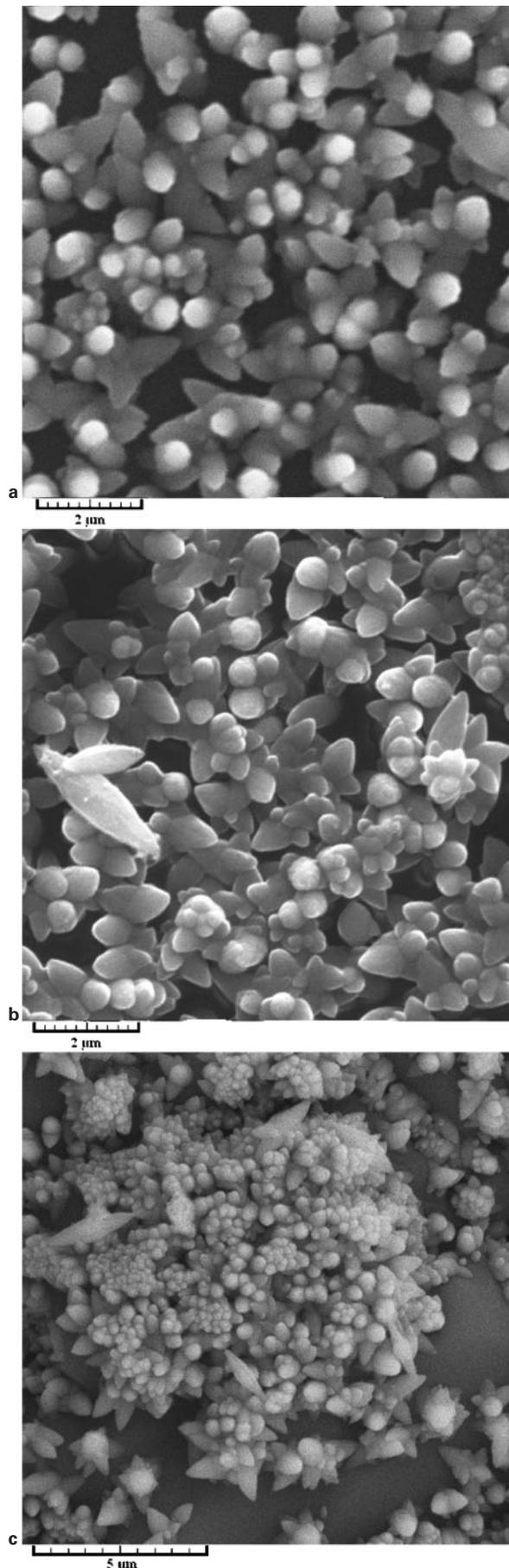


2 SEM micrographs showing morphology of zinc oxide deposits without annealing treatment on *a* QG, *b* SLG and *c* HPA substrates
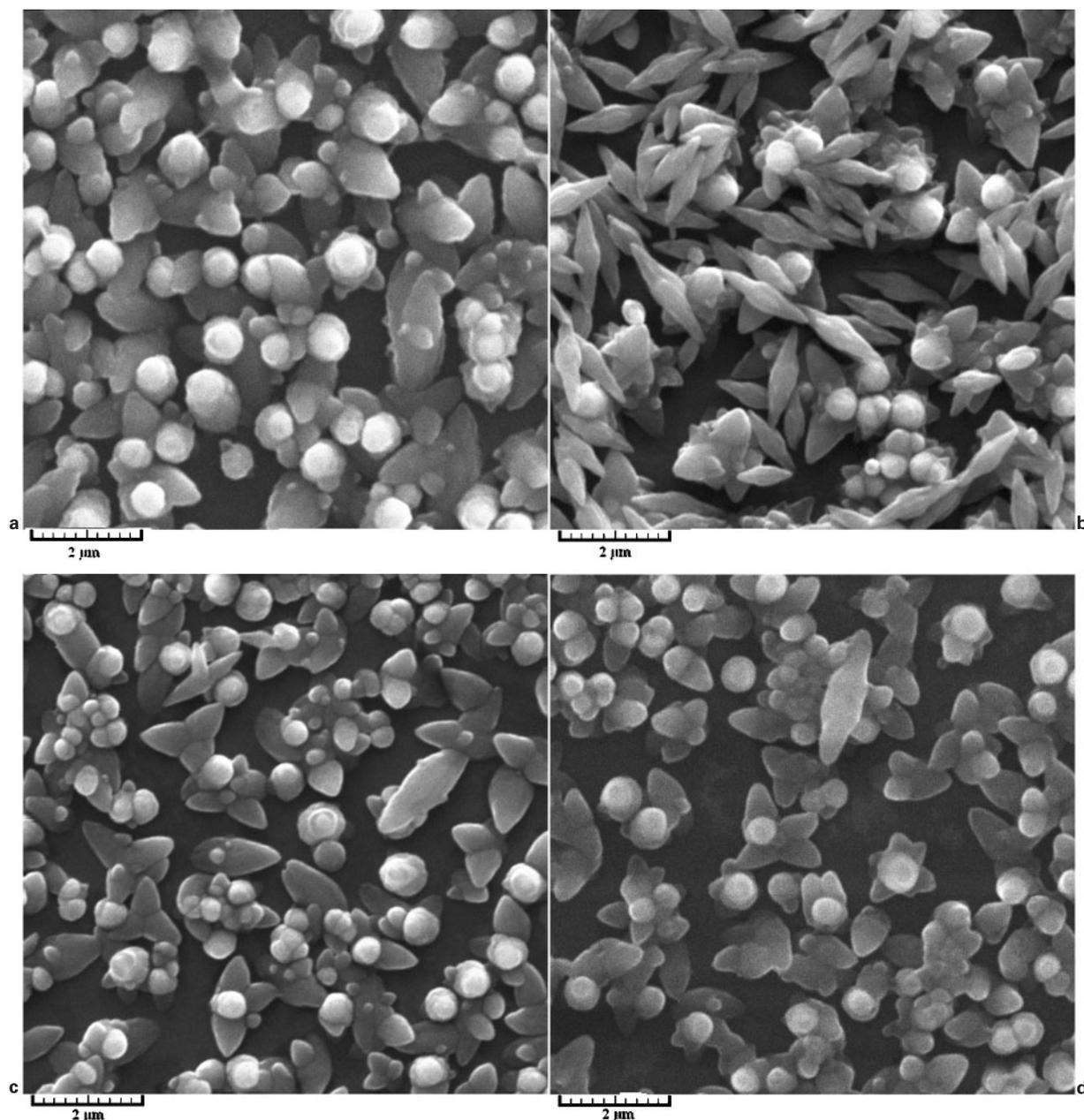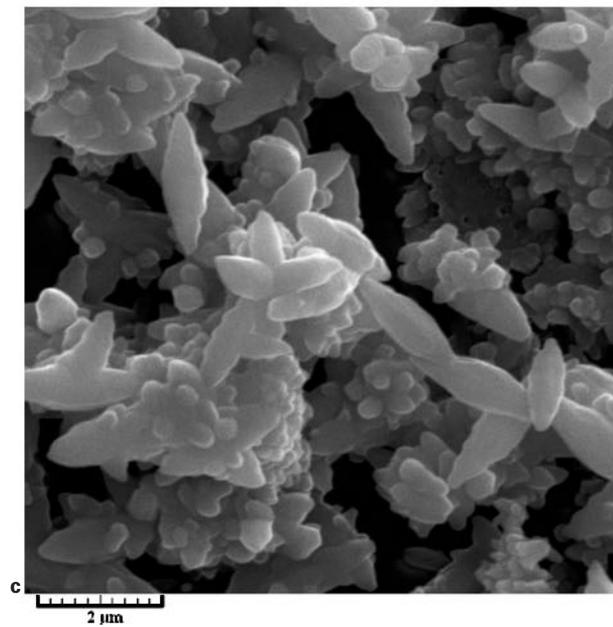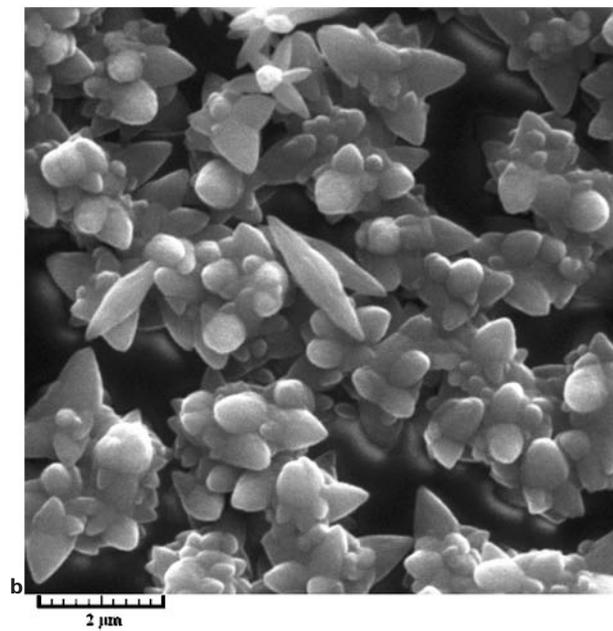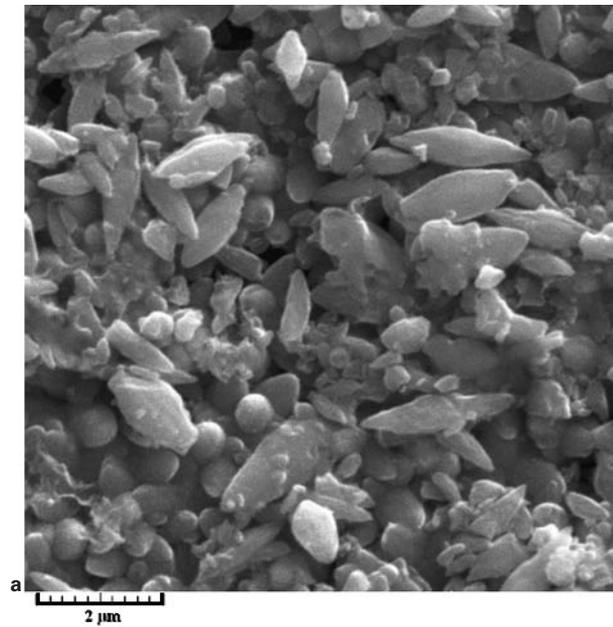
**3 SEM micrographs showing morphology of zinc oxide deposits on QG substrate annealed at *a* 180°C, *b* 300°C, *c* 500°C and *d* 800°C**

coatings is of both fundamental scientific interest and potential technological significance. In general, the characteristics of chemically deposited coatings may be dependent on the substrate type. For example, the substrate type influences some of the deposit and deposit/substrate interface properties such as stress and adhesion.[11]

In the present work, the chemical deposition of ZnO was studied using QG, SLG and HPA substrates. The experimental deposition conditions used to study the deposition of ZnO on the above mentioned substrates were the same. All deposits had the same thickness. These conditions are outlined in Table 1.

Figure 1 shows the effect of number of dips on the growth rate of the deposits formed on the substrate. As can be seen, the increasing rate of the thickness of the layers for QG and SLG substrates is about the same. This rate is, however, much greater for HPA substrate. All thicknesses increase linearly with the dipping number

of the samples. The curve for the HPA substrate is obviously shifted up towards higher thicknesses. The thickness value for the deposits formed on QG, SLG and HPA substrates at 100 times dipping are, for example, 1·21, 1·10 and 2·16 μm respectively. This finding may be attributed to differences in the adsorption of a layer of complex solution when immersed in it for three substrates. However, this fact should only affect the early stages of the TSCD process. In addition, the difference in the growth behaviour when the adequate nuclei are formed, may also contribute to the obvious variations in the thickness. Another possible explanation for the higher affinity of oxide layer to deposit on HPA may be lower surface energy barrier between those two ceramic materials (ZnO and HPA), which facilitates the formation of nuclei of a ZnO layer with an increased thickness. These nuclei form the basis for further growth and show the progressive growth. It should be noted

4   SEM micrographs showing morphology of zinc oxide deposits on SLG substrate annealed at *a* 180°C, *b* 300°C and *c* 500°C
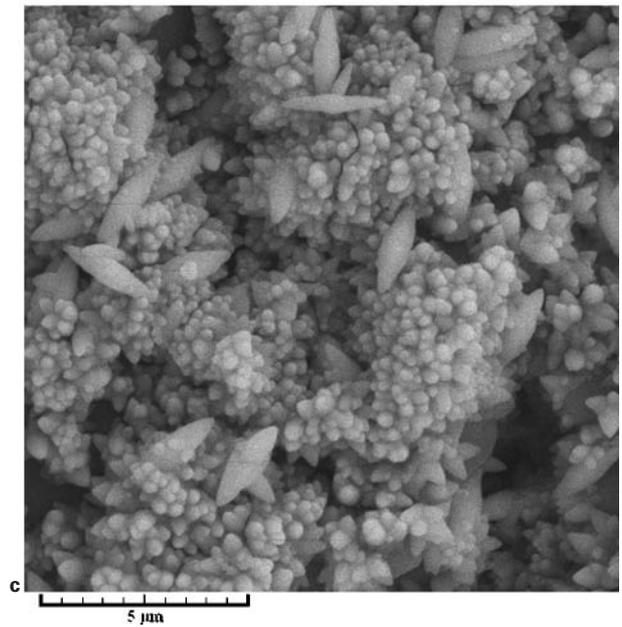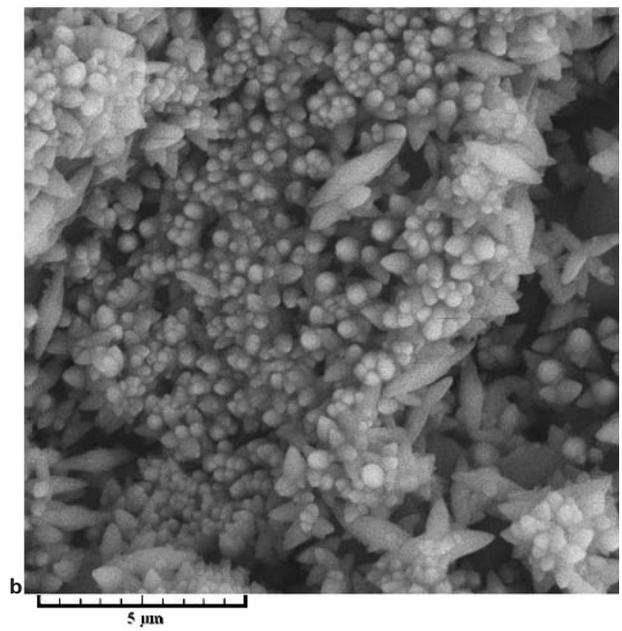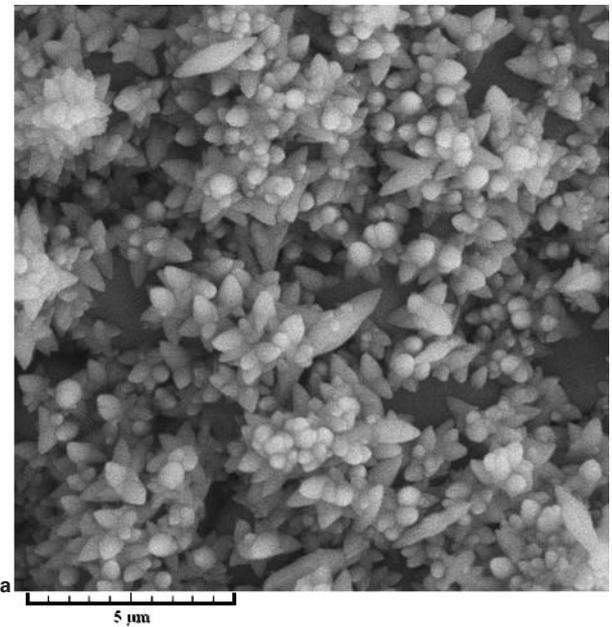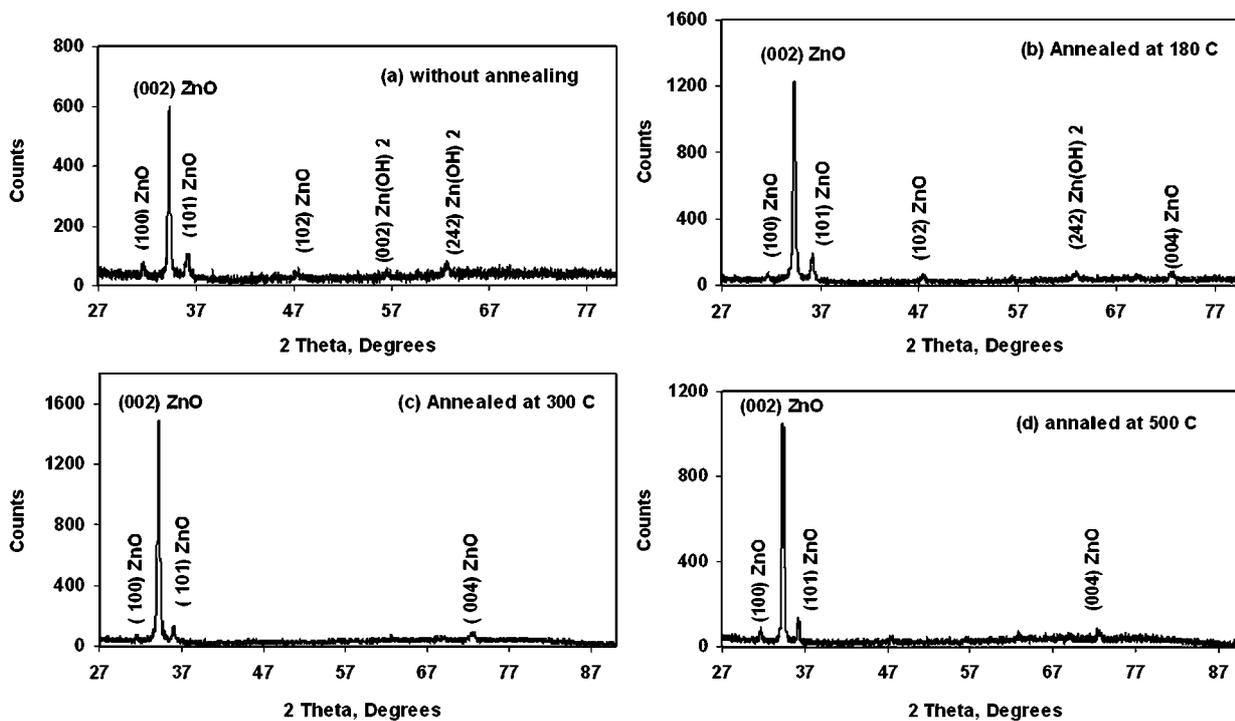


5   SEM micrographs showing morphology of zinc oxide deposits on HPA substrate annealed at *a* 180°C, *b* 300°C and *c* 800°C
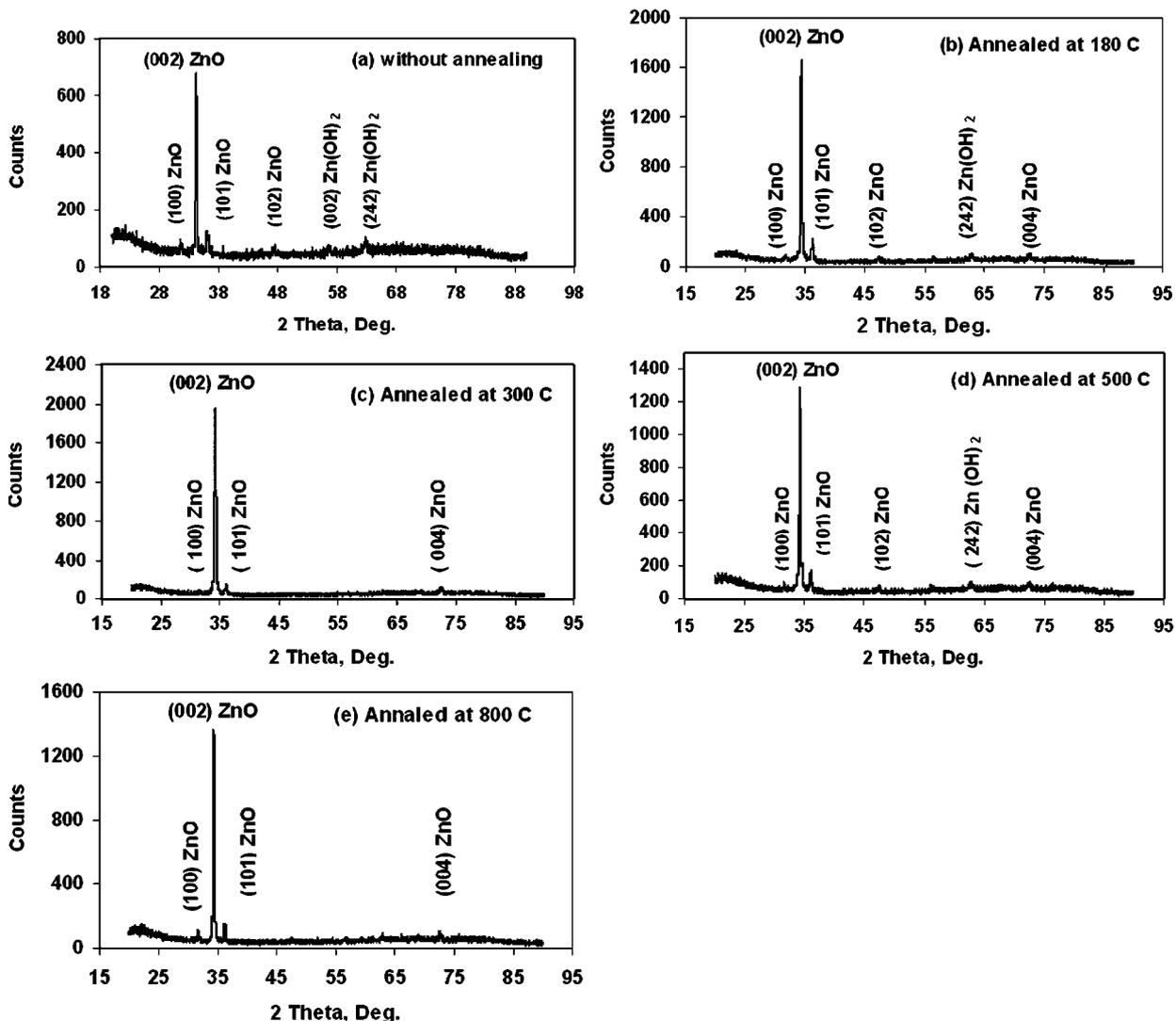
*a* without annealing; *b* annealed at 180°C; *c* annealed at 300°C; *d* annealed at 500°C; *e* annealed at 800°C

**6   XRD patterns for ZnO deposits on QG substrate**



*a* without annealing; *b* annealed at 180°C; *c* annealed at 300°C; *d* annealed at 500°C

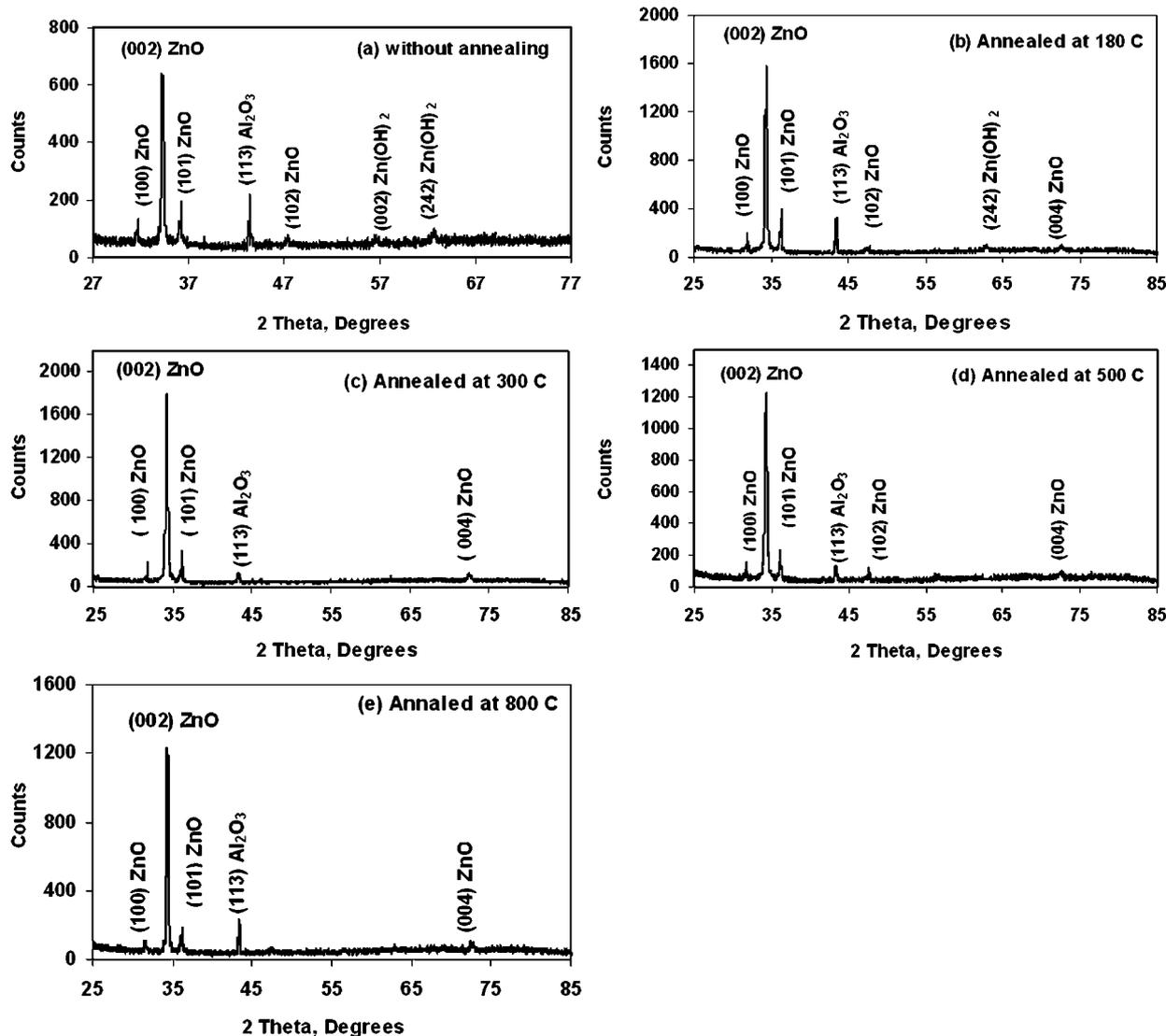**7   XRD patterns for ZnO deposits on SLG substrate**

*a* without annealing; *b* annealed at 180°C; *c* annealed at 300°C; *d* annealed at 500°C; *e* annealed at 800°C

**8 XRD patterns for ZnO deposits on HPA substrate**

that the progressive growth has been proved from the surface morphologies of the oxide layers produced on SLG and QG substrates (Figs. 2–4)

The surface morphologies of the non-annealed deposits after dipping 100 times are shown in Fig. 2. A slight morphology change is observed when the substrate changes from QG to SLG, while a much more distinguishable change occurs when HPA is used for this purpose. HPA substrate causes clustering of the ZnO crystallites, while QG and SLG substrates do not distinguishably show this effect. The SEM micrographs clearly indicate that the zinc oxide layers deposited on all three substrates are composed of oval shaped crystallites preferably oriented perpendicular to the surface of the substrate. Crystallites deposited on the HPA substrate are more compact than those deposited on the other two.

Observations show that clustering is intensified by annealing at temperatures >180°C (Figs. 3–5). As can be seen, the average size of the oval shaped crystallites reduces from left to right in the following order: QG>SLG>HPA.

Semioval shaped crystallites have apparently formed in some of the samples. Figure 3 clearly indicates the presence of such grains.

XRD patterns for deposits produced on Q–G, SL–G and HPA substrates are shown in Figs. 6–8. Effects of annealing temperature on XRD patterns of the deposited layers are demonstrated in these figures. It is concluded that changing of the substrate type influences the intensity of the preferred crystallite orientation, but not on the growth direction. In these X-ray diffraction spectra, the peaks at $2\theta=31\cdot3$, $34\cdot6$, $36\cdot2$ and $47\cdot6$ correspond to the planes (100), (002), (101) and (102) of the hexagonal ZnO respectively. The preferred orientation peak occurred at $2\theta=34\cdot6$. These spectra indicate a good crystalline character for the deposited layer showing a preferential orientation with the *c* axis perpendicular to the substrate. The same preferred orientation of the films was found in the case of ZnO films prepared using other methods.[12–14] The substrate material have no influence on the preferred growth directions.

Samples without annealing or annealed at lower temperatures show the characteristic peaks of $Zn(OH)_2$ at the $2\theta$ angles of $56\cdot1$ and $63\cdot1$. As it is shown in Figs. 6–8, increasing annealing temperature up to 300°C causes an increase in the intensity of the peak corresponding to the (002) plane. If the annealing temperature exceeds
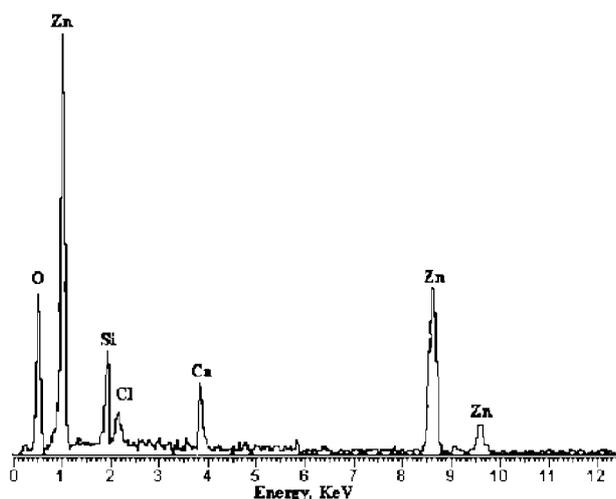
**9 EDAX result of ZnO film dipped for 100 times**

300°C, the intensity of the peak corresponding to the (002) plane decreases and the peaks belonging to $Zn(OH)_2$ are eliminated. It was concluded that the most appropriate temperature for annealing was ~300°C.

EDAX spectrum of the ZnO film shows the presence of Zn, O, Ca, Si and a trace amount of Cl. The source of Si is the substrate (Fig. 9). Ca may have come from either the source material or the SLG substrate as an impurity. The Cl species may have come from the aqueous complex solution. As a typical example, one of the samples was also analysed by wet chemistry using AAS. AAS analysis showed 76·4 wt-%Zn, while EDAX analysis indicated 78·2 wt-%Zn. The difference is within the acceptable range of the experimental errors.

## Conclusions

SEM, EDAX and XRD techniques were used to evaluate the effect of substrate materials (QG, SLG and HPA) on the morphology, orientation, crystallite shape and chemical composition of the chemically deposited ZnO layers. It is shown that the substrate material has no influence on the chemical composition. It does, however, change the surface compaction, clustering and sizes of the grown crystallites. These variations may be attributed to the changes in physorption of cold complex solution on the substrate, the growth behaviour of the nuclei and possibly the surface energy of the substrate material. Increasing the annealing temperature up to 300°C causes an increase in the intensity of the (002) plane peak. Higher temperatures eliminate the characteristic peaks of $Zn(OH)_2$. Morphological differences described in the present study dictate that the ZnO coatings grown on QG and SLG should lead to alternative properties with respect to ZnO films coated traditionally on HPA substrates. Electrical properties are the specific example to be studied further.

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