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Abstract

Zinc oxide (ZnO) thin films have been reported to suffer from degradation in electrical properties, when exposed to elevated heat and humidity, often leading to failures of electronic devices containing ZnO films. This degradation appears to be linked to water and oxygen penetration into the ZnO film. However, a direct observation in the ZnO film morphological evolution, detailing structural and chemical changes has been lacking. Here, we systematically investigated the chemical and morphological heterogeneity of ZnO thin films caused by elevated heat and humidity, simulating an environmental aging. X-ray fluorescence microscopy, X-ray absorption spectroscopy, grazing incidence small angle and wide angle X-ray scattering, scanning electron microscopy (SEM), ultra-high-resolution SEM and optical microscopy were carried out to examine ZnO, and Al-doped ZnO thin films, on two different substrates – silicon wafers and flexible PET films. In the un-doped ZnO thin film, the simulated environmental aging

resulting in pin-holes. In the Al-doped ZnO thin films, significant morphological changes occurred after the treatment, with an appearance of platelet-shaped structures that are 100-200 nm wide by 1 μ m long. Synchrotron x-ray characterization further confirmed the heterogeneity in the aged Al-doped ZnO, showing the formation of anisotropic structures and disordering. X-ray diffraction and X-ray absorption spectroscopy indicated the formation of a zinc hydroxide in the aged Al-doped films. Utilizing advanced characterization methods, our studies provided information with unprecedented level of details and revealed the chemical and morphologically heterogeneous nature of the degradation in ZnO thin films.

Text

Zinc oxide (ZnO) possesses many unique properties and attracts great attention in both fundamental research and industrial applications, from conventional electronics, solar cells ⁶⁻⁸, humidity sensors, to emerging applications in chemical energy technologies ⁹, piezoelectric nanogenerators ¹⁰, energy scavenging ¹¹, and electromechanically coupled sensors ³. In many applications, an increased electrical conductivity is desirable, which is usually achieved by doping the ZnO with other elements. In particular, Al-doped ZnO possesses high conductivity, as well as good optical transmission properties in the visible and near infrared range. Thus, Al-doped ZnO is particularly suitable for applications that require both transparency and electrical conductivity such as organic light-emitting devices ⁵ and solar cells ^{12, 13}. However, ZnO thin films, especially with Al-dopants, are not stable under harsh environments such as elevated heat, humidity and UV exposure, which limits the applicability of ZnO-based materials in devices requiring long-term stability ¹⁴. Therefore, it is important to understand the long-term stability and degradation phenomena in ZnO thin films.

Most of the studies on ZnO thin films focus on structural, electrical, optical properties and sensing abilities^{6-8, 14, 16-24}, but only a few report on the chemical and morphological changes of ZnO under environmental treatment such as high temperature and high humidity, (the so-called ‘damp heat’ treatment). The influence of deposition methods, film thickness, dopant type and film quality on the degradation of ZnO films under damp heat treatment were previously studied^{6, 16-18, 25}. In general, after the damp heat treatment, an increase in resistivity with a decrease in mobility and carrier density was reported for Al-doped ZnO thin films¹⁸. Penetration of water and oxygen along the grain boundaries and formation of Zn(OH)₂ were reported to be responsible for the degradation of the electrical and optical properties^{14, 18, 20, 21}. It was previously reported that when an Al-doped zinc oxide thin film is subjected to the damp heat treatment, the surface of the film exhibited morphological heterogeneity, where large and small spots were formed on the samples exposed to high temperature (100°C) and high humidity (100% relative humidity)^{6, 22}. However, the nature of this heterogeneity, such as the chemical and elemental composition, remains unclear, with the detailed morphological analysis particularly lacking.

Here, we focus on studying the chemical and morphological heterogeneity of ZnO thin films when the materials are subjected to steam treatment and compared with the untreated pristine samples. Al-doped and undoped ZnO thin films on two substrates were studied: Si and polyethylene terephthalate (PET). The transparency and flexibility of PET are attractive for applications such as flexible electronics. However, it is unclear if the type of substrate may contribute to the evolution of the samples, in particular, considering the polymer swelling and deforming in the steam treatment. Si substrate is mechanically more stable during steam treatment and can serve as a comparison.

A wide range of techniques were utilized to characterize the pristine and aged samples. Optical Microscopy (OM) was used to characterize the surface appearance. Scanning Electron Microscopy (SEM, Jeol 7600F), Ultra-high resolution SEM (Hitachi SU9000) and Energy Dispersive X-ray Spectroscopy (EDS, Jeol 7600F) were used to characterize the surface morphology and chemical distribution. X-ray Diffraction (XRD) measurements were performed (Rigaku Ultima III) to investigate the chemical and structural changes. OM, SEM, EDS and XRD were performed at the Center for Functional Nanomaterials (CFN) of the Brookhaven National Laboratory (BNL). X-ray Fluorescence (XRF) and Micro X-ray Absorption Near Edge Structure spectroscopy (μ -XANES) measurements were carried out by utilizing the Sub-micron Resolution X-ray Spectroscopy (SRX) beamline at the National Synchrotron Light Source II (NSLSII) of BNL. XRF elemental mapping was used to observe the morphology of the film surface and XANES was used to verify the chemical change before and after the treatment. Grazing Incidence X-ray Scattering (small angle and wide angle) measurements (GISAXS and GIWAXS, respectively) were performed at beamline 7.3.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory.

Pristine samples were first characterized by the techniques detailed above, and were then treated to purposely introduce degradation (see supplementary material for experimental setup). Steam treatment was carried out to age the samples where an environment of 100% relative humidity at 100°C was created to simulate the harsh environment under an accelerated aging condition. Such conditions of both high humidity and elevated temperature (often referred as ‘damp heat’ treatment, or ‘accelerated aging’) is widely adapted in academic research and industrial testing^{6, 16, 18, 21, 25}. By comparing the results from the treated samples and the pristine ones we aim to study the environmentally induced heterogeneity in ZnO thin films.

Analysis of ZnO and Al-doped ZnO pristine films by high-resolution SEM prior to treatment showed subtle differences in morphology. Al-doped ZnO on Si exhibited pinholes and slightly wider gaps between grains as compared to the denser packing of grains observed in pristine undoped ZnO thin film on Si (see supplementary material for Figure S7 high resolution SEM of pristine ZnO and Al-doped ZnO on Si). Al doping likely deteriorates the crystallinity of the ZnO films, which may be due to the formation of stress by the smaller radius of Al^{3+} ions (0.054 nm) compared with Zn^{2+} ions (0.074 nm). In comparison with other dopant such as Ga, where there is smaller difference in radius between Ga^{3+} ions (0.062 nm) and Zn^{2+} (0.074 nm) ions, Al-doped ZnO likely develops more defects³¹⁻³³. This may attribute to the degradation and morphological changes during the treatment as discovered below.

For ZnO on the Si and PET substrates after treatment, little morphological change was observed with OM and SEM. In contrast, for Al-doped ZnO on both the Si and PET substrate, significant morphological changes were observed in the treated sample compared with the pristine one. On larger scale, the OM images of pristine and aged Al-doped ZnO thin films on the Si substrates shows that: for the pristine samples, the surface morphology is homogeneous, while bright and dark regions were formed in the aged sample, with crack-like structures observed in both regions (see supplementary material for more OM & SEM images of pristine and aged Al-doped ZnO on Si). A higher resolution visualization of changes on a smaller scale was provided by SEM. Figure 1(a,b) show overview SEM images of the pristine and aged Al-doped ZnO films on the Si substrate, respectively. The film displays a homogeneous surface morphology before treatment (Figure 1(a)). After the treatment, flake-like platelets with bright contrast (marked by blue arrows in Figure 1(b)) and dark contrast (marked by red arrows in Figure 1(b)) were formed, which are also observed in the film grown on the PET substrate, as

shown in Figure 1(c). The size of the bright-contrast platelets is $\sim 100\text{-}200$ nm wide by $1\text{ }\mu\text{m}$ long. The bright and dark platelets are believed to be the same type of platelets, with dark and light SEM contrast arising as a result of different orientations, as follows. The darker platelets lie on the surface, and thus are better connected to the partially-conductive substrate, while brighter platelets are oriented perpendicularly to the surface of the thin film, and therefore are subject to well-known “edge effect”²⁶. Furthermore, the platelets perpendicular to the surface have much smaller contact area, which may cause higher charging of the platelets and results in a brighter contrast in the SEM images.

Figure 1 SEM images of Al-doped ZnO films on a Si substrate: (a) pristine. (b) aged (blue and red arrows indicate the formation of bright and dark platelets, respectively). (c) SEM images of aged Al-doped ZnO films on a PET substrate (crosses indicate the positions where EDS were performed). Ultra-high resolution SEM Al-doped ZnO films on a Si substrate: (d) 3 kV, SE mode. (e) 1 kV, HA-BSE mode with energy filtering, pristine sample. (f) 1 kV, HA-BSE mode with energy filtering, aged sample (arrows indicate the formation of pinholes).

In order to conduct elemental analysis of the films, EDS measurements were performed on selected positions (marked with yellow crosses in the SEM images, Figure 1(c)), and EDS mapping was performed in the entire sample area shown in Figure 1(c). The elemental composition in areas with brighter and darker contrast platelets, as well as regular areas, have

been investigated (see supplementary material for Table S2 EDS data). No clear elemental differences were detected amongst the entire films in EDS, while the expected elements (O, Zn, Al, Si, C) were detected from either the sample composition or the sample mounting. These results show that the Zn and O are the major components of the platelet-shaped structures created during the steam treatment. However, an overall reduction in Zn quantity was observed after the treatment in Al-doped ZnO sample on the PET substrate with higher Zn content in the platelet-shaped structures.

To further study the morphological changes upon aging in the undoped and Al-doped ZnO films on a smaller length scale, ultra-high resolution SEM studies have been performed (Hitachi SU9000). A specific feature of this instrument is an energy filter on the top high-angular back-scattered electron (HA-BSE) detector, which, in combination with low-voltage imaging conditions²⁷, was used to enhance the contrast originating from the crystallinity and the orientation of ZnO features on the surface.

Figure 1(e) HA-BSE images of pristine ZnO with energy filtering. Unlike the SE image (see supplementary material for Figure S10 Ultra high resolution SEM), which only shows surface morphological contrast, the HA-BSE image shows many of the ZnO grains appearing brighter. Since the compositional contrast can be ruled out (material is compositionally uniform ZnO), the brighter contrast here is due to ordering/crystalline structure of the ZnO grains. In the SEM images, collected from the treated sample (Figure 1(f)), the HA-BSE image shows that a considerably fewer number of ZnO grains appearing as bright, compared with pristine sample (Figure 1(e)), suggesting that treatment causes reduction in crystalline ordering of the crystal grains. This corresponds well with the GISAXS data presented in the later section. Furthermore, pinholes ~ 10 nm in size, as well as deeper, more pronounced gaps between individual ZnO

grains are observed after treatment (Figure 1(f)), an evidence of the reduction in packing density and structural ordering. This may also lead to potential mechanical instability and reduction in conductivity, which can lead to device degradation and/or failure.

However, no platelet-shaped structures were formed in the undoped ZnO film, in contrary to the Al-doped ZnO film shown previously in Figure 1(a). Figure 1(d) show ultra-high resolution SEM images of the aged Al-doped ZnO films on the Si substrate. The detailed view of the platelets formed due to aging confirms that the platelets with brighter and darker contrast were the same type of features, with different orientations. Considering the process of water condensation on the film surface during the steam treatment and water drying, it is likely that the water droplets during drying caused the platelets to align along different orientations. The platelets were also found to exhibit a rough surface morphology, which can only be observed in the ultra-high resolution SEM.

The crystal structure of the film before and after treatment was studied by XRD which was carried out on all the samples grown on a Si substrate. The bare Si wafer was also measured as a reference. Figure 2 shows the XRD results of the pristine and aged Al-doped ZnO thin films (see supplementary material for Figure S9 XRD pattern of pristine and aged ZnO thin film on Si substrate). The Si (400) peak from the substrate appears at 69.2° , consistent with the surface cut of the substrate. The peak at 34.4° corresponds well with ZnO (002). An additional peak appears at 23.3° which is only present in the aged Al-doped ZnO thin film.^o. This peak was identified as Zn(OH)_2 peak, and was previously reported to appear at 23.35° after damp heat treatment¹⁴. Water can be absorbed at the grain boundaries of ZnO and forms Zn(OH)_2 ^{2, 8, 11}. All other peaks are also present in the bare Si wafer and are thus considered to be originating from the substrate (see supplementary material for Figure S7 rocking curve of Si wafer).

Figure 2 XRD pattern of pristine and aged Al-doped ZnO on a Si substrate and the bare Si wafer.

The crystallinity and grain size of the inorganic thin films were also studied by means of GIWAXS and GISAXS, respectively. Both techniques provide information about the lateral and normal ordering at a surface or inside a thin film and require smooth films on a flat substrate. Therefore, only the films deposited on the Si wafer were studied here. The measurements were performed with an incidence angle of 0.26° and the energy of the x-rays was set to 10 keV.

Figure 3 shows the raw 2D GIWAXS patterns for the ZnO films undoped and doped with Al, before and after steam treatment, respectively. The different crystal planes are indicated as well. The distance between the lattice planes of the main peak, corresponding to the (002) crystal planes is 0.259 nm. For the Al-doped film after the steam treatment, the area highlighted by a red rectangle show two strong reflections (not seen in other samples) , indicating a strongly anisotropic crystal structure with the lamellar d spacing of about 0.773 nm (Figure 3). This corresponds well with the platelet-shaped structures observed in SEM images and Zn(OH)_2 formation seen in XRD data.

Figure 3 2D GIWAXS patterns of the ZnO films, undoped and doped with Al, before and after steam treatment. An anisotropic structure was only observed in Al-doped ZnO, highlighted by the red rectangle.

An example GISAXS pattern is shown in Figure 4(a) in the top right corner for the pristine ZnO film. The yellow box indicates the integration area and in order to evaluate the in-plane ordering, a vertical integration was performed. The resulting line cuts for all films are summarized in Figure 4(a). The positions of the shoulders provide information on the domain size. These domain sizes most likely correspond to the grain sizes of the films, as observed by the ultra-high resolution SEM data (see Figure 1). The in-plane domain size was extracted based on the position of the shoulder and conversion with the Scherrer equation²⁸, which leads to sizes of about 38 nm for the ZnO film, 39 nm for the Al-doped ZnO. After the steam treatment, a flattening can be observed of the line cuts, indicating a reduction in ordering. This is consistent

with the high resolution SEM data, where the pinholes formation and reduction in grain ordering on the surface of the homogeneous pristine thin films was observed after aging (Figure 1(f)).

Figure 4 (a) The resulting line-cuts following the same procedure for all ZnO films, undoped and doped with Al, before and after steam treatment(see supplementary material for raw GISAXS pattern of pristine ZnO). The yellow box with double-arrow indicates the integration area and direction, with detail can be found in supplementary materials). (b) XRF Zn mapping results: ZnO on PET substrate, pristine and aged. (c) XRF Zn mapping results: Al-doped ZnO on PET substrate, pristine and aged. (d) XANES spectra of ZnO and Al-doped ZnO thin films on the PET substrate, before and after steam treatment.

XRF mapping of the Zn distribution was done on ZnO and Al-doped ZnO on the PET substrate before and after treatment (see supplementary material for Figure S11 XRF spectra of Al-doped and undoped ZnO thin film on PET substrate). The data fitting of XRF spectrum was accomplished using PyXRF (in-house development at NSLS-II)²⁹. Little changes were observed in the ZnO on the PET substrate after treatment (Figure 4(b)). In contrast, the Zn spatial heterogeneity is evident in the aged Al-doped ZnO on the PET substrate (Figure 4(c)), consistent with the SEM results as shown in Figure 1. For the pristine Al-doped ZnO on the PET substrate, the image shows that the Zn is homogeneous across the entire scanned region of interest. Spatial

heterogeneity of Zn is observed for the aged Al-doped ZnO (Figure 4(c)). Higher Zn concentration regions with a size of 20-30 μm were observed, which is about the size of the clusters of the platelet-shaped structures observed with SEM (Figure 1). There is a reduction of the Zn concentration for the Al-doped ZnO film after steam treatment, which is also observed in the ZnO film, consistent with the EDS analysis. This may be attributed to the mechanical instability of the films deposited on the PET substrates or the swelling of PET substrate during steam treatment, which leads to loss of thin film material as a result of the treatment process.

Local XANES spectra in micron-sized regions (μ -XANES) were collected from regions with relatively higher (marked with black crosses) and lower (marked with red crosses) concentrations of Zn on the XRF 2D maps. As no clear differences could be observed in the XANES spectra between the different points from the same sample, the corresponding spectra were averaged and are shown in Figure 4(d). Both ZnO and Al-doped ZnO on the PET substrate before and after treatment showed almost no differences in the XANES spectra. Although, according to the literature ³⁰, XANES spectra of ZnO and Zn(OH)_2 are nearly identical, in combination with the XRD data, our results suggest the formation of Zn(OH)_2 in the aged Al-doped ZnO thin film.

In summary, we systematically investigated the degradation of ZnO thin films (undoped and Al-doped) on Si and PET substrates due to environmental factors. Undoped ZnO exhibit only slight morphological changes after aging. Subtle structural changes (i.e. pin-holes) developed in ZnO due to steam treatment, as observed by ultra-high resolution SEM. In contrast, after the steam treatment, Al-doped ZnO on both the Si and PET substrates showed significant morphological changes. Platelet-like structures in different orientations, likely to be containing Zn(OH)_2 , were formed in the Al-doped ZnO films. The deterioration of ZnO crystallinity caused

by doping Al might contribute to more defects and pinholes in pristine Al-doped ZnO structure compared with undoped ZnO, which created path for water to go through and formed Zn(OH)_2 after steam treatment. This might attribute to the difference in ion radius in Al^{3+} (0.054 nm) vs. Zn^{2+} (0.074 nm), and insertion of smaller radius ions may lead to an additional stress and disorder, leading to defects development. This increase in grain disorder is likely contribute to more significant morphological changes after aging, which has been observed here. Ultra-high resolution SEM, GISAXS and GIWAXS also show the reduction of ordering in the structure in the thin films after the steam treatment. In particular, a highly anisotropic structure was found in the GIWAXS study, likely corresponding to the formation of the platelet-like structures formed in the aged Al-doped ZnO films. A reduction in Zn quantity was observed in both EDS and XRF microscopy, with a higher heterogeneity of Zn observed by XRF in the aged Al-doped ZnO sample. The XANES data is consistent with the XRD results, indicating that the structure can be a mixture of ZnO and Zn(OH)_2 . The development of pinholes and structural disordering in all ZnO thin films, with additional platelet-shaped structure and Zn(OH)_2 formation in Al-doped ZnO are believed to be predominant mechanisms of degradation and is likely the main cause of failure of ZnO-based devices. Overall, our study highlights the mechanism of environmentally induced degradation for ZnO thin films, in light of morphological, structural, and chemical evolutions.

Supplementary Material

See supplementary material for experimental setup, additional EDX, OM, SEM, ultra-high resolution SEM, and XRD data, XRF spectra, and GISAX data.

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