Observation of the Evolution of Etch Features on Polycrystalline ZnO:Al Thin-Films

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ABSTRACT

The transparent conducting oxide (TCO) ZnO:Al is often used as the window layer and a source of light trapping in thin-film silicon solar cells. Light scattering in sputtered zinc oxide is achieved by wet chemical etching, which results in craters distributed randomly over the ZnO surface. To gain a better understanding of the etching process on ZnO thin films, a method for atomic force microscope (AFM) realignment between etching steps is developed. Using this method, the evolution of the HCl etch on a polycrystalline ZnO thin-film is observed. Results showed that this observation method did not modify the etching behavior, nor did stopping and restarting the etching change the points of attack, indicating that the points of HCl attack are built into the films as they are grown. Additionally, we investigated the evolution of the HCl etch on a ZnO surface previously etched in KOH, and found that the etch sites for both the acidic and basic solution are identical. We conclude that “peculiar” defects, which induce accelerated etching, are built into the film during growth, and that these defects can extend part or all the way though the thin-film in a similar way as screw dislocations in single crystalline ZnO.

INTRODUCTION

ZnO is a wide bandgap semiconductor that can be doped to act as a transparent conducting oxide (TCO) for use in both inorganic and organic photovoltaic devices [1, 2, 3]. In Si thin-film solar cells, the ZnO layer is also often also used as a source of light trapping [1, 3]. The texturization of polycrystalline ZnO films can be done through various means, such as wet chemical etching in HCl, or as grown in low pressure chemical vapor deposition (LPCVD), for example [3].

While the etching process for the ZnO single crystals is well understood, there is still no model for polycrystalline ZnO [4, 5, 6]. Despite there being no model, trends have been observed [6, 7]. For example, using a series of reactively mid-frequency (MF)-sputtered ZnO films, Hüpkes et. al. showed that even though the resultant structure from the various chemical (both acidic and basic) and physical etching methods vary, the density of the points of attack decreased for all etch types as the oxygen partial pressure was decreased [6]. From this they concluded that the number of points of attack is built into the material itself.

To verify these observations and better understand the nature of the ZnO etching process, we developed a method for reproducibly aligning and imaging a sample between short etching steps using an atomic force microscope (AFM) in non-contact mode, which minimizes modifications made to the surface. Using this stepwise imaging process, we have been able to observe the evolution of various etches on a ZnO surface indirectly. This paper contains two examples of applications of this method. First, the evolution of the standard HCl etch on the surface of a polycrystalline ZnO thin-film is explored. Second, we investigate the observations of Hüpkes et. al. further.
The discussion will focus on three major areas: first, the applicability and limitations of this alignment method; second, the evolution of the HCl etch on polycrystalline ZnO; and third, the evolution of an acidic etch on a sample previously etched in a base.

EXPERIMENT

Polycrystalline ZnO:Al thin-films were prepared by depositing approximately 800 nm of ZnO:Al on a cleaned Corning glass (Eagle 2000) substrate using radio-frequency (RF)-sputtering (VISS 300, VAAT) from a ceramic target consisting of ZnO:Al2O3 with 1 % wt. Al2O3. The deposition was carried out at a substrate temperature of 300°C, discharge power of 1.5 kW, and 0.1 Pa deposition pressure of pure argon. More details on this and similar films are described by Berginski et. al. [7].

To position the sample on the µm-scale between the multiple etching steps reproducibly, four progressively smaller alignment methods were used as indicated in Figure 1: a) large scale manual marks were made using a diamond tip for the mm-scale alignment of the sample. b) A photolithographically prepared grid was used to align the sample within ±30 µm. The grid consisted of thermally evaporated silver dots of approximately 3-4 µm in diameter with a spacing of 8 µm and a thickness of 50 nm. Defects were chosen as markers and areas to scan since they were uniquely spread across the ZnO surface and provided large available areas to scan. c) A large AFM (SIS nanostation 300) scan was used to further localize (within 1 µm) the defect of interest in the Ag grid. d) The area of interest, which in this case was approximately 12*12 µm², was aligned accurately along the silver dots and scanned.

We applied this stepwise etch-imaging process to track the evolution of the HCl (0.5%) etch on a polycrystalline ZnO thin film with incremental etching times of either 2 or 4 seconds. The method was also used to image a ZnO sample after a 400 seconds etch in KOH (30%), followed by incremental 5 or 10 second etches in the HCl solution. All etches were performed at room temperature. Following all etching steps, the process was stopped by rinsing the sample with deionized (DI) water and dried with nitrogen.
To compare line scans and estimate the remaining ZnO, the AFM data was shifted by setting the glass level to zero in the sample when the etch had progressed far enough to expose it. For the other line scans the maximum AFM value was assumed to fit to the maximum thickness measured by surface profiler (Dektak 3030). This approach fit quite well as the AFM and surface profiler thickness measurements had an error of less than 30 nm.

RESULTS AND DISCUSSION

Strengths and weaknesses of the alignment method

Figure 2 (a) and (b) show SEM images of the resultant HCl etch structure after 30 seconds without and with the Ag grid, respectively. Note that despite the additional process steps required to deposit the Ag grid the resultant etch features appear unchanged. In contrast, realignment in an SEM, which may be faster and easier, contaminates the surface by depositing carbon during the imaging process; this acts as a barrier in subsequent ZnO etching steps. Due to the partly isotropic nature of the HCl etch on ZnO, the ZnO under the Ag grids was also etched causing many of the markers to wash away after repeated etches. Figure 2 (c) and (d) show AFM images in the same location after two and ten cumulative seconds of etching, respectively. Notice that all eight Ag grid points are still present after the single etching step, while only half remain after five etching steps, which provides further evidence that the presence of an Ag grid does not modify the HCl etch. Despite the loss of some of the Ag markers, repositioning the sample in the AFM was still possible using the remaining Ag dots and larger manual marks. After approximately five etch steps, the surface developed unique features that could be identified and remained fairly consistent between etching steps. Once the surface has evolved to this point, the Ag grid is helpful but no longer necessary for realignment. In this case, realignment could alternatively be done using a modified keystone technique [8]. The intact grid is, however, necessary for realignment during the initial etching steps.

![Figure 2](image)

While the etch features remained unchanged, it is important to note that the etch rates of the samples in this experiment are faster than those observed in the static etching in HCl 0.5% solution. This is most likely due to the dynamic nature of these very short etches, which prevents the shielding of the ZnO by used acid solution. We have observed that samples are etched more quickly when they are kept in motion or placed in a sonicator (not shown). The etch rates observed in this work were a factor of about two larger than similar samples which were statically etched. The higher etch rate observed in these samples is also partly due to the etching that occurs during the transfer of the sample from the etching bath to DI water rinse; this error in actual etching time is compounded with each additional etching step.
HCl etch evolution

Figure 3 shows AFM images taken at the same location on a ZnO surface at various steps in the etching process. Notice that even though the etching process was stopped and restarted many times, the same points of attack were picked in subsequent etching steps.

![AFM images](image)

Figure 3. 12x12 µm² AFM images taken at cumulative etch times of 2, 4, 8, 12, 16, and 30 seconds shown in (a), (b), (c), (d), (e), and (f), respectively. The line in (e) indicates the area of the line scan analysis.

This is even more evident in the evolution of single line scans at the same location, as shown in Figure 4 (a). The location of the lines relative to the total scanned area is indicated in Figure 3 (e). While some etching sites are present during the first etching steps and then disappear, and others appear only later, most are present throughout the entire etching process. After 18 seconds of etching, the glass was reached at some points (see Figure 4 (a, red)), while other points still had thicknesses over 660 nm, showing that the etching rate can vary by a factor of about 4.5 between etch sites and other locations on the film surface.

![Graphs](image)

Figure 4. (a) Line scans at approximately the same location throughout the etching process. The original thickness is marked in blue, and the thickness when the glass was first observed is marked in red. (b) Percentage of the sample remaining as a function of the cumulative etch time.
Further AFM data analysis yielded the fraction of the original ZnO material remaining, depicted in Figure 4 (b) as a function of the cumulative etch time. A linear fit matches the data very well up to 18 seconds, showing that the ZnO was etched at a constant rate of 3.9 %/s. The deviation to another linear fit of 1.9 %/s at longer times can be attributed to a couple of factors. First, 18 seconds is the point at which the glass first appeared, exposing less ZnO to the HCl solution than during earlier etching steps. Second, after the glass appeared, longer etching steps were taken (4 rather than 2 seconds). This longer etching time may allow larger shielding effects.

**KOH followed by HCl etches**

To study the development of etch sites further we now apply this method to etching in acidic and basic solutions. AFM images taken at the same location on a polycrystalline ZnO:Al surface after a 400 second KOH etch (Figure 5 (a)), and subsequent HCl etches (Figure 5 (b)-(d)) are shown in Figure 5. While the surface structures from the KOH etch are softer, the density of the etching points is similar to the ones observed in Figure 3, which agrees with previous conclusions [6].

From AFM data we extracted the line traces for the different etching steps, see Figure 5 (e). Notice that while the points of attack become more pronounced in the HCl etch, the points of attack are in general already present in the KOH etch (see markers in Figure 5 (e)). Since ZnO is an amphoteric oxide, it is not surprising that it etches in both basic and acidic solutions. It is interesting, however, that these solutions attack the same points, while in single crystals, the etching of O- and Zn-terminated surfaces are prohibited in bases and acids, respectively, and is only possible at defects [4].

From the evolution of the HCl etch we can conclude that the points of attack are built into the film during growth. If the points of attack were due to the state of the sample in the HCl solution or particular adsorbates on the ZnO surface, subsequent etching steps would attack
different points. This conclusion is supported by the observation that KOH and HCl attack the
same points. We further conclude that the etch attack is induced by a structural defect rather than
a local chemical property like polarity, which would act differently in acids and bases.

These polycrystalline ZnO:Al films have an approximate grain size between 50 and 200
nm, and thus have a much higher density of defects than etching points. To explain the etching
behavior of ZnO we assume the presence of certain “peculiar” defects that etch more rapidly in
acidic and basic solutions. These defects often reach all the way through the film, but they appear
to also have shorter range effects: etching sites may begin at the surface or somewhere in the
bulk of the ZnO film, and may extend part or all the way through the film.

CONCLUSIONS

Using an AFM repositioning method we have been able to image the same location
between small etching steps. With this technique, the evolution of the HCl etch on
polycrystalline ZnO, and the relation between etching in acidic and basic solutions were studied.
Specifically, we observed that stopping and restarting the etching process did not change the
points of attack, and that both acidic and basic solutions attack the same points. From these
observations we ruled out the status of the solution close to the film surface and adsorbed
molecules as etching catalysts, since both of these factors would change between etching steps.
We also ruled out a local chemistry effect such as the polarity of the ZnO crystallites, as the
points of attack would be different for etching in acidic and basic solutions. We concluded that
there are peculiar defects that induce accelerated etching built into the film during growth, and
that these defects can extent part or all the way though the thin-film in a similar way to screw
dislocations in single crystalline ZnO.

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