Influence of the film properties on the plasma etching dynamics of rf-sputtered indium zinc oxide layers

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The etching characteristics of indium zinc oxide (IZO) films were investigated using a high-density plasma in Ar, Ar/Cl2, and Ar/CH4/H2 chemistries. The IZO layers were deposited by means of rf magnetron sputtering, in which the target composition and growth temperature were varied to selectively tune the film properties. X-ray diffraction, elastic recoil detection, and Rutherford backscattering spectroscopy were used to determine the crystallization quality, atomic density, and composition of the as-deposited IZO films. As the In/(In+Zn) composition ratio in the IZO layer increases, the etch yield in Ar and Ar/Cl2 plasmas remains fairly constant, indicating that the etching dynamic is essentially independent of the film properties. In sharp contrast, a strong increase of the IZO etch yield with the In/(In+Zn) fraction is observed in Ar/CH4/H2 plasma due to the preferential desorption of the group-III etch products. By comparing these experimental data to the predictions of a simple rate model accounting for preferential desorption effects, it is concluded that the balance between etching and polymer deposition in the Ar/CH4/H2 plasma plays an important role in the evolution of the IZO etch rate with the In concentration fraction. © 2007 American Vacuum Society. [DOI: 10.1116/1.2736679]

I. INTRODUCTION

Because of their high electrical conductivity and high optical transparency, transparent conducting oxides (TCOs) have been extensively studied for transparent electrodes in various optoelectronic devices such as liquid-crystal displays, solar cells, and light-emitting diodes (LEDs). Although SnO2–In2O3 (ITO) is the most commonly used TCO for transparent electrodes,1–11 there is significant interest in developing new alternatives to this material because the scarcity of indium imparts a very high cost to ITO.13 To this end, numerous studies on binary, ternary, or even quaternary compound oxides composed of combinations of In, Zn, Cd, Sn, and Ga have been reported in the literature.14–27 Among these materials, the In2O3–ZnO (IZO) system has attracted a lot of attention because of the absence of toxic cadmium and the use of inexpensive zinc. In addition, compared to ITO, IZO layers are characterized by a larger work function13,28 and a superior transmission in the 1–1.5 μm range.29 Promising results on the use of IZO films for fabricating Ohmic contacts to n-type ZnO for LED applications were also recently reported.30

So far, IZO films have been prepared by metal organic chemical vapor deposition,31 sputtering,32–34 pulsed-laser deposition,35 and sol-gel.36 Although the growth characteristics of IZO layers are relatively well understood, the development of a reliable pattern transfer process for IZO is still in its infancy. Among the various patterning techniques, plasma etching is preferred because it allows high-resolution pattern transfer for device structures. Recently, the etch rate of IZO films in Ar/Cl2 and Ar/CH4/H2 plasma chemistries was shown to be influenced by the plasma characteristics such as reactive neutral density, positive ion density, and ion energy.37 However, in addition to the plasma parameters, it is also expected that the film properties somewhat impact the etching characteristics.

In this work, we investigate the influence of the film properties on the plasma etching dynamics of IZO layers through an extensive characterization. We first examine the effect of the target composition and deposition temperature on the properties of rf-sputtered IZO layers using x-ray diffraction (XRD), elastic recoil detection (ERD), and Rutherford backscattering spectroscopy (RBS). Based on this full characterization, it is shown that although the etch rates in Ar and Ar/Cl2 plasmas are independent of both the crystallization quality and film composition, the etching characteristics in Ar/CH4/H2 chemistries strongly depend on the In concentration fraction.

II. EXPERIMENTAL SETUP

IZO films were deposited on glass substrates (Corning EAGLE2000) using rf magnetron sputtering.
The layer thickness. To obtain the atomic density of the film integrated over the results of this fit provided the concentration fraction of each element and the atomic density of the film integrated over the film thickness. For all samples, we found that the atomic density $N_t$ is determined by dividing the areal atomic density obtained from the fit by the film thickness. The angle between the He beam and the surface normal was 7° to minimize channeling. The detector was placed at a scattering angle of 170°. The RBS spectra were then analyzed using SIMNRA simulations to take into account the non-Rutherford cross section on oxygen. The results of this fit provided the concentration fraction of each element and the atomic density of the film integrated over the layer thickness. To obtain the atomic density $N_t$, the integrated atomic density was divided by the film thickness measured by a KLA-Tencor surface profilometer. For further analysis, ERD measurements were also performed using a 4.57 MeV $^4$He$^{++}$ ion beam at normal incidence. The angle between the target and substrate was fixed at 70 mm. The deposition temperature was varied from room temperature (RT) to 500 °C.

High-density plasma etching of IZO films was realized using an Oerlikon (formerly UNAXIS) 790 inductively coupled plasma (ICP) reactor. The 2 MHz power applied to the ICP source and the rf (13.56 MHz) chuck power were held constant at 300 and 200 W, respectively. Etching was performed in Ar, Ar/Cl$_2$, and Ar/CH$_4$/H$_2$ chemistries. The Ar concentration in Ar/Cl$_2$ and Ar/CH$_4$/H$_2$ was controlled by varying the Ar mass flow rate between 0 and 20 sccm (Sccm denotes cubic centimeter per minute at STP), while keeping the Cl$_2$ and CH$_4$/H$_2$ mass flow rates constant (10 Sccm Cl$_2$ for Ar/Cl$_2$; 3 Sccm CH$_4$ and 10 Sccm H$_2$ for Ar/CH$_4$/H$_2$). The total gas pressure before plasma ignition was set to 5 mTorr. The IZO etch rate was determined from stylus profilometry measurements. During the current experiments, the plasma exposure time was set to 2 min for investigations realized in Ar/CH$_4$/H$_2$ and 5 min for those performed in Ar and Ar/Cl$_2$.

III. RESULTS AND DISCUSSION

A. Film properties

Figure 1 presents a typical RBS spectrum obtained from the IZO layer grown using a In$_2$O$_3$(ZnO)$_4$ target under RT conditions. The peaks observed in Fig. 1 correspond to O, Zn, and In, respectively, the O peak being superimposed to the broad glass substrate contribution. The results of the SIMNRA simulations are also shown for comparison. To account for the substrate contribution in the simulations, the back side of the sample was analyzed to determine the composition of the glass substrate. As mentioned above, $N_t$ can be determined by dividing the areal atomic density obtained from the fit by the film thickness. For all samples, we found $N_t \approx 82 \pm 5$ nm$^{-3}$. This value is very similar to that expected from bulk, single-crystal IZO. For example, for In$_2$O$_3$(ZnO)$_4$, the volume of the IZO lattice is 162 Å$^3$ with 13 atoms per unit cell, which yields $N_t = 80$ nm$^{-3}$.

The results for the concentration fraction of each element in the IZO films are displayed in Fig. 2 as a function of the $k$ value in the In$_2$O$_3$(ZnO)$_4$ target. The composition of the target is also shown for comparison. For both growth temperatures investigated, the Zn content is lower than that in the target, with this difference being larger for IZO films grown at 500 °C. This may result from a lower sticking coefficient and/or a higher vapor pressure of Zn compared to that of In. Figure 2 further shows that the oxygen content is fairly in-
dependent of the \( k \) value in both RT- and 500 °C-deposited IZO layers, with these values being similar to those expected from the target composition.

Because the O peak in the RBS spectra is weak and superimposed to the broad glass substrate contribution, there could be some errors in our determination of the O concentration. For validation, we have compared our RBS results to those of ERD. This technique is known to be more suitable for the analysis of light elements such as O in solids containing heavy atoms such as Zn and In. The results obtained for IZO films grown using the \( \text{In}_2\text{O}_3(\text{ZnO})_4 \) target at either RT or 500 °C are shown in Fig. 3 as typical examples. It can be seen that the concentration fractions of Zn and In in RT-deposited IZO films are about 29% and 17%, respectively, in excellent agreement with the results obtained by RBS. As for oxygen, the concentration fraction is 53±2%, which is also similar to the RBS results (54±2%). Figure 3 further shows that the depth profiles are smooth, with a relatively thick interface. Indeed, in both cases, the thickness of the interfacial region is about \( 35 \times 10^{16} \text{ at. cm}^{-2} \), which corresponds to an actual thickness of 40±5 nm.

Changes in the target composition can also induce modification of the microstructural properties of the film. To illustrate this behavior, Fig. 4 presents the influence of the \( k \) value in the \( \text{In}_2\text{O}_3(\text{ZnO})_4 \) target on the XRD spectra of IZO layers deposited at either RT [Fig. 4(a)] or 500 °C [Fig. 4(b)]. The films grown at RT are essentially amorphous for \( k \leq 4 \), whereas a small peak can be seen for \( k = 5 \) and \( k = 7 \). On the other hand, for IZO films grown at 500 °C, Fig. 4(b) shows a broad peak between 30.5° and 32.3°, which indicates that the films are crystalline and textured. According to Dupont et al., the broad XRD peak of IZO layers can be related to a distribution of \( \text{In}_2\text{O}_3 \) and \( \text{In}_2\text{O}_3(\text{ZnO})_k \) polytypes. The films grown using the \( k = 2 \) target show the lowest overall peak position at 30.5°, with this position being linked to the (222) plane of \( \text{In}_2\text{O}_3 \). For higher \( k \) values, the overall XRD peak is shifted toward higher diffraction angles. These higher 2\( \theta \) values can be attributed to the (00l) reflections of the \( \text{In}_2\text{O}_3(\text{ZnO})_k \) compounds.

**B. Etching characteristics**

Figure 5 presents the influence of the In concentration fraction on the sputter-etch yield of IZO films obtained in a
The sputter-etch yield $Y_{\text{phys}}$ can be determined from $ER = J_+ Y_{\text{phys}}/N_e$, where $ER$ is the sputter-etch rate and $J_+$ is the positive ion flux impinging onto the material surface. As the exact value of $J_+$ is unknown for the plasma under investigation, $J_+ Y_{\text{phys}}$ is displayed in Fig. 5 instead of $Y_{\text{phys}}$. Within the uncertainties, $J_+ Y_{\text{phys}}$ is seen to be independent of both the crystallization quality and composition of the IZO films. In Ref. 43, it was shown that the sputter-etch characteristics of pulsed-laser-deposited SrTiO$_3$ films can be influenced by the film microstructural properties. In particular, it was found that polycrystalline SrTiO$_3$ layers grown under relatively high oxygen background pressure present an atomic density much lower than that expected from bulk, single-crystal SrTiO$_3$ due to the presence of micropores within grain boundaries. For this latter system, the sputter-etch rate was found to be inversely proportional to the film atomic density, whereas the sputter-etch yield was constant for all deposition conditions. By comparison, the atomic densities of the IZO films investigated in the present work are similar independently of the growth conditions, and as a consequence, the sputter-etch rate and the sputter-etch yield are independent of both the crystallization quality and film composition.

Table I. Binding energies used in the Monte Carlo simulations.

<table>
<thead>
<tr>
<th></th>
<th>In</th>
<th>Zn</th>
<th>O</th>
</tr>
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<tbody>
<tr>
<td>Displacement energy (eV)</td>
<td>25</td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td>Lattice binding energy (eV)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Surface binding energy (eV)</td>
<td>2.49</td>
<td>1.35</td>
<td>2</td>
</tr>
</tbody>
</table>

We have compared our experimental results for the sputter-etch yield to those predicted by Monte Carlo simulations. For these simulations, we used the mass densities calculated from the RBS results. The binding energies used in the present simulations are those provided by the software. These values are listed in Table I. The energy of the argon ions was kept constant at 300 eV, which is similar to the value expected from the sum of bias voltage (−275 V) and sheath potential (−25 V) in the experiments. The results of our simulations are shown on the right axis of Fig. 5. It can be seen that the sputter-etch yield decreases only slightly with increasing In concentration fraction, with the mean value being $2.2 \pm 0.2$ atoms/ion. This dependence of the calculated etch yield is in very good agreement with that deduced from the experimental data. On the other hand, assuming that $J_+$ is in the typical $10^{16}$ cm$^{-2}$ s$^{-1}$ range for inductively coupled argon plasmas operated at low pressure, we estimate $Y_{\text{phys}} \sim 0.3$ from the experimental data presented in Fig. 5. Our experimental results are thus lower than those predicted by the Monte Carlo simulations. Among the possible explanations, this discrepancy is likely to result from the redeposition of sputtered species following their interaction with the gas phase, resulting in a lower effective sputter-etch yield. Indeed, it was shown that the degree of redeposition of sputtered metals such as Pt and complex oxides such as (Ba,Sr)TiO$_3$ and SrBiTa$_2$O$_9$ reaches $\approx 90\%$ in the 5–15 mTorr range.

Figure 6 presents the influence of the In concentration fraction on the normalized sputter-etch yield of O, In, and Zn obtained from the Monte Carlo simulations. This normalized sputter-etch yield was calculated according to

$$\text{Normalized etch yield} = \left( \frac{Y_j}{Y_{\text{tot}}} \right) / \xi_j,$$

where $Y_j$ is the etch yield of the element $j$, $Y_{\text{tot}}$ is the total etch yield (i.e., $Y_O + Y_{Zn} + Y_{In}$), and $\xi_j$ is the concentration fraction of the element $j$ in the as-deposited IZO films. Over the whole range of In concentration investigated, the normalized etch yield of Zn is found to be higher than 1. It is also higher than those of In and O by about a factor of 2. This indicates that during sputter etching of IZO layers by noble argon ions, there is preferential sputtering of the Zn atoms.
This result is in excellent agreement with our previous Auger electron spectroscopy measurements that showed a Zn-depleted IZO surface following sputter etching in a pure argon plasma. The influence of the indium concentration fraction on the etch yield of IZO layers in Ar/Cl₂ plasmas is shown in Fig. 7. Over the whole range of Ar concentrations investigated, the etch yield is seen to be similar for both amorphous and crystalline IZO layers. In addition, the IZO etch yield is independent of the film composition within experimental errors. Figure 7 further shows that \( J_+ Y \) increases with the Ar concentration. Assuming that the etch rate is ion-flux limited, i.e., \( ER = J_+ Y_{\text{sat}} / N_t \), where \( Y_{\text{sat}} \) is the ion-assisted chemical etch yield on an IZO surface saturated with reactive neutrals; the higher \( J_+ Y \) values can be attributed to the expected higher positive ion flux.

Figure 8 presents the influence of the indium concentration fraction on the etch yield of IZO films in Ar/CH₄/H₂ plasma. As in Figs. 5 and 7, there are no differences within the uncertainties between the etch yield of amorphous and crystalline IZO layers. Nevertheless, the IZO etch yields in Ar/CH₄/H₂ are, on the average, much higher than those presented in Figs. 5 and 7 for Ar and Ar/Cl₂ plasmas. In a previous paper, it was found that the depth profile of IZO layers after etching in CH₄/H₂/Ar plasmas presents a relatively thick In-depleted region, in which the Zn concentration fraction largely exceeds that in as-deposited IZO films. The higher etch yields displayed in Fig. 8 can therefore be understood from the preferential desorption of In-containing reaction products. Figure 8 further shows that the IZO etch yield increases only slightly at low indium concentration and then strongly increases beyond 17%. Similar results are obtained for all Ar concentrations in Ar/CH₄/H₂ investigated, with the etch yield simply increasing with the Ar concentration.

To gain further insights into the meaning of our results, we developed a simple rate model accounting for preferential etching effects. Generally, the etch yield of a multicomponent material can be written as the sum of the etch yields of each element. Indeed, despite possible variations in the surface composition upon preferential etching, conservation of mass implies that for sufficiently long etching times, the fraction of the etch yield of each element is given by its concentration fraction in the material. Therefore, for IZO films, one can write

\[
Y = \sum_i \xi_i Y_i = \xi_O Y_O + \xi_{Zn} Y_{Zn} + \xi_{In} Y_{In}.
\]

Since \( \xi_{O} + \xi_{Zn} + \xi_{In} = 1 \), Eq. (2) can then be rewritten as

\[
Y = \xi_O Y_O + (1 - \xi_O - \xi_{In})Y_{Zn}\left(1 + \frac{\xi_{In} Y_{In}}{(1 - \xi_O - \xi_{In})Y_{Zn}}\right).
\]

For the IZO films investigated in the present work, Fig. 2 has shown that \( \xi_{O} \) is approximately the same, independent of the target composition and growth temperature. Thus, for given plasma etching conditions, the only variable in Eq. (3) is \( \xi_{In} \).

We calculated the etch yield of the IZO films as a function of the In concentration fraction using Eq. (3). The results are shown in Fig. 9 for two \( (Y_{In}, Y_O, Y_{Zn}) \) calculation sets. Set 1 is \( Y_{In} = Y_O = 1; Y_{Zn} = 2 \). This set of individual etch yields is based on the normalized etch yields deduced from the Monte Carlo simulations for physical sputtering with Ar ions displayed in Fig. 6. In this framework, the calculated IZO etch yield is seen to only slightly decrease with increasing In concentration, in excellent agreement with both the experimental data and the simulations shown in Fig. 5. The dependence of the etch yield on \( \xi_{In} \) obtained from this set of calculations is also similar to the experimental data for IZO etching in Ar/Cl₂ plasmas presented in Fig. 7. This suggests that the relative values for the individual etch yields in the Ar/Cl₂ plasma are similar to those in a pure argon atmo-
sphere, in excellent agreement with the similar surface composition reported previously.\textsuperscript{37} Note that in the Cl\textsubscript{2} plasma, one would expect a very high fragmentation level of the Cl\textsubscript{2} molecules for the high-power-density conditions investigated.\textsuperscript{53} As a consequence, Cl\textsuperscript{+} should be the dominant chlorine charge carrier.\textsuperscript{54,55} Because the mass of Cl\textsuperscript{+} is close to that of Ar\textsuperscript{+}, the energy transferred by the incident ions through nuclear collisions in the material is similar for both ions, thereby yielding comparable individual etch yields.

Set 2 is $Y_{\text{Zn}}=Y_{\text{O}}=2$; $Y_{\text{In}}=20$. This set of etch yields corresponds to a situation where there is preferential desorption of In, as expected for IZO etching in Ar/CH\textsubscript{4}/H\textsubscript{2} plasmas (see Fig. 8). In this case, Fig. 9 shows a linear increase of the IZO etch yield with increasing $Y_{\text{In}}$. However, this linear dependence differs from that of the experimental data presented in Fig. 8, with the latter exhibiting a smoother variation at low In concentrations. This difference in the etch yield behavior can probably be attributed to the formation of the polymer layer during etching in methane-containing plasmas. Indeed, after ignition of the plasma, CH\textsubscript{4} deposition takes place on the IZO surface. Ion bombardment then results in breaking bonds and mixing of the near-surface region, and, thus, in the formation and release of the reaction products.\textsuperscript{56-58} However, due to the significant difference in the desorption rates of In- and Zn-containing reaction products, the rate of CH\textsubscript{4} consumption by the IZO layer will depend on the In concentration fraction, resulting in different balances between etching and deposition for the various IZO layers.\textsuperscript{59} This mechanism is not considered in the simple model presented above. Therefore, in the presence of polymer deposition, additional physics is required to adequately simulate the influence of the film composition on the etching characteristics of IZO layers.

IV. CONCLUSION

In this work, we examined the influence of the film properties on the plasma etching dynamics of IZO films in Ar, Ar/Cl\textsubscript{2}, and Ar/CH\textsubscript{4}/H\textsubscript{2} plasmas. In all plasma conditions investigated, the etching characteristics were found to be independent of the film crystallization quality. As the In/(In + Zn) composition ratio in the IZO layer increases, the etch yield in Ar and Ar/Cl\textsubscript{2} plasmas remained approximately the same, in excellent agreement with both Monte Carlo simulations and the predictions of a simple rate model accounting for preferential etching effects. In sharp contrast, a strong increase of the IZO etch yield with the In/(In + Zn) fraction was observed in Ar/CH\textsubscript{4}/H\textsubscript{2} plasma because of the preferential desorption of the group-III etch products. However, for this latter system, it was suggested that the balance between IZO etching and polymer deposition plays an important role in predicting the evolution of the IZO etch rate with the indium concentration fraction.

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