Etching mechanisms of (In, Ga, Zn)O thin films in CF$_4$/Ar/O$_2$ inductively coupled plasma
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Etching mechanisms of (In, Ga, Zn)O thin films in CF₄/Ar/O₂ inductively coupled plasma

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The authors investigated the etching characteristics and mechanisms of (In, Ga, Zn)O (IGZO) thin films in CF₄/Ar/O₂ inductively coupled plasmas. The etching rates of IGZO as well as the IGZO/SiO₂ and IGZO/Al₂O₃ etching selectivities were measured as functions of O₂ content in a feed gas (0%–50%) and gas pressure (p = 4–10 mTorr) at fixed input power (W_{inp} = 700 W) and bias power (W_{dc} = 200 W). It was found that the IGZO etching rate decreases monotonically toward O₂ rich plasma but exhibits a maximum under gas pressure conditions. The zero-dimensional plasma model with Langmuir probe diagnostics data provided the information on plasma parameters and densities of plasma active species. The model-based analysis shows the dominance of the ion-flux-limited etching regime at p/C₂ > 6 mTorr as well as the noticeable influence of CFₓ radicals on the overall etching kinetics. © 2015 American Vacuum Society [http://dx.doi.org/10.1116/1.4913735]

I. INTRODUCTION

Recently, a lot of new materials have been studied to evaluate their potentialities for modern micro and nanoelectronics technology. Among these materials, there is the family of transparent conductive oxides (TCOs) used for electrodes in flat panel displays, solar cells, and organic light emitting diodes. Initially, the dominant attention was attracted to the indium tin oxides (In₂O₃(SnO₂)ₓ (ITO)). The attractive properties of the ITO thin films were their low electrical resistivity and high optical transparency in the visible range of the spectrum. Later, it was found that ZnO-based TCOs have advantages compared to ITO with nontoxicity, lower cost, and higher thermal and chemical stabilities. Furthermore, it has been reported that the properties of the ZnO thin films can be effectively improved by some dopants, including In and Ga. Therefore, development and optimization of the dry etch process for (In, Ga, Zn)O (IGZO) thin films is an important task to be solved to allow accurate pattern transfer and stable device parameters.

Most existing work on the etching characteristics of the ZnO-based TCOs relates to the undoped ZnO. The results can be summarized as follows:

1. Hydrocarbon-based etching chemistries (CH₄, C₂H₆) provide the highest etching rates (up to 200 nm/min) due to the formation of highly volatile metal-organic compounds, but suffer from polymer deposition and degradation of the photoluminescence properties of the etched surface.

2. In chlorine-based (Cl₂, BCl₃) plasmas, the ZnO etching process occurs mostly in the ion flux-limited etching regime and is characterized by a relatively low etching rate (~80–90 nm/min).

3. Bromine-based (HBr) etching chemistry provides the lowest etching rate (~30–40 nm/min), while the etching process occurs in the reaction rate-limited etch regime with Br atoms acting as the main chemically active species. The addition of even a small amount of fluorine-containing gas decreases the ZnO etching rate [by a factor of 3 at 15% CHF₃ in HBr (Ref. 14)]. The same etching mechanism was also found for the Gadoped ZnO thin films.

These features are in general agreement with the volatilities of reaction products, which can be characterized by their melting points (Fig. 1). For the IGZO thin films, there are only few reports on their etching characteristics and mechanisms in Cl₂ and BCl₃ based plasmas. In particular, it was found that BCl₃-based plasma provides higher IGZO etching rate compared with Cl₂-based plasmas, and the BCl₃ radicals play the dominant role in the etching process. Also, the addition of O₂ to BCl₃ accelerates the IGZO etching process as has been repeatedly mentioned for many other oxide materials. The etching characteristics and mechanisms of IGZO thin films with fluorine-based gas chemistries have received little attention and, in fact, have not been explored in detail.

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In this work, we focused on investigating the etching characteristics and mechanisms for IGZO thin films with CF$_4$/Ar/O$_2$ gas chemistry. Our main goal was to understand how variations of gas mixing ratio and gas pressure influence the IGZO etching rate through the changes of internal plasma characteristics and composition. For this purpose, model-based analysis of plasma chemistry and etching kinetics was applied. Our interest in both SiO$_2$ and Al$_2$O$_3$ was due to their frequent use as the under- or overlaying layers in the IGZO-based devices. Therefore, these two materials were examined only to obtain the etching selectivity over IGZO. For both SiO$_2$ and Al$_2$O$_3$, the etching mechanism(s) in CF$_4$-based plasmas is not the key issue in this work because of much previous research.

II. EXPERIMENTAL AND MODELING DETAILS

A. Film preparation techniques

The IGZO thin films were deposited on thermally oxidized (300 nm) Si (100) substrate using radio frequency magnetron sputtering. The target was composed of In:Ga:Zn = 2:2:1 at. %. The process was performed in 8 sccm Ar + 2 sccm O$_2$ gas mixture at chamber pressure 0.75 mTorr and input power 400 W. The thickness of the IGZO films was ~100 nm. The film composition, determined by Auger analysis, was In:Ga:Zn:O at 19:18:8:55 atomic percentages, respectively.

B. Experimental setup and plasma diagnostics

Both etching and plasma diagnostics experiments were performed in a planar inductively coupled plasma (ICP) reactor. The reactor had a cylindrical (r = 16 cm) chamber made from anodized aluminum and a five-turns copper coil located above a 10 mm horizontal quartz window. The coil was connected to a 13.56 MHz power supply. The distance (l) between the window and the bottom electrode, used as a substrate holder, was 12.8 cm. The bottom electrode was connected to a 12.56 MHz power supply to maintain a negative dc bias voltage (−$U_{dc}$). The temperature of the bottom electrode was stabilized at 17 °C, using a water flow cooling system. The etched samples, ~2 × 2 cm$^2$, were placed in the center of the bottom electrode. Etched depths were measured using a surface profiler (Alpha-step 500, Tencor). For this purpose, we developed line striping of the photoresist (PR) (AZ1512, positive) with line width/spacing ratio 2 μm/2 μm. The initial thickness of the PR layer was ~1.5 μm.

Plasma diagnostics were measured by double Langmuir probe (LP) (DLP2000, Plasmart, Inc.). The probes were installed through the viewport on the sidewall of the reactor chamber at 5.7 cm above the bottom electrode and centered in a radial direction. The treatment of $I−V$ curves aimed at obtaining electron temperature (T$_e$) and ion saturated current density ($J_s$) was carried out using the software supplied by the equipment manufacturer. The calculations were based on Johnson and Malter double probe theory with the one-Maxwellian approximation for the electron energy distribution function (EEDF). In order to obtain the total positive ion density ($n_+$) from the measured $J_s$, we used Allen–Boyd–Reynolds’ approximation $J_s \approx 0.61e n_+ v_b$, where $v_b = \sqrt{e T_e / m_i}$ is the ion Bohm velocity. The effective ion mass, $m_i$, was evaluated using Blank’s law, assuming $y_i = k_i y$, where $y_i$ is the mole fraction of each ion inside $n_+$, $k_i$ is the ionization rate coefficient, and $y$ is the mole fraction of the corresponding neutral particle.

To investigate the effects of O$_2$ mixing ratio, the experiments were performed at fixed total gas flow rate ($q = 40$ sccm), gas pressure ($p = 6$ mTorr), bias power ($W_{dc} = 200$ W), and input power ($W_{inp} = 700$ W). In Figs. 2, 4, and 6, the corresponding series of experiments (or model runs) are marked by label “1.” The initial compositions of the CF$_4$/Ar/O$_2$ mixtures were set by adjusting the flow rates of the corresponding gases. In these experiments, the CF$_4$ flow rate $q_{CF_4}$ was fixed at 20 sccm, while O$_2$ and Ar were mixed at various ratios within $q_{O_2} + q_{Ar} = 20$ sccm. Accordingly, the fraction of CF$_4$ in the initial gas mixture $y_{CF_4} = q_{CF_4}/q$ was always 0.5, and the remainder was represented by the different amounts of O$_2$ and Ar. The variation of O$_2$ content in a feed gas in the range of 0%–50% corresponds to the transition between CF$_4$/Ar and CF$_4$/O$_2$ gas systems.

To investigate the effects of gas pressure, we employed Ar rich (50% CF$_4$ + 38% Ar + 12% O$_2$) and O$_2$ rich (50% CF$_4$ + 12% Ar + 38% O$_2$) plasmas. In Figs. 2, 4, and 6, the corresponding series of experiments (or model runs) are marked by labels “2” and “3,” respectively. The experiments were carried out for $p = 4$–10 mTorr at $q = 40$ sccm, $W_{dc} = 200$ W and $W_{inp} = 700$ W.

In all cases, each experimental point was reproduced for 5–7 times in order to control the experimental error. The relative error was ~10%–12% for the etching rate measurements and about ~3%–5% for the LP measurements.

C. Plasma modeling

To obtain data on densities and fluxes of plasma active species, we used a simplified zero-dimensional model with one-Maxwellian EEDF and the experimental data on $T_e$ and $n_+$ as input parameters. Such simplification for the CF$_4$
based low-pressure ($p < 50$ mTorr) ICPs provides reasonable agreement between the plasma diagnostics and modeling.\textsuperscript{22–24}

The electron density ($n_e$) was estimated from simultaneous solution of the steady-state ($dn/dt = 0$) equation of chemical kinetics for negative ions and the quasineutrality equation

$$n_e \approx \frac{k_{ia}n_i^2}{\sum k_{ja}n_j + k_{ii}n_i}.$$  

The rate coefficients of dissociative attachment $k_{ia}$ for neutral species with partial densities of $n$ were taken from Refs. \textsuperscript{25–27} as functions of $T_e$. The ion–ion recombination rate coefficient, \( k_{ii} = 1 \times 10^{-7} \text{ cm}^3/\text{s} \), was assumed to be the same for all types of positive and negative ions.\textsuperscript{26,27}

The steady-state densities of neutral species were obtained from the system of chemical kinetics equations in the general form $R_F - R_D = (k_F + 1/\tau_R)n$, where $R_F$ and $R_D$ are the volume averaged formation and decay rates in bulk plasma for a given species, $k_F$ is the first order heterogeneous decay rate coefficient, and $\tau_R = \pi \sigma^2 \lambda p / q$ is the residence time. The list of processes included in the model is given in Table \textbf{I}. Compared with our previous work,\textsuperscript{24} this table contains only those reactions with a principal influence on the particle balance for the given range of experimental conditions. The rate coefficients for electron impact reactions (R1–R16) were calculated using the fitting expressions $\kappa = AT^\alpha \exp(-C/T_e)$,\textsuperscript{24–27} The rate coefficients for R17–R48 were taken from Bose \textit{et al.}\textsuperscript{26} and NIST chemical kinetics database\textsuperscript{28} for the gas temperature ($T$) of 700 K. The last was assumed to be independent of the variable operating parameters. The rate coefficients for heterogeneous loss of atoms and radicals, R49–R55, were taken similarly to Ref. 21 as $k_S = (\lambda^2 / D + (2r / \nu_T)^2)^{-1}$, where $D$ is the effective diffusion coefficient, $\gamma$ is the sticking probability,\textsuperscript{25,27} $\lambda^{-2} = (2.405/r)^2 + (\pi / l)^2$ is the diffusion length, and $\nu_T = (8kBT / \pi m)^{1/2}$. All reaction pathways between the adsorbed (marked by the $s$ index) and gaseous species inside R49–R55 were assumed to be of equal probabilities. The rate coefficients for heterogeneous loss of ions R56 were calculated as $k_5 = v / d_1$, where $d_1 = 0.5r l / (ph_2 + lh_2)$. The correction factors for axial, $h_1$, and radial, $h_2$, sheath sizes are given by low pressure diffusion theory.\textsuperscript{29}

### III. RESULTS AND DISCUSSION

#### A. Etching rates and selectivities

Figure 2(a) shows that an increase in O$_2$ fraction in a feed gas at constant chamber pressure results in the monotonic decrease in the IGZO etching rate from 27.8 to 4.6 nm/min for 0%–50% O$_2$. Therefore, the IGZO etching rate in the CF$_4$/O$_2$ gas system is reduced by a factor $\sim$6 compared to that in the CF$_4$/Ar gas system. An increase in gas pressure in the range of 4–10 mTorr causes the nonmonotonic IGZO etching rates in both Ar rich and O$_2$ rich plasmas, with the maximum etching rates correspond to $p = 6$ mTorr. The relative heights of maxima in both Ar rich and O$_2$ rich plasmas are also quite close and occupy the range of 1.7–1.8 times compared with the etching rate corresponding to the lowest pressure end.

The etching rates of SiO$_2$ and Al$_2$O$_3$ exhibit weakly non-monotonic behaviors with increasing O$_2$ mixing ratio. For both materials, the etching rates in the CF$_4$/O$_2$ gas system are significantly higher compared with those in the CF$_4$/Ar gas system, so that the IGZO/SiO$_2$ and IGZO/Al$_2$O$_3$ etching selectivities show deep (about an order of magnitude) falls toward more oxygenated plasmas [Fig. 2(b)]. Whereas the behaviors of both SiO$_2$ and Al$_2$O$_3$ etching rates versus gas pressure are similar to that for IGZO. Thus, the corresponding etching selectivities may be characterized by the constant averaged values.

#### B. Plasma parameters and densities of active species

Figure 3 presents the results of plasma diagnostics by Langmuir probes. Figure 3(a) shows that substitution of Ar for O$_2$ results in decreasing $T_e$ in the range of 3.63–3.82 eV at $p = 6$ mTorr. This is due to an increase in the electron energy loss for the low-threshold excitations (vibrational, electronic) of O$_2$ and other molecular species, which appear in a gas phase as products of plasma chemical reactions. The similar behavior of $T_e$ with increasing gas pressure...
<table>
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<th>$\epsilon_{th}$ (eV)</th>
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<td>$F_2 + CF = CF_2 + F$</td>
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<td>$F_2 + O(1d) = FO + F$</td>
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<td>$F_2 + CFO = CFO_2 + F$</td>
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<td>$CF_2 + O = CFO + F$</td>
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<td>$CF_2 + O(1d) = CFO_2 + F$</td>
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<td>$CF_2 + F = CF_3$</td>
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<td>$CF_2 + O = CFO + F$</td>
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<tr>
<td>R28</td>
<td>$CF_2 + O = CO + 2F$</td>
<td>$3.98 \times 10^{-12}$</td>
</tr>
<tr>
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<td>$CF_2 + O(1d) = CO + 2F$</td>
<td>$3.98 \times 10^{-12}$</td>
</tr>
<tr>
<td>R30</td>
<td>$CF + F = CF_2$</td>
<td>$5.01 \times 10^{-15}$</td>
</tr>
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<td>$CF + O = CO + F$</td>
<td>$6.31 \times 10^{-11}$</td>
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<tr>
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<td>$CF + O(1d) = CO + F$</td>
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<tr>
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<td>$CF + O_2 = CFO + O$</td>
<td>$3.16 \times 10^{-11}$</td>
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<td>R34</td>
<td>$FO + O = F + O_2$</td>
<td>$2.51 \times 10^{-11}$</td>
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<td>$FO + O(1d) = F + O_2$</td>
<td>$5.01 \times 10^{-11}$</td>
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<td>R36</td>
<td>$2FO = F_2 + O_2$</td>
<td>$2.51 \times 10^{-12}$</td>
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<td>R37</td>
<td>$3.89$</td>
<td>$2.51 \times 10^{-16}$</td>
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<td>R38</td>
<td>$CFO + CF_2 = CF_3 + CO$</td>
<td>$1.00 \times 10^{-11}$</td>
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<td>$1.00 \times 10^{-11}$</td>
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<tr>
<td>R45</td>
<td>$CFO + F = CFO_2$</td>
<td>$7.94 \times 10^{-11}$</td>
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<td>R46</td>
<td>$CFO + O(1d) = F_2 + CO_2$</td>
<td>$2.00 \times 10^{-11}$</td>
</tr>
<tr>
<td>R47</td>
<td>$C + O_2 = CO + O$</td>
<td>$1.58 \times 10^{-11}$</td>
</tr>
<tr>
<td>R48</td>
<td>$CO + F = CFO$</td>
<td>$1.29 \times 10^{-11}$</td>
</tr>
<tr>
<td>R49</td>
<td>$F = f(\gamma) + CF_2 = CF_4$</td>
<td>$f(\gamma), \gamma = 0.05$</td>
</tr>
<tr>
<td>R50</td>
<td>$CF_3 = CF_2 + F = CF_4$</td>
<td>$f(\gamma), \gamma = 0.05$</td>
</tr>
</tbody>
</table>
CF4/Ar/O2 gas mixture on the densities of neutral species. In 0%–50% O2 at where gas changes from CF4/Ar to CF4/O2, we obtain constant chamber pressure. As the composition of the feed and CF2O (R16). The acceleration of R8 compared with the behavior of n+, while the gap between n+ and ne increases with more oxygenated plasmas and higher pressures. In our opinion, such effects are caused by a combination of two phenomena. First, a decrease in T e suppresses the ionization through the decreasing ionization rate coefficients for all types of neutral species. The high sensitivity of ionization rate coefficients to Te is due to εi ≈ 12–15 eV > (3/2)Te, where εi is the threshold energy for ionization, and (3/2)Te is the mean electron energy. Second, the substitution of Ar for O2 as well as an increase in gas pressure, results in increasing densities of electronegative species due to both O2 itself and oxygen-containing reaction products. This increases plasma electronegativity (n−/ne = 0.14–0.41 for 0%–50% O2 at p = 6 mTorr, 0.13–0.32 for p = 4–10 mTorr in Ar rich plasma and 0.22–0.56 for p = 4–10 mTorr in O2 rich plasma) and accelerates the decay for positive ions and electrons through ion–ion recombination and dissociative attachment, respectively.

Figure 4 illustrates the influence of O2 content in the CF4/Ar/O2 gas mixture on the densities of neutral species. In the presence of oxygen, the F atom formation kinetics in electron-impact processes is noticeably influenced by several stepwise channels involving F2 (R8), FO (R14), CFO (R15), and CF2O (R16). The acceleration of R8 compared with the nonoxygenuated plasmas is due to increasing F2 density (nF2 = 6.84 × 1011–2.99 × 1013 cm−3 for 0%–50% O2), because of increasing formation rates in R46 and R49. The high density of FO (8.18 × 1010–6.23 × 1012 cm−3 for 12%–50% O2) is provided by a combined effect of R20, R49, and R54. The high formation rate for CFO species is supported by R16 and R48 while CF2O is effectively formed in R39, R44, and R45. Furthermore, when the O2 fraction in a feed gas exceeds 25% (i.e., yO2 > yAr), the contribution of atom–molecular reactions R35–R37 and R42 to the F atom formation rate reaches the level of R14–R16. Consequently, in the 50% CF4 + 50% O2 gas mixture, the total effect from the electron-impact dissociations of reaction products (R8 and R14–R16) and atom–molecular reactions (R35–R37 and R42) exceeds the formation rate of F atoms due to the dissociation of CFO in R1–R3. As a result, the efficiency of all electron-impact reactions are slightly suppressed by decreasing Te and ne, the substitution of Ar for O2 in the CF4/Ar/O2 gas mixture under the given process conditions provides a continuous increase in the total F atom formation rate and F atom density. The density of CF3 radicals decreases toward O2 rich plasmas due to increase decomposition rates in R23, R24 with the participation of O, O(1D) and in R38, R39, with the participation of CFO. Similar mechanisms result in decreasing densities for CF2 and CF.

The behavior of F atom density versus gas pressure was found to be similar for both Ar rich (nF = 1.68 × 1013–4.01 × 1013 cm−3 for p = 4–10 mTorr) and O2 rich (nF = 2.83 × 1013–7.09 × 1013 cm−3 for p = 4–10 mTorr) plasmas. The first case is mainly supported by increasing rates of R1–R3 and R14–R16 while in the second case the dominant role belongs to R14–R16 and R35–R37. The density of CFx (x = 1–3) radicals in Ar rich plasma increases monotonically toward higher pressures (for example, nCF3 = 1.27 × 1012–2.29 × 1012 cm−3 for p = 4–10 mTorr) following formation rates of these species in R1, R2, R4, and R5. In the highly oxygenated plasmas, this effect is over-compensated by the faster growth of decay frequencies of the CFx species in the processes involving O, O(1D), and CFO. As a result, CFx densities decrease monotonically.
toward higher pressures (e.g., \( n_{\text{CF}_4} = 1.92 \times 10^{10} - 7.01 \times 10^9 \text{ cm}^{-3} \) for \( p = 4 - 10 \text{ mTorr} \)).

**C. Etching mechanism approaches**

It is well known that, when a chemically active gas is used for the etching process, the etching mechanism is determined by two main factors: the type of dominant active species and the volatility of reaction products. From Fig. 1, it can be understood that all IGZO-related metal fluorides are low volatile compounds. This allows one to neglect the spontaneous (thermally activated) desorption of reaction products and assume the IGZO etching mechanism to be the ion assisted chemical reaction. For further analysis, let us first account for the simplest situation with following assumptions:

1. The main chemically active species are the fluorine atoms. Since all three oxide bonds are weaker than the fluoride ones (Fig. 5), a spontaneous chemical reaction between F atoms and IGZO-forming oxides at nearly room temperatures is possible. This means that the rate
of chemical etching pathway is not limited by the ion-induced destruction of oxide bonds. Accordingly, it can be characterized by $\gamma_R \Gamma_F$ \cite{30,32}, where $\Gamma_F$ is the flux of F atoms, and $\gamma_R$ is the averaged reaction probability. For a given composition of reaction products, $\gamma_R = \text{const}$ at constant surface temperature.

(2) The main role of ion bombardment is the ion stimulated desorption of reaction products. The rate of this process is given by $Y_\perp \Gamma_\perp$ \cite{30,32}, where $\Gamma_\perp \approx J_\perp/\epsilon$ is the total flux of positive ions on the etched surface, and $Y_\perp$ is an averaged desorption yield. For ion bombardment energy $\epsilon < 500$ eV, one can assume $Y_\perp \sim \epsilon^{1/2}$ \cite{32}. Therefore, the rate of the physical etching pathway can be characterized by the parameter $\sqrt{\epsilon} \Gamma_\perp$ (the ion energy flux), where $\epsilon \approx \epsilon^f - U_{\text{f}} - U_{\text{dc}}$, and $U_f \equiv 0.5T_i \ln(m_i/2.5m_e)$ is the floating potential.

(3) The etching mechanism is not affected by the fluorocarbon polymerization on the surface. This means that the thin steady-state (nonreactive) fluorocarbon layer does not limit the transport of F atoms to the etched surface, and hence does not result in sufficient energy loss for ions. At the least, this same assumption will not disturb the good agreement between measured and model-predicted SiO$_2$ etching rates in CF$_4$/Ar/O$_2$ plasma under the close range of the experimental conditions \cite{24}.

These allow one to consider the IGZO etching mechanism as a simple sequential two-step process

\begin{equation}
\text{(In, Ga, Zn)O + F} \rightarrow \text{(In, Ga, Zn)F + O}, \tag{1}
\end{equation}

\begin{equation}
\text{(In, Ga, Zn)F + ion} \rightarrow \text{desorbed (In, Ga, Zn)F}. \tag{2}
\end{equation}

Figure 6(a) shows that an increase in both O$_2$ fraction in the feed gas and gas pressure is accompanied by similar increasing tendencies for $U_{\text{dc}}$ and thus, for ion bombardment energies ($\epsilon_0 = 235–274$ eV for 0%–50% O$_2$ at $p = 6$ mTorr, 254–263 eV for $p = 4–10$ mTorr in Ar rich plasma and 262–275 eV for $p = 4–10$ mTorr in O$_2$ rich plasma). However, this effect is overcompensated by decreasing $\Gamma_\perp$, so that a monotonic decrease in $\sqrt{\epsilon} \Gamma_\perp$ toward more oxygenated plasmas and higher pressures occurs [Fig. 6(b)]. On the contrary, the fluxes of F atoms show a monotonic increase [Fig. 6(c)] following the densities of these species in a gas phase. The comparison of Figs. 2(a), 6(b), and 6(c) allows one to propose the IGZO etching mechanism as follows: It seems that for $p \geq 6$ mTorr, the ion bombardment does not provide effective cleaning of the etched surface from the reaction products. As a result, the IGZO etching process occurs in the ion-flux-limited etching regime, and the etching rate follows $\sqrt{\epsilon} \Gamma_\perp$. For lower pressures, the etched surface is clean enough. Probably, such a condition is provided by the combination of lower fluorination rate and higher rate of ion-stimulated desorption. Here, the etching process occurs in the neutral-flux-limited mode, and the rate reflects the behavior of $\Gamma_F$. Therefore, the nonmonotonic change of the IGZO etching rate versus gas pressure results from the change of the process limiting condition from stages (1) to (2).

Though the above explanation appears reasonable, it somewhat suffers from the quantitative disagreement between the changes of etching rate and ion energy flux. As the O$_2$ fraction in the CF$_4$/Ar/O$_2$ plasma increases from 0% to 50%, the IGZO etching rate decreases by a factor $\sim$6, while $\sqrt{\epsilon} \Gamma_\perp$ loses only 30% of its original value. To remove such inconsistency, we propose the following three
additional reaction pathways influencing the overall etching kinetics:

\[(\text{In}, \text{Ga, Zn}) \text{O} + \text{CF}_x \rightarrow \text{COF}_x + (\text{In}, \text{Ga, Zn}), \quad (3)\]
\[(\text{In}, \text{Ga, Zn}) + \text{CF}_x \rightarrow (\text{In}, \text{Ga, Zn})\text{CF}_x, \quad (4)\]
\[(\text{In}, \text{Ga, Zn})\text{CF}_x + \text{ion} \rightarrow \text{desorbed (In, Ga, Zn)}\text{CF}_x. \quad (5)\]

The possibility of stage (3) at nearly room temperatures directly follows from the comparison of bond strengths in Fig. 5. The possibility of stage (4) is confirmed by the data where the authors have found Zn(CFx) compounds on the ZnO surface treated in CF4/Ar plasma under a close range of experimental conditions. If one assumes a higher yield of ion-stimulated desorption for (In, Ga, Zn)CFx compared with (In, Ga, Zn)F, the situation becomes clear. Since the fluxes of F atoms and CFx radicals have opposite behaviors versus gas mixing ratio [Fig. 6(c)], an increase of O2 fraction in a feed gas changes the composition of reaction products and leads to decreasing effective desorption yield. Therefore, the deep fall in the IGZO etching rate toward O2 rich plasmas is probably provided by the simultaneous decrease of both multiplicands in \(Y_d\Gamma_e\).

IV. CONCLUSION

In this work, we investigated etching characteristics and mechanisms of IGZO thin films in CF4/Ar/O2 inductively coupled plasmas. The variable parameters were the fraction of O2, and hence Ar, in the feed gas and the gas pressure. It was found that the IGZO etching rate decreases monotonically toward O2 rich plasma (27.8–6.4 nm/min for 0%–50% O2), but exhibits a maximum versus gas pressure at \(p = 6\) mTorr for both Ar rich and O2 rich plasmas. To obtain the data on plasma parameters, densities, and fluxes of plasma active species needed for the analysis of the etching mechanism, we used a combination of plasma diagnostics from Langmuir probes and the zero-dimensional plasma model. The model-based analysis of etching kinetics showed the basic features of the IGZO etching mechanism to be as follows: (1) at \(p \geq 6\) mTorr the etching process occurs in the ion-flux-limited etching regime, and (2) CFx radicals have significant influence on the overall etching chemistry.

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