A Study of Etch Characteristics of ITO Thin Film using the Plasma Diagnostic Tools

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Abstract

In this study, high-density plasma etching characteristics of ITO(indium tin oxide) films used for transparent electrodes in display devices have been investigated. The etch characteristics of ITO as a function of Ar/CH_4 gas mixtures were analyzed using QMS(quadrupole mass spectrometry), OES(optical emission spectroscopy), and ESP(electrostatic probe). ITO etch rates were increased with the addition of moderate amount of CH_4 to Ar due to the increased chemical reaction between CH_3 or H and ITO in addition to the physical sputtering of ITO by Ar ion bombardment. However, the addition of excess amount of CH_4 decreased the ITO etch rates possibly due to the increased polymer formation on the ITO surface. Also, the measurement data obtained by QMS and OES suggested that CH_3 radicals are more activity involved in the etching of ITO compared to H radicals.

Introduction

Indium tin oxide (90wt.%In_2O_3, 10wt.%SnO_2; ITO) thin films used for the fabrication of display devices require high optical transmittance and excellent electrical conductivity, and the properties of the ITO thin films depend on the deposition methods. However, the wet etching methods currently used for ITO etching tend to produce different ITO etch rates depending on the deposition methods in addition to isotropic etching and selective grain-boundary etching. Therefore, it may not be suitable for the fabrication of fine patterns required for next generation display devices.[1] Recently, the necessities of the research on the dry etching of ITO thin films have been increased to improve fine line patterning of ITO lines and also to obtain optimized selectivities over SiO_2 and Si_3N_4 underlayers used in the pixel electrode applications.[2]

In this study, dry etching characteristics of ITO films and etch selectivities over SiO_2 and Si_3N_4 were investigated using Ar/CH_4 and Ar/H_2 inductively coupled plasmas and the etching mechanism of ITO thin films was studied using plasma diagnostic tools(QMS, OES, and ESP).

Experiment

In this study, ITO thin films and underlayers (Si_3N_4 and SiO_2) were etched using a planar inductively coupled plasma etching equipment described elsewhere.[3] ITO films used in this experiment were sputter deposited on the glass to the thickness of 180nm and showed the resistivity of $2\sim3\times 10^{-4}\Omega$ cm. SiO_2 ($\sim$300nm) and Si_3N_4($\sim$270nm) used for the underlayers were deposited by PECVD (plasma enhanced chemical vapor deposition). ITO etchings were performed as a function gas combination of Ar/CH_4 and Ar/H_2 while other etch parameters such as rf power, pressure, and bias voltage were fixed at 500W, 15mTorr, and -200V respectively. The etch rates of ITO, SiO_2, and Si_3N_4 were measured using a surface profilometer after stripping the photoresist masked on the film.

To observe the effects of plasma conditions on the etch characteristics of ITO films, QMS(Hiden Analytical Inc.; PSM500), OES (SC Technology; PCM402), and Langmuir probe (electrostatic probe; Hiden analytical Inc.) located on the sidewall of the process chamber were used.

Results and Discussion

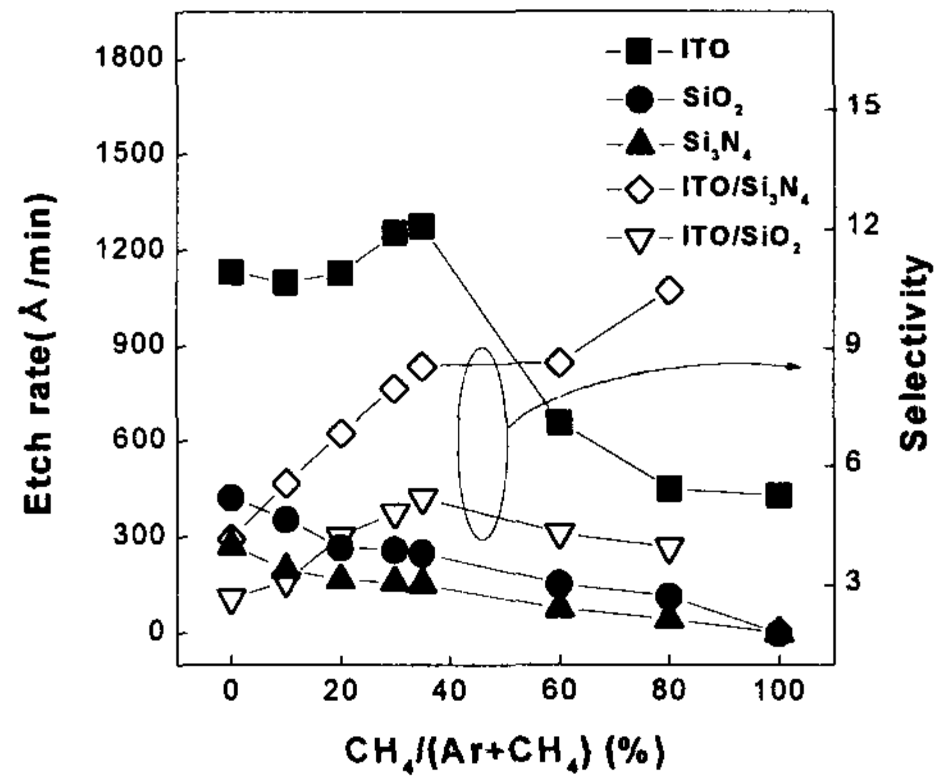


Fig. 1. Etch rates of ITO films and underlayers (SiO_2, Si_3N_4) and ITO etch selectivities over the underlayers as a function of gas ratio of CH_4/(Ar+CH_4). (500W, -200V, 15mTorr)

Figure 1 shows the etch rates of ITO, SiO_2, and Si_3N_4 as a function of CH_4 in the gas mixture of CH_4/Ar at 500 Watts of rf power, -200 Volts of dc-self bias voltage, and 15mTorr of operational pressure. The ITO etch selectivities over SiO_2 and Si_3N_4 were also included in the figure. As shown in the figure, with the increase of CH_4, ITO etch rates increased until 35% of CH_4 is reached, however, the further increase of CH_4 decreased ITO etch rates. In the cases of SiO_2 and Si_3N_4, the etch rates decreased monotonically with the increase of CH_4 percentage in the gas mixture. The ITO etch selectivity over Si_3N_4 was generally higher than that over SiO_2, and, when CH_4 was added more than 80%, the etch selectivity over Si_3N_4 was infinite due to the etch stop of Si_3N_4.

To study the effects of CH_4/Ar plasma conditions on the ITO etch rates, the characteristics of CH_4/Ar plasmas were investigated using QMS, OES, and Langmuir probe for the etch conditions measured for Figure 1, and the results are shown in Figure 2 (a) for QMS, (b) for OES, and (c) for Langmuir probe. When the radicals dissociated from CH_4 in the CH_4/Ar plasmas were measured using QMS, the peaks from H_2, H, CH_2, and CH_3 were observed and, among these, the peak intensity from CH_2 was the smaller compared to the other peak intensities throughout the CH_4/Ar gas mixtures used in the experiment. Also, it is known from the other researchers that H radicals and CH_3 radicals are the main reactive radicals affecting the ITO etch rates.

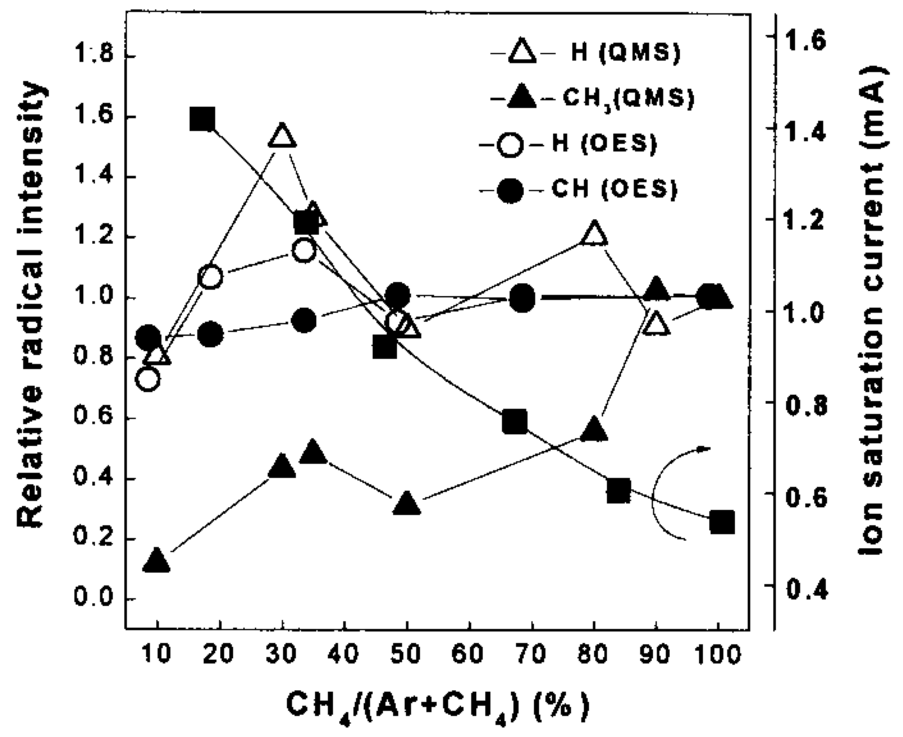
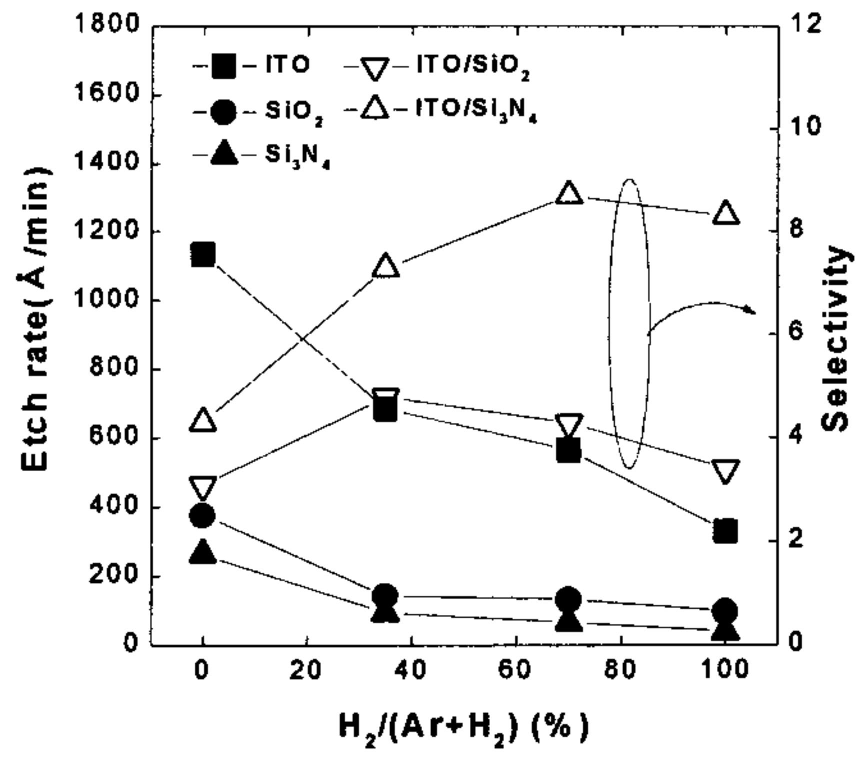


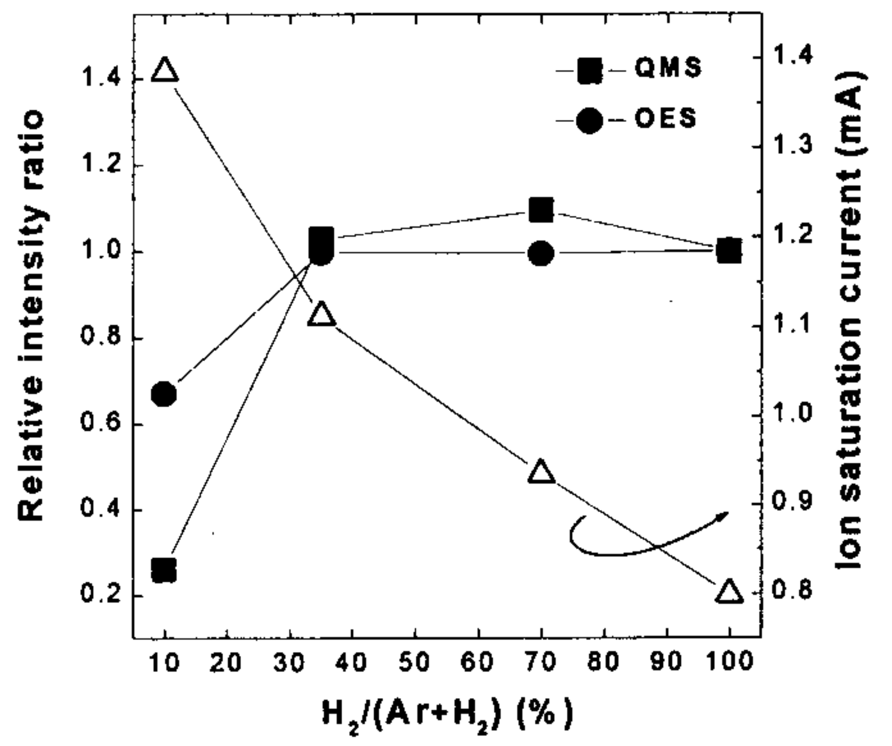
Fig. 2. Relative radical intensities measured by (a) QMS and (b) OES and ion saturation currents measured by (c) a Langmuir probe as a function of gas ratio $CH_4/(Ar+CH_4)$ for the etching condition shown in Fig. 1.

Therefore, in Figure 2(a), relative variations of H radicals and CH_3 radicals were plotted as a function of CH_4 percentage. As shown in Figure 2(a), in the range from 0% to 35% of CH_4, the density of hydrogen atom generally increased with the increase of CH_4 in the CH_4/Ar gas mixture, however, in the range from 35% to 100% of CH_4, the increase of CH_4 generally decreased the density of hydrogen atom. In the case of CH_3 radical density, the increase of CH_4 in the gas mixture increased CH_3 radical density monotonically. Using the OES, the optical emission peaks from the dissociated species such as hydrogen atom (656.1nm) and CH (431.9nm) were also measured as shown in Figure 2(b), and the results showed the similar trends with the QMS results. The optical emission peak from hydrogen atom showed a maximum at near 35% of CH_4 and the peak from CH increased with the increase of CH_4 even though the peak appears to saturate at around 50% of CH_4. The increase of hydrogen atoms with the increase of CH_4 in the range from 0% to 35% of CH_4 appears to be due to the increased dissociation of CH_4, however, the decrease of hydrogen atoms with the further increase of CH_4 appears to be related to the increased recombination of hydrogen atoms into H_2 molecules and the increased formation of CH_3 from CH with hydrogen atom. Ion current densities obtained from the Langmuir probe biased at -40 volts were measured as a measure of ion densities in the plasmas and the results are shown in Figure 2(c). As shown in Figure 2(c), the increase of CH_4 percentage in CH_4/Ar gas mixtures decreased the ion current density possibly due to the higher ionization energy related to CH radicals and H atom compared to Ar, which suggests the decrease of ion density in the plasma with the increase of CH_4 percentage.

The increase of ITO etch rate shown in the range under 35% of CH_4 appears to be related to the increase of reactive radicals such as hydrogen and CH_3 even though ion density bombarding the surface of the specimen, therefore, physical sputtering effect was decreased. However, the decrease of ITO etch rate in the range from 35% to 100% of CH_4 needs more investigation because of the opposite behavior of reactive radicals such as hydrogen atoms and CH_3 radicals even though the ion density is still decreased with the increase of CH_4 percentage.



(a)



(b)

Fig. 3. (a) Etch rates of ITO films and underlayers and ITO etch selectivities over the underlayers as function of gas ratio of $H_2/(Ar+H_2)$. (500W, -200V, 15mTorr) (b) Relative H radical intensities measured by OES and QMS and ion saturation currents measured by a Langmuir probe as a function of gas ratio $H_2/(Ar+H_2)$.

To separate the effects of hydrogen atoms from those of CH_3 radicals on the etching of ITO thin films, ITO thin films were etched using Ar/H_2 gas mixtures and the results are shown in Figure 3(a) for 500 Watts of rf power, -200 Volts of dc self-bias voltage, and 15mTorr of operational pressure. As shown in Figure 3(a), the ITO etch rate was decreased almost linearly with the increase of hydrogen percent in the Ar/H_2 mixture. The densities of hydrogen atoms and ion current densities for the conditions shown in Figure 3(a) were also measured and the results are shown in Figure 3(b). The results from QMS were similar to those from OES as shown in Figure 3(b), and the increase of H_2 percents increased the density of hydrogen atoms until 35% of H_2 is reached and the further increase of H_2 percents saturated the density of hydrogen atoms. The increase of H_2 percents in the Ar/H_2 mixture generally decreased the ion current density of the plasma. From the results in Figure 3(a) and (b), the increase of hydrogen atoms in the plasma appears not to affect the ITO etch rate significantly, therefore, the decrease of ITO etch rate in Figure 3(a) is more related to the decrease of physical sputtering effect originated from the decrease of ion density with the increase of H_2 in the plasma. Therefore, ITO etch rate in Figure 1 should be more related to the CH_3 radical density and ion density in the plasma than hydrogen density in the plasma. In fact, the increase of ITO etch rate in the Figure 1 is more related to the formation of volatile compounds such as $In(CH_3)_x$ and $Sn(CH_3)_y$[4-5] by the increase of reactive CH_3 radicals under the sufficient ion bombardment even though the flux of the ion bombardment is decreased with the increase of CH_4. However, the further increase of CH_3 in the plasma with non-sufficient ion bombardment to the specimen generates hydrocarbon polymer on the surface of the specimen and, therefore, the ITO etch rate begins to decrease with the further increase of CH_4 in the CH_4/Ar mixture. The formation of hydrocarbon polymer on the ITO surface which is responsible for the decrease of etch rate has been also reported by other researchers.[6-9]

If the etch rates of SiO_2 and Si_3N_4 in Figure 1 and 2 are compared as a function of CH_4 percentage, the SiO_2 etch rate was always higher than that of Si_3N_4. The higher etch rate of SiO_2 compared with that of Si_3N_4 appears to be not only from the higher sputter yield of SiO_2 but also from the higher reactivity of SiO_2 with CH_3 radicals. Oxygen in SiO_2 can react with carbon in CH_4 during the etching, and it decreases the possibility of the formation of fluorocarbon. However, no such element exists for Si_3N_4, therefore, the increased possibility of the fluorocarbon formation appears to decrease the Si_3N_4 etch rate compared to the SiO_2 etch rates. If both SiO_2 and Si_3N_4 could be used for the underlayers of ITO in the display devices, the use of Si_3N_4 as the underlayer would be beneficial in the viewpoint of etching because of the higher etch selectivity.

Conclusions

In this study, etching characteristics of ITO thin film and its etch selectivities over the underlayers such as SiO_2 and Si_3N_4 were investigated using CH_4/H_2 inductively coupled plasmas. The characteristics of the plasmas were analyzed using QMS, OES, and Langmuir probe. When a certain amount of CH_4 was added to Ar, due to the reaction between ITO and CH_3 radical enhanced by sufficient ion bombardment, the ITO etch rate was increased. However, the further increase of CH_4 in CH_4/Ar mixtures decreased ITO etch rates possibly due to the increased formation of fluorocarbon polymer on the ITO surface with high CH_3 radicals and insufficient ion bombardment. Hydrogen atom formed by the dissociation of CH_4 in the CH_4/Ar mixtures appears not to affect the ITO etch rate significantly compared to CH_3 radicals. The etch selectivity of ITO over Si_3N_4 was higher than that over SiO_2 because of the reduced polymer formation on SiO_2 by the oxygen in SiO_2 during the etching compared to that on Si_3N_4.

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