ELSEVIER

Surface and Coatings Technology 131 (2000) 247–251

SURFACE & COATINGS TECHNOLOGY

www.elsevier.nl/locate/surfcoat

A study on the etch characteristics of ITO thin film using inductively coupled plasmas

J.Y. Park[a,*], H.S. Kim[a], D.H. Lee[a], K.H. Kwon[b], G.Y. Yeom[a]

[a] *Department of Materials Engineering, Sungkyunkwan University, Suwon 440-746, South Korea*
[b] *Department of Electronic Engineering, Hanseo University, Seosan 356-820, South Korea*

Abstract

In this study, the high-density plasma etching of indium tin oxide (ITO) 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 quadrupole mass spectrometry (QMS), optical emission spectroscopy (OES), and electrostatic probe (ESP). 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 amounts of CH_4 decreased the ITO etch rates, possibly due to the increased polymer formation on the ITO surface. Also, the data obtained by QMS and OES suggested that CH_3 radicals are more actively involved in the etching of ITO compared to H radicals. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Indium tin oxide (ITO) films; Inductively coupled plasmas; High density

1. Introduction

Indium tin oxide (90 wt.% In_2O_3; 10 wt.% 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 of display devices. Also, since ITO etching by the wet etching methods depends on the physical and chemical characteristics of the film itself, the small variation in the film characteristics over the substrate could cause ITO residues to be left on the substrate after the etching and also could cause excess sidewall etching of ITO films [1]. Recently, the pixel electrode applications have increased in the need for the research on the dry etching of ITO thin films. Improved fine line patterning of ITO lines and also optimized selectivity over SiO_2 and Si_3N_4 underlayers is required [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).

2. 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 by Kim et al. [3]. The inductively coupled plasmas (ICP) used in the experiment were generated by applying 13.56 MHz r.f. power to the planar spiral Cu coil located on the top of the process chamber and separated by a 1.5-cm thick

* Corresponding author.

0257-8972/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0257-8972(00)00788-X

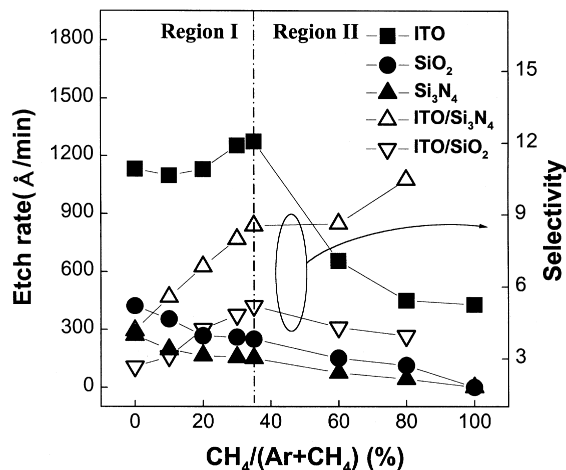
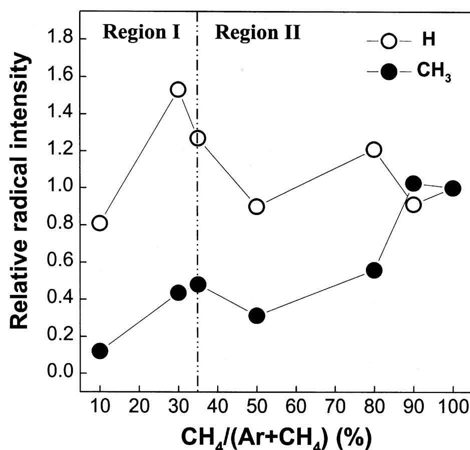
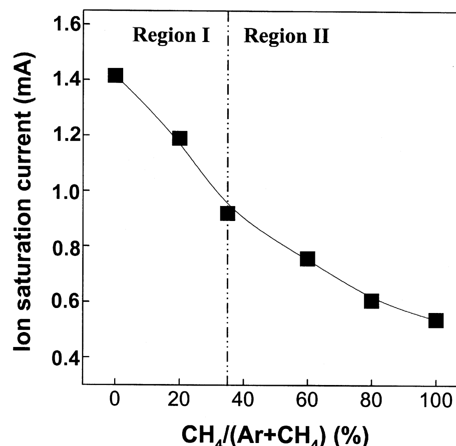


Fig. 1. Etch rates of ITO films and underlayers (SiO_2, Si_3N_4) and ITO etch selectivities over the underlayers as a function of pressure ratios of $CH_4/(Ar + CH_4)$ (500 W, −200 V, 15 mtorr).

quartz window. A separate 13.56 MHz r.f. power was also applied to the bottom electrode to supply ion bombardment to the substrate by generating d.c. self-bias voltage. ITO films used in this experiment were sputter deposited on the glass to a thickness of 180 nm and showed the resistivity of $2–3 \times 10^{-4}$ Ω/cm. SiO_2 (~300 nm) and Si_3N_4 (~270 nm) 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 r.f. power, pressure, and bias voltage were fixed at 500 W, 15 mtorr, and −200 V, respectively. Gas combination, therefore, gas percentage was controlled by changing the partial pressure at the fixed total pressure. 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.





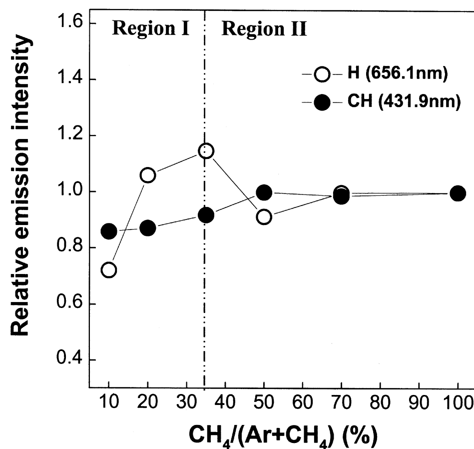


Fig. 2. (a) Relative radical intensities measured by QMS; (b) relative optical emission intensity measured by OES; and (c) ion saturation currents by a Langmuir probe as a function of pressure ratios of $CH_4/(Ar + CH_4)$ for the etching condition shown in Fig. 1.

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.

3. Results and discussion

Fig. 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 W of r.f. power, −200 V of d.c.-self bias voltage, and 15 mtorr operational pressure. The ITO etch selectivities over SiO_2 and Si_3N_4 were also included in the figure. As shown, with the increase of CH_4, ITO etch rates increased until CH_4 reaches 35% of the operational pressure (region I), however, the further increase of CH_4 decreased ITO etch rates (region II). 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 for both regions I and II. The ITO etch selectivity over Si_3N_4 was generally higher than that over SiO_2, and, when CH_4 was above 80%, the etch selectivity over Si_3N_4 was infinite due to the etch stop on 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 Fig. 1, and the results are shown in Fig. 2a for QMS, Fig. 2b for OES, and Fig. 2c 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 small 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. Therefore, in Fig. 2a, relative variations of H radicals and CH_3 radicals were plotted as a function of CH_4 percentage. As shown in Fig. 2a, in region I, the density of the hydrogen atoms generally increased with the increase of CH_4 in the CH_4/Ar gas mixture, however, in region II, the increase of CH_4 generally decreased the density of the hydrogen atoms. In the case of CH_3 radical density, the increase of CH_4 in the gas mixture increased CH_3 radical density monotonically for both regions I and II.

Using the OES, the optical emission peaks from the dissociated species such as the hydrogen atom (656.1 nm) and CH (431.9 nm) were also measured as shown in Fig. 2b, and the results showed similar trends to the QMS results. The optical emission peak from the hydrogen atom showed a maximum close to 35% of CH_4 and the peak from CH increased with the increase of CH_4 even though the peak appears to saturate at approximately 50% of CH_4. The increase of hydrogen atoms with the increase of CH_4 in region I appears to be due to the increased dissociation of CH_4, however, the decrease of hydrogen atoms with the further increase of CH_4 in region II appears to be related to the increased recombination of hydrogen atoms into H_2 molecules and the increased formation of CH_3 from CH_x with hydrogen atom. Ion current densities obtained from the Langmuir probe biased at −40 V were measured as a measure of ion densities in the plasmas and the results are shown in Fig. 2c. As shown in Fig. 2c, the increase of the percentage of CH_4 in CH_4/Ar gas mixtures decreased the ion current density possibly due to the higher ionization energy related to CH_x radicals and H atoms compared to Ar, which suggests a decrease of ion density in the plasma with an increase in the percentage of CH_4.

The increase of ITO etch rate shown in region I of Fig. 1 appears to be related to the increase of reactive radicals such as hydrogen and CH_3 even though the ion density bombarding the surface of the specimen and, therefore, the physical sputtering effect was decreased. However, the decrease of ITO etch rate in region II of Fig. 1 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 increased percentage of CH_4.

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 Fig. 3a for 500 W of r.f. power, −200 V of d.c. self-bias voltage, and 15 mtorr operational pressure. As shown in Fig. 3a, 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 Fig. 3a were also measured and the results are shown in Fig. 3b. The results from QMS were similar to those from OES as shown in Fig. 3b. Higher levels of H_2 increased the density of hydrogen atoms until 35% of H_2 is reached. Any further increase in H_2 percentage saturated the density of hydrogen atoms. The increase of H_2 in the Ar/H_2 mixture generally decreased the ion current density of the plasma. From the results in Fig. 3a,b, the increased level of hydrogen atoms in the plasma appears not to affect the ITO etch rate significantly, therefore, the decrease of ITO etch rate in Fig. 3a is more related to the decrease in physical sputtering originating from the decrease in ion density with increased H_2 in the plasma. Therefore, the ITO etch rate in Fig. 1 should be more related to the CH_3 radical density and ion density in the plasma than hydrogen density in the plasma. In

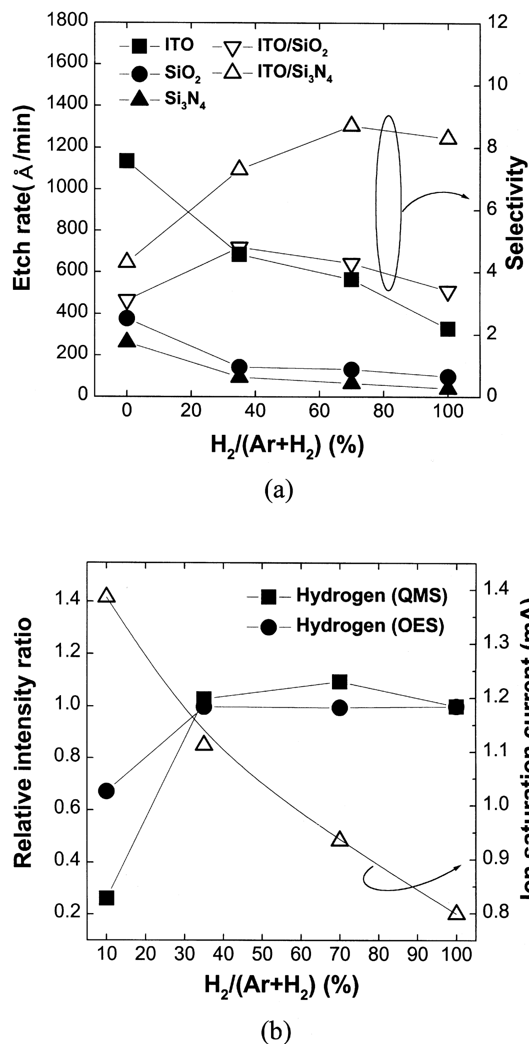


Fig. 3. (a) Etch rates of ITO films and underlayers (SiO_2, Si_3N_4) and ITO etch selectivities over the underlayers as a function of pressure ratios of $H_2/(Ar + H_2)$ (500 W, −200 V, 15 mtorr). (b) Relative H radical intensities measured by OES and QMS and ion saturation currents measured by a Langmuir probe as a function of pressure ratios of $H_2/(Ar + H_2)$.

fact, the increase of ITO etch rate in region I of Fig. 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 insufficient 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 Mohri et al. [6] and Kuo et al. [7–9].

If the etch rates of SiO_2 and Si_3N_4 in Figs. 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.

4. 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/Ar 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 atoms 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.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-98-016-E00100).

References

[1] M. Takabatake, Y. Wakui, N. Konishi, J. Electrochem. Soc. 142 (1995) 2470.

[2] A.H. Shih, A. Demos, R.D. Beer, Solid State Technol. 39 (1996) 71.
[3] H.S. Kim, G.Y. Yeom, J.W. Lee, T.I. Kim, J. Vac. Sci. Technol. A17 (1999) 2214.
[4] S.J. Pearton, J.C. Zolper, R.J. Shul, F. Ren, J. Appl. Phys. 86 (1999) 33.
[5] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 77th ed, CRC Press, New York, 1996–1997.
[6] M. Mohri, H. Kakinuma, M. Sakamoto, H. Sawai, Jpn. J. Appl. Phys. 29 (1990) L1932.
[7] Y. Kuo, J. Appl. Phys. 36 (1997) L629.
[8] Y. Kuo, J. Appl. Phys. 29 (1990) 2243.
[9] Y. Kuo, T.L. Tai, J. Electrochem. Soc. 145 (1998) 4313.