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

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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\textsubscript{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\textsubscript{4} to Ar due to the increased chemical reaction between CH\textsubscript{4} or H and ITO in addition to the physical sputtering of ITO by Ar ion bombardment. However, the addition of excess amounts of CH\textsubscript{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\textsubscript{4} radicals are more actively involved in the etching of ITO compared to H radicals.

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1. Introduction

Indium tin oxide (90 wt.% In\textsubscript{2}O\textsubscript{3}; 10 wt.% SnO\textsubscript{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\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} underlayers is required [2].

In this study, dry etching characteristics of ITO films and etch selectivities over SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} were investigated using Ar/CH\textsubscript{4} and Ar/H\textsubscript{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\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{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...
Fig. 1. Etch rates of ITO films and underlayers (SiO$_2$, Si$_3$N$_4$) 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).

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.; PSM5000), 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, SiO₂, and Si₃N₄ as a function of CH₄ in the gas mixture of CH₄/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 SiO₂ and Si₃N₄ were also included in the figure. As shown, with the increase of CH₄, ITO etch rates increased until CH₄ reaches 35% of the operational pressure (region I), however, the further increase of CH₄ decreased ITO etch rates (region II). In the cases of SiO₂ and Si₃N₄, the etch rates decreased monotonically with the increase of CH₄ percentage in the gas mixture for both regions I and II. The ITO etch selectivity over Si₃N₄ was generally higher than that over SiO₂, and, when CH₄ was above 80%, the etch selectivity over Si₃N₄ was infinite due to the etch stop on Si₃N₄.

To study the effects of CH₄/Ar plasma conditions on the ITO etch rates, the characteristics of CH₄/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 CH₄ in the CH₄/Ar plasmas were measured using QMS, the peaks from H₂, H, CH₂, and CH₃ were observed and, among these, the peak intensity from CH₂ was small compared to the other peak intensities throughout the CH₄/Ar gas mixtures used in the experiment. Also, it is known from the other researchers that H radicals and CH₂ radicals are the main reactive radicals affecting the ITO etch rates. Therefore, in Fig. 2a, relative variations of H radicals and CH₂ radicals were plotted as a function of CH₄ percentage. As shown in Fig. 2a, in region I, the density of the hydrogen atoms generally increased with the increase of CH₄ in the CH₄/Ar gas mixture, however, in region II, the increase of CH₄ generally decreased the density of the hydrogen atoms. In the case of CH₂ radical density, the increase of CH₂ in the gas mixture increased CH₂ 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 CH₄ and the peak from CH increased with the increase of CH₄, even though the peak appears to saturate at approximately 50% of CH₄. The increase of hydrogen atoms with the increase of CH₄ in region I appears to be due to the increased dissociation of CH₄, however, the decrease of hydrogen atoms with the further increase of CH₄ in region II appears to be related to the increased recombination of hydrogen atoms into H₂ molecules and the increased formation of CH₃ from CH₄ 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 CH₄ in CH₄/Ar gas mixtures decreased the ion current density possibly due to the higher ionization energy related to CH₂ radicals and H atoms compared to Ar, which suggests a decrease of ion density in the plasma with an increase in the percentage of CH₄.

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 CH₃ 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 CH₃ radicals even though the ion density is still decreased with the increased percentage of CH₄.

To separate the effects of hydrogen atoms from those of CH₃ radicals on the etching of ITO thin films, ITO thin films were etched using Ar/H₂ 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/H₂ 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 H₂ increased the density of hydrogen atoms until 35% of H₂ is reached. Any further increase in H₂ percentage saturated the density of hydrogen atoms. The increase of H₂ in the Ar/H₂ 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 H₂ in the plasma. Therefore, the ITO etch rate in Fig. 1 should be more related to the CH₃ radical density and ion density in the plasma than hydrogen density in the plasma. In
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(CH₃)ₓ and Sn(CH₃)ₓ [4,5] by the increase of reactive CH₃ radicals under the sufficient ion bombardment even though the flux of the ion bombardment is decreased with the increase of CH₄. However, the further increase of CH₃ 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 CH₄ in the CH₄/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 SiO₂ and Si₃N₄ in Figs. 1 and 2 are compared as a function of CH₄ percentage, the SiO₂ etch rate was always higher than that of Si₃N₄. The higher etch rate of SiO₂ compared with that of Si₃N₄ appears to be not only from the higher sputter yield of SiO₂ but also from the higher reactivity of SiO₂ with CH₃ radicals. Oxygen in SiO₂ can react with carbon in CH₄ during the etching, and it decreases the possibility of the formation of fluorocarbon. However, no such element exists for Si₃N₄, therefore, the increased possibility of the fluorocarbon formation appears to decrease the Si₃N₄ etch rate compared to the SiO₂ etch rates. If both SiO₂ and Si₃N₄ could be used for the underlayers of ITO in the display devices, the use of Si₃N₄ 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 SiO₂ and Si₃N₄ were investigated using CH₄/Ar inductively coupled plasmas. The characteristics of the plasmas were analyzed using QMS, OES, and Langmuir probe. When a certain amount of CH₄ was added to Ar, due to the reaction between ITO and CH₃ radical enhanced by sufficient ion bombardment, the ITO etch rate was increased. However, the further increase of CH₄ in CH₄/Ar mixtures decreased ITO etch rates possibly due to the increased formation of fluorocarbon polymer on the ITO surface with high CH₃ radicals and insufficient ion bombardment. Hydrogen atoms formed by the dissociation of CH₄ in the CH₄/Ar mixtures appears not to affect the ITO etch rate significantly compared to CH₃ radicals. The etch selectivity of ITO over Si₃N₄ was higher than that over SiO₂ because of the reduced polymer formation on SiO₂ by the oxygen in SiO₂ during the etching compared to that on Si₃N₄.

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References