Etch characteristics of gallium indium zinc oxide thin films in a HBr/Ar plasma

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ABSTRACT
Gallium indium zinc oxide (GIZO) thin films patterned with a photoresist (PR) were dry etched using inductively coupled plasma (ICP) of HBr/Ar gas. The etch rate of the GIZO films and the etch selectivity of GIZO/PR decreased gradually as HBr gas was added to Ar. In addition, the etch rate increased with increasing ICP power and dc-bias voltage to the substrate. However, the etch rate was decreased with increasing gas pressure. X-ray photoelectron spectroscopy and atomic force microscopy revealed Br compounds on the film surface during the etching process. It can be concluded that the high density plasma etching of GIZO films using HBr/Ar gas follows a sputtering etching mechanism with the assistance of a chemical reaction on the films.

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1. Introduction

Recently, various oxide-based thin-film transistors (TFTs) have been proposed as a replacement for conventional TFTs including hydrogenated amorphous silicon (a-Si:H) or polysilicon semiconductors [1–5]. Among the many candidates for TFTs containing oxide semiconductor materials, high-performance amorphous gallium indium zinc oxide (a-GIZO) based TFTs, which are used in active matrix liquid crystal displays (AMLCDs) or active matrix organic light-emitting diodes (AMOLEDs), have been reported [6–9]. These a-GIZO TFTs showed high mobility (≥10 cm²/V·s) and an excellent subthreshold gate swing (0.20 V/decade) with a reasonable on/off ratio even in the amorphous phase.

Some processes need to be solved before a-GIZO TFTs can be realized. One of them is to etch GIZO thin films with a fine geometry without etch damage. Wet etching studies of GIZO thin films have been reported [10,11] but there are no reports on the dry etching of GIZO films. In the case of wet etching, undesirable results including a severe undercut and low slope of the etched sidewall are typically obtained. Moreover, it is difficult to control the etch uniformity of a large wafer. There are many reports of the etching of zinc oxide, indium tin oxide (ITO), and indium zinc oxide (IZO) thin films using a range of gases including Cl₂, BCl₃, CF₄, C₂F₆, HBr, and CH₃/CH₂ [12–15]. It was reported that ZnO and ITO thin films are etched mainly using chlorine- and fluorine-based gases. Those studies reported that chlorine chemistry causes rapid etching of the photoresist. Hence, a hard mask, such as an oxide and metal, is needed for the improved etch profile. On the other hand, fluorine chemistry showed a very slow etch rate and poor etch profile. CH₄/H₂ chemistry showed the highest etch rate of ZnO films at room temperature but the electrical and optical properties of the devices deteriorated. In the case of etching IZO thin films, the etch rate was moderate but a good etch profile with a high degree of anisotropy was obtained using HBr/Ar gas.

In this study, inductively coupled plasma reactive ion etching (ICPRIE) of GIZO thin films patterned with a photoresist (PR) was performed using HBr/Ar gas. The HBr concentration in the HBr/Ar gas and other etch parameters including ICP rf power, dc-bias voltage to the substrate, and gas pressure were varied to obtain the etch characteristics and etch mechanism of GIZO films. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) of the etched surfaces were carried out to determine the etch mechanism of GIZO thin films using HBr/Ar gas.

2. Experimental details

The a-GIZO thin films were deposited on SiO₂/Si substrates by rf magnetron sputtering at room temperature. It was confirmed that the deposited a-GIZO films consisted of Ga₂O₃:In₂O₃:ZnO = 1:1:1 as an atomic ratio by inductively coupled plasma mass spectroscopy. The films were patterned by a lithography process using a 1.2 μm thick photoresist. The films were etched using a commercial ICPRIE equipment (A-Tech, Korea) that can generate high density plasma. The ICPRIE system consisted of a main process chamber and load lock chamber. The coil installed at the top of the main process chamber was connected to a 13.56 MHz rf power supply to generate the high density plasma. A self dc-bias voltage induced by rf power at 13.56 MHz was capacitively coupled to the substrate susceptor to control the ion energy in the plasma. The main process chamber was evacuated to a base pressure of 2 × 10⁻⁶ Torr using a turbomolecular pump. The substrate susceptor was cooled with chilled fluid at a constant temperature of 15 °C and the substrate was then cooled through cold helium gas filled between the substrate and susceptor.

HBr/Ar gas was used as an etch gas and fed into the main chamber at a rate of 30 sccm. The etch rates and etch profiles of the GIZO thin film were measured using an inductively coupled plasma mass spectrometer and scanning ion microscopy.
films were examined by varying the HBr gas concentration. The effects of the ICP rf power, dc-bias voltage to substrate, and gas pressure on the etch rate were investigated.

An alpha step (Tencor P-1) was used to measure the etch rates. The etch profiles were observed by field emission scanning electron microscopy (FESEM: Hitachi S-4300) at a 20 kV operating voltage. The surface chemistry and surface morphology of the etched films were observed by XPS (Thermo Scientific K-Alpha) using an Al Kα x-ray source and AFM (NS4A) in tapping mode, respectively, to elucidate the etch mechanism of the GIZO films in a HBr/Ar plasma.

3. Results and discussion

Fig. 1 shows the etch rates of GIZO thin films and photomask (PR) in different HBr concentrations. The etching conditions were as follows: ICP rf power of 700 W, dc-bias voltage of 200 V, and gas pressure of 5 mTorr. The etch rate of GIZO films decreased gradually with increasing HBr concentration. On the other hand, the etch rate of the photoresist increased with increasing HBr concentration up to 40% and then decreased slowly with further increases in HBr concentration. As the HBr concentration increased from 0% to 40%, the sputtering effect by Ar ions is reduced but the formation of Br radicals is increased to attack the photoresist films. With further increase of HBr, the passivation layer containing hydrogen is formed on film surface by hindering the attack by Br radicals. The etch rate of GIZO films decreased monotonously. The etch rate of the GIZO films decreased gradually due to reduced sputtering by Ar ions despite the increase in bromine radicals. The etching of GIZO thin films in HBr/Ar plasma does not follow a reactive ion etching mechanism (Fig. 1).

Fig. 2 shows FESEM micrographs of GIZO thin films etched at various HBr concentrations. Redeposited materials were observed around the patterns of the GIZO films when the GIZO films were etched in pure Ar. This is because there was no chemical reaction between the GIZO films and Br radicals, and only sputtering by Ar ions occurred. As the HBr concentration was increased to 80%, the redeposited materials were still produced around the etched patterns.
Only the GIZO film etched at 100% HBr showed a clean sidewall. This suggests that etching in 100% HBr gas proceeded mainly by a chemical reaction between the GIZO films and Br radical.

In order to shed light on the etching mechanism, it is important to examine the etched surfaces of GIZO thin films at different HBr concentrations. First of all, AFM analysis of the etched surfaces of the GIZO films was carried out. Bare IZO films without a PR were used for AFM analysis, and were etched to a depth of 500 Å. The scan area was 1 × 1 μm². As the HBr concentration was increased, the surface morphology changed dramatically from 20% HBr, 60% HBr to 100% HBr, as shown in Fig. 3. The root mean square (RMS) surface roughness of the as-deposited GIZO film, the GIZO films etched at 20% HBr and 60% HBr, and 100% HBr were 0.675 nm, 1.348 nm, 3.881 nm and 1.541 nm, respectively. The surface of the as-deposited GIZO film was smoother than those of the etched GIZO films. Moreover, the film surface etched in 60% HBr was much rougher than that etched in 20% HBr. This suggests that a chemical reaction between GIZO films and Br radicals had occurred under these etching conditions. This also indicates that by the addition of HBr gas to Ar caused surface modification of the GIZO films due to an increase in hydrogen and bromine radicals, whereas the sputtering effect by Ar ions decreased. However, the GIZO film etched in 100% HBr showed a lower RMS than in the case of 60% HBr etching. This was due to both the pure chemical reaction and greatly decreased sputtering in pure HBr plasma and/or a passivation layer containing hydrogen. Ion sputtering and a chemical reaction are very important factors that determine the etch rate and etch profile.

Fig. 4 shows the XPS full spectra of the as-deposited GIZO and the GIZO films etched in 20% HBr/Ar, 60% HBr/Ar and 100% HBr. Bare GIZO thin films without photoresist masks were used as specimens for this analysis. From a comparison of the full spectra, Br 3d peaks were observed from the surfaces of all etched specimens. This suggests the presence of bromine compounds on the etched surfaces. Narrow scans for the Ga, In and Zn peaks were performed. Fig. 5(a) shows narrow scans of the Ga 2p peaks. The peak for the as-deposited GIZO specimen showed the chemical state of Ga₂O₃ (1118.2 eV). The peaks for the etched GIZO specimen were shifted to slightly higher binding energy states corresponding to 1119.2 eV. This means that the film surface contained compounds with Ga. Fig. 5(b) shows the narrow scans of the In 3d peaks. The chemical state of In₂O₃ was detected on the surface of the as-deposited specimen, and corresponded to a binding energy of 445.2 eV.
energy of 445.2 eV. For the etched IZO specimens, the main peaks were shifted to a higher binding energy of approximately 445.8–446 eV. This peak shift suggests the formation of chemical compounds containing In on the etched film surface, such as InBr₃ [16]. Fig. 5(c) shows the narrow scans of the Zn 2p peaks. The as-deposited film presented the chemical state of ZnO, which had a
dramatically by adding HBr gas. The surface morphology of the etched HBr showed a clean etch profile. Increasing HBr concentration and heavy etch residues were formed during the etching of GIZO films in HBr/Ar gas.

As the next step, this study examined the effect of the etch parameters, i.e. ICP rf power, dc-bias voltage to substrate, and gas pressure, on the etch rate. The standard etch conditions were 80% HBr/20% Ar gas, 700 W ICP rf power, 200 V dc-bias voltage, and 5 mTorr gas pressure. When one parameter was varied, the other parameters including the gas concentration were fixed. Fig. 6(a) shows the change in etch rate and etch selectivity as the ICP rf power was increased from 600 W to 800 W. As the ICP rf power was increased, the etch rates and etch selectivity of the GIZO film and PR mask increased considerably. This was attributed to an increase in Ar ions and bromine radicals by the increase in plasma density at high coil rf power. With increasing dc-bias voltage to the substrate, the etch rate showed a similar trend to that observed for the ICP power variations. The etch rates of the GIZO film and PR mask increased rapidly but the etch selectivity decreased with increasing dc-bias voltage from 100 V to 300 V, as shown in Fig. 6(b). This was attributed to the increased bombardment energy of Ar ions at high dc-bias voltage. Both the coil rf power and dc-bias voltage can control the ion bombarding energy on the GIZO films, and are the main factors determining the etch rate. The etch rates of the films and etch selectivity increased gradually with decreasing gas pressure from 10 mTorr to 1 mTorr (Fig. 6(c)). This suggests that the gas pressure has a strong influence on the etch rate of the GIZO thin films. The vertical sputtering effect is enhanced because the mean free path of ions at low gas pressure is longer than that at high gas pressure. In addition, the optical emission spectroscopy showed that the plasma density at 1 mTorr was higher than that at 10 mTorr. Overall, GIZO thin films can be etched with fine pattern transfer without any redepositions or etch residues.

4. Conclusion

High density plasma etching of GIZO thin films patterned with a photoresist was carried out in inductively coupled plasma of HBr/Ar gas. The etch rates and etch selectivity of GIZO/PR decreased with increasing HBr concentration and heavy etch residues were formed along the etched sidewall of the films. Only GIZO films etched in 100% HBr showed a clean etch profile.

The surface morphology of the etched GIZO films was changed dramatically by adding HBr gas. The surface morphology of the etched GIZO films became increasingly rough with increasing HBr concentration up to 80% and smooth in 100% HBr. This change in the etched surface was attributed to both sputtering by Ar ions and a chemical reaction between the GIZO films and bromine radicals, and/or the passivation layer containing hydrogen. XPS analysis also revealed some chemical reactions between the GIZO films and bromine radicals. The change in the etch rate and surface morphology of the GIZO films depends on the predominant factor between ion sputtering and surface chemical reaction.

The etch rate of the GIZO thin films increased with increasing ICP rf power and dc-bias voltage and increased gradually with decreasing gas pressure. These results show that the etching of GIZO thin films follows a sputter etching mechanism with the assistance of a surface chemical reaction.

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