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High-density plasma etching characteristics of aluminum-doped zinc oxide thin films in Cl₂/Ar plasma

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Abstract
We investigated the etching characteristics of aluminum-doped zinc oxide (AZO) thin films in an adaptively coupled plasma (ACP) system. The dry etching characteristics of AZO films were studied by changing the Cl₂/Ar gas mixing ratio, RF power, DC bias voltage. We determined the following optimized process conditions: RF power of 500 W, DC bias voltage of −100 V, process pressure of 15 mTorr. In Cl₂/Ar plasma (=50:50%), the maximum etching rate of AZO films is 70.45 nm min⁻¹. The ion composition of Cl₂/Ar plasma was determined by optical emission spectrometry (OES). The chemical reactions on the surface of AZO films were analyzed by x-ray photoelectron spectroscopy (XPS).

1. Introduction

The transparent conductive oxide (TCO) layer is often used as an electrode that is transparent to visible light. And the common TCO materials ITO (In₂O₃:SnO₂), SnO, ZnO is widely used in photovoltaic applications, such as transparent electrodes in touch pads, flat panel displays (FPD), and other future devices [1, 2]. Among these materials, ITO is the most studied and widely used now. However, the main raw material of ITO is In, a rare metal, which is expensive and can pollute the environment and the chemical properties are unstable [3]. For many years, people have been looking for a common and widely available material to effectively use as transparent electrodes to replace ITO. Compared with ITO, aluminum-doped zinc oxide (AZO) is ubiquitous, and has good light transmittance, electrical conductivity and processability at low temperature and infrared band, low resistivity (∼10⁻⁴ Ω cm), simple chemical etching, has become the most likely place of ITO material [4–6].

Patterning of AZO is also required for the fabrication of optoelectronic devices. Therefore, how to use the plasma etch to the transparent electrode should be investigated. We investigated the etching characteristics of AZO thin films using Cl₂/Ar mixtures in an adaptively coupled plasma (ACP) system [7, 8]. The reaction of the etching AZO thin film was been analyzed using a series of equipment such as X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), optical emission spectroscopy (OES).

2. Experiment

In this experiment, we deposed the AZO (Al doping concentration 2%) thin film on Silicon wafer (100) by RF Sputtering with the Ar. The process condition is gas flow rate of 30 sccm, RF power of 60 W, substrate temperature of 150 °C and the AZO thin film thickness about 100 ∼ 150 nm [9].

Two commonly used etching instruments are capacitive coupled plasma (CCP) and inductively coupled plasma (ICP) systems. The advantage of CCP is that good process reproduction and the PR mask have the high selectivity. Compared with CCP, ICP has high plasma density and low power consumption. Adaptively coupled plasma (ACP) equipment combined the advantages of ICP and CCP, so this time we used ACP to etch the film [10]. During the experiment, all the factors are as the total gas flow rate of 100 sccm, the RF power of 500 W, the
DC-bias voltage of −100 V, and the substrate temperature of 25 °C. As for the analysis of the results of this experiment, used the optical emission spectroscopy (OES) to realize the species in the plasma and the x-ray photoelectron spectroscopy (XPS) to examine chemical binding states and the composition of the AZO thin film surface. At the same time, we confirm the depth of etching and the surface morphology by atomic force microscope (AFM).

3. Result and discussion

The etch rates and selectivity of the AZO thin films as shown as figure 1. The etch rate varied by the Cl2/(Cl2 + Ar) flow ratios from 0% to 100% in the conditions where RF power of 500 W, working pressure of 15 mTorr, and bias voltage of 100 V. As shown in figure 1(a), with the increasing of Cl2 gas in the Cl2/Ar mixture until the ratio is 50%, the etching rate increases significantly, reaching a maximum value of 70.45 nm min⁻¹. With the increasing of the Cl2 gas ratio over 50%, etching rate decreases rapidly. As the concentration of Cl2 increases to 50%, the amounts of the Cl free radicals increasing, the potential of chemical reactions and the chemical products like ZnClx, AlClx, ClxOx will be increased. The Ar ion act as a physical sputtering in the etching reaction which will remove chemical by-products (Al2Ox, AlClx) attached on the thin film [11]. The etching rate was declined after flow ratio 50%, the reason is that the surface physical sputtering effect weakened as decreasing the Ar gas ratio, and the by-products are more easily attached to the AZO thin film. Figure 1(b) shows the etch selectivity values of the AZO thin film to the PR and SiO2 thin films. The etch selectivity of SiO2 thin film was generally higher than PR in Cl2/Ar plasma.

In plasma etching, DC-bias is related to physical ion bombardment and sputtering yields. As the collision force of ions increases, it is easier to break the bonding of by-products on the surface of the thin film [12]. Figure 2 shows the etch rate of the AZO thin film as a function of DC-bias voltage in the conditions where Cl2/(Cl2 + Ar) = 50:50%, gas flow rate of 100 sccm, RF power of −100 V, and process pressure of 15 mTorr. The etch rate of the AZO thin film increases with the increase of DC-bias voltage. In particular, as DC-bias increases from 50 V to 100 V, the etch rate increases dramatically, while the etch rate increases gradually from 100 V to 200 V. This means that the threshold force of ion bombardment to break the bonding of by-products is at DC-bias of 100 V or less. Figure 3 shows the etch rate of the AZO thin film as a function of RF power in the conditions where Cl2/(Cl2 + Ar) = 50:50%, gas flow rate of 100 sccm, DC-bias voltage of −100 V, and process pressure of 15 mTorr. The etch rate of AZO thin film increases with the increase of RF power. As the increasing of RF power, the ion volume density, ion current density and even the desorption ratio will be increased, which makes the reaction faster, and the etch rate goes up [13, 14].

In order to study the AZO thin film etching mechanism, we determined the ionic composition of Cl2/Ar plasma using OES analysis. The optical emission spectra from the dissociated species, such as Ar radical [419.8 nm], Cl radical [579.8 nm], Cl2 radical [468.14 nm], Al radical [308.07 nm], Zn radical [472.05 nm], O radical [725.4 nm], are shown in figure 4. As shown in figure 4(a), the emission intensities of Cl, Cl2 radicals increased with increasing Cl2 concentration from 0 to 50%. However, the emission intensity of these radicals slightly decreased when the Cl2 concentration increase from 50 to 100%. Under the physical sputtering action of Ar⁺, Cl2 dissociated and reacts with surface chemicals in the form of Cl and Cl2 radicals. When the Cl2 ratio increases to 50%, Cl and Cl2 showed an upward trend. With the Cl2 ratio increasing, the number of Cl/Cl2...
radicals increased under the Ar$^+$ physical sputtering yield. When the Cl$_2$ ratio over to 50%, the ratio of Ar$^+$ decreased gradually, which means the yield of Ar$^+$ decreasing, Cl$_2$/Cl$_2$ shows the downward trend, resulting in the decrease of etch rate (figure 1). Figure 4(b) shows the variation of Al, Zn, and O intensity, all the three elements have shown an upward trend until the gas etching rate is Cl$_2$/Ar = 50:50%, and then showed down trend until Cl$_2$/Ar ratio is 100%. As the increase of Cl radical and the action of Ar$^+$ physical sputtering, the intensity of the elements Al, Zn, O in the plasma reaches the maximum when Cl$_2$ ratio is 50%. when the ratio of Cl$_2$ over 50%, the intensity of the three elements declined, that is because Ar$^+$ physical sputtering weakened, and
more chemical by-products attached on the thin film surface. This reflects the reason why etch rate changes with different proportion of Cl$_2$/Ar. In addition, it can be seen the figure 4(b), comparing other elements, O was removed the most in this etching experiment, Moreover, it well be known that the etching of AZO is affected the chemical reaction and physical sputtering by the OES analysis.

Figure 5(a) shows the XPS narrow scan of Zn 2p peak. There are 2 peaks in the Zn 2p XPS narrow scan spectra 1042.87 eV, 1019.86 eV [15]. As the ratio of Cl$_2$ increasing to 50%, the position of the main peak changes and the value of binding energy becomes 1044.02 eV, 1020.98 eV. As the ratio of Cl$_2$ increased to 100%, the binding energy peak shift is $\Delta E = 1.55$ eV comparing the value of binding energy before etching, due to Cl radicals enters the chemical reaction, the chemical by-products formed and attached on the thin film surface, and meanwhile the physical sputtering of the Ar$^+$ weakened. And the figure 5(b) shows the O 1s narrow scan XPS. The binding energy changes significantly in the reaction process of O 1s. The value of binding energy is 529.42 eV before etching. When the Cl$_2$:Ar = 50:50%, the intensity of ZnI and ZnII declined and a new peak ZnIII appeared, was Zn-Cl (1021.29 eV). The reason for this result is that some of the Cl elements binding to Zn attached on the thin film surface, some else Cl elements bind...
to O removed under the physical sputtering of the Ar\(^+\). Figure 6(c) shows the Zn 2p\(_{1/2}\) binding energy in the pure Cl\(_2\), the peak intensity of ZnIII showed an upward trend\([16, 17]\).

Figure 7(a) shows the XPS narrow scanning spectrum of O1s as-deposited. There are three peaks which we named as O\(_{Ii}\), O\(_{II}\), O\(_{III}\), and determined as Al-O-Zn (529.39 eV), Al-O (530.44 eV) and Zn-O (531.44 eV), respectively. With the progress of etching and the addition of new Cl elements, O\(_{Ii}\) peak Al-O-Zn was broken and a new peak O\(_{III}\) (532.31 eV) appeared, and the intensity of the O\(_{II}\) (Al-O), O\(_{III}\) (Zn-O), O\(_{IV}\) (Cl-O) peaks shows increasing trend, as shown in the figure 7(b). It can be seen that when Cl enter the chemical reaction system, and under the action of Ar\(^+\) physical sputtering, the chemical bond of Al-O-Zn was broken, and a series of chemical reactions occur with Cl, the products Zn-O, Al-O and Cl-O increase to adhere to the surface, and their intensity increased. With the increasing of Cl, the physical sputtering of Ar\(^+\) weakening, the intensity of Cl-O increased until the Cl ratio is 100%\([18, 19]\).

As shown in figure 8(a), Al 2p\(_{3/2}\) contains two peaks, namely, Al\(_{I}\) peak Al-O (73.65 eV) and Al\(_{II}\) peak Al-O-Zn (74.48 eV). The intensity of two peaks is not obvious as-deposited, because Al elements content is not large. When Cl\(_2\)/Ar = 50:50%, Cl bind to Al, the new peak Al\(_{III}\) (75.08 eV) appeared in the figure 8(b). Al elements are attached to the surface of the film in other forms of uniform combination, and the intensity increased gradually with the Cl increasing. The intensity of Al\(_{III}\) (Cl-Al) shows upward trend until the Cl\(_2\) ratio is 100%, because the element Al is a non-volatile substance, Al-Cl easily adhered to the surface\([20, 21]\).

Table 1 shows the surface atomic ratio from XPS analysis in each reaction stage as-deposited, Cl\(_2\)/Ar = 50:50%, Cl\(_2\)/Ar = 100:0%. O can be seen from the table 1 in the as-deposited stage, contain quantity of up to 58.04%, when in pure Cl\(_2\), O content accounted for only 21.59%. When Cl enter the etching system, part of them combine to O removed, that can well explain the O1s XPS binding energy why changed obviously. In addition, the ratio of Zn increased from 40.37% to 72.95%, which verified that Zn was the element with the most adhesion on the film surface. Compared with other elements, the content of Al element is relatively small. The change of Al element changes from 1.58% to 5.45%, combines well with Cl, O element, and adheres to the surface.

In order to investigate the surface properties of the AZO thin film, AFM were used to the measured the surface states at three ratios of Cl\(_2\)/Ar plasma were measured, as shown in figure 9. Figures 9(a)–(c) shows the AFM morphologies of as-deposited AZO thin film and etched AZO film in a Cl\(_2\)/Ar = 50:50% plasma and in a pure Cl\(_2\) plasma, respectively. The corresponding RMS (root mean square) values of surface roughness were 0.82 nm, 35.44 nm and 57.69 nm, respectively. The surface roughness of AZO thin film significantly increased.
after the Cl$_2$ plasma etching. Under the Cl$_2$/Ar plasma, it becomes smoother than that of the etched sample in pure Cl$_2$ plasma. As shown in Table 1, the etching of AZO thin films under Cl$_2$/Ar plasma is relatively selective. O element has a relatively high reaction with Cl$_2$ compared to Al and Zn elements, resulting in the lowered element ratio after the etching process. This means that oxygen vacancies are generated on the surface of the AZO thin film after the etching process. Therefore, the high roughness of the thin film after the etching process can be explained by oxygen vacancies and byproducts on the surface. And, the smoother surface under Cl$_2$/Ar plasma can be explained that the physical sputtering of Ar ions can effectively remove the by-products on the surface of AZO thin film, thus reducing the surface roughness of the film [22].

4. Conclusion

In this work, we studied the etch properties of AZO films using ACP systems. Etching performance is determined by changing process conditions (gas mixing ratio, RF power, and DC bias voltage). When the concentration of Cl$_2$ increases from 0 to 50%, the etch rate of AZO films reaches the maximum. When the concentration of Cl$_2$ is greater than 50%, the etch rate of AZO films decreases as the deposition rate of surface products increases. By the analysis of OES, Cl$_2$ were broken by Ar$^+$ sputtering and then reacted with the AZO thin films and the etching of AZO is affected the chemical reaction and physical sputtering. From XPS analysis, the chemical by-products Al$_x$O$_y$, AlCl$_x$ attached the film was be proved, physical sputtering yield of Ar$^+$ destroying Al-O-Zn and Al-Zn bonds to promote the chemical reaction. The AZO surface morphology analysis
by AFM proves that physical sputtering of Ar ions can effectively remove the by-products on the surface of AZO film, it can effectively avoid the damage caused by the pattern of the membrane. Finally, it is proved that the etching rate of AZO films in Cl2/Ar plasma was controlled by chemical reaction and Ar\(^+\) physical sputtering.

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