Inductively coupled plasma reactive ion etching of titanium thin films using a Cl₂/Ar gas

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1. Introduction

Titanium materials have been applied in many commercial products including microelectronics, optoelectronics, and other electronic devices [1–3]. In particular, titanium thin films are used widely in submicron semiconductor devices to form silicides that reduce the contact resistance between aluminum and silicon, and as a barrier between metal and silicon to prevent aluminum spiking [4]. Additionally, titanium thin films have been used as a hard mask in a plasma etching process owing to its high etch selectivity to other materials [5–7]. In many applications, a photoresist mask is generally used for pattern transfer, but it has its own disadvantages such as poor durability and fast etch rate under harsh etching conditions of the reactive ion etching process. Therefore, inorganic etching masks such as metals and metal oxides must be used to achieve a complete pattern transfer. Among the mask materials suitable for this purpose, titanium films are good candidate materials owing to their low sputtering yield and strong adhesion.

Some reports examining the etching of titanium thin films employed various etching gases, such as CCl₄/O₂, CCl₄/Cl₂/Ar/O₂, Cl₂/BCl₃, Cl₂/N₂, and Cl₂ [4,8–11]. However, in most cases, the etch rates of Ti films were relatively slow and no good etching profiles were provided. In this study, the etching of Ti thin films was evaluated using inductively coupled plasma reactive ion etching (ICPRIE) equipment with Cl₂/Ar gas chemistry. The etching parameters including the coil rf power, dc-bias voltage, gas pressure and Cl₂ concentration were varied to investigate the etch characteristics. In addition, X-ray photoelectron spectroscopy (XPS) was used to examine the etch mechanism.

2. Experimental details

Ti thin films were prepared on Si substrates by a rf magnetron sputtering and the films were patterned by conventional lithography process using a photoresist of AZ1512. The thicknesses of the Ti and photoresist films were 100 nm and 1200 nm, respectively. The pattern of photoresist films was composed of the lines and spaces of 1, 5, 10, 50, and 100 μm in width. The Ti films were etched using commercial ICPRIE equipment (A-Tech, Korea) that can generate high density plasma. The ICPRIE system consists mainly of a main process chamber and a 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 high density plasma. A self dc-bias voltage induced by the 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 pressure of 2.66–3.99 × 10⁻⁶ Pa using a turbomolecular pump. The substrate susceptor was cooled to a constant temperature of 7–10 °C with chilled fluid and the substrate was then cooled with cold helium gas between the substrate and susceptor.

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A B S T R A C T

Inductively coupled plasma reactive ion etching of titanium thin films patterned with a photoresist using Cl₂/Ar gas was examined. The etch rates of the titanium thin films increased with increasing the Cl₂ concentration but the etch profiles varied. In addition, the effects of the coil rf power, dc-bias voltage and gas pressure on the etch rate and etch profile were investigated. The etch rate increased with increasing coil rf power, dc-bias voltage and gas pressure. The degree of anisotropy in the etched titanium films improved with increasing coil rf power and dc-bias voltage and decreasing gas pressure. X-ray photoelectron spectroscopy revealed the formation of titanium compounds during etching, indicating that Ti etching proceeds by a reactive ion etching mechanism.

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AC l₂/Ar gas mix was used as the etch gas and fed into the main chamber at a flow rate of 50 sccm. The etch rates and etch profiles of the Ti thin films were examined by varying the Cl₂ gas concentration. In addition, the effects of the etch parameters i.e. coil rf power, dc-bias voltage to substrate and gas pressure, on the etch rate and etch profile 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). The surface chemistry of the etched films was examined by XPS to determine the etch mechanism of the Ti films in a Cl₂/Ar plasma.

3. Results and discussion

Ti thin films patterned with the photoresist masks were etched using a Cl₂/Ar gas mix with various Cl₂ concentrations to determine the optimal gas concentration. Fig. 1 shows the changes in etch rates of the Ti films and photoresist mask as a function of the Cl₂ concentration. The etch conditions were fixed: a coil rf power of 800 W, dc-bias voltage of 300 V, and gas pressure of 0.665 Pa. The etch rates of the Ti films increased gradually from 35 nm/min in 100% Ar to 200 nm/min in 100% Cl₂. The increase in etch rate with increasing Cl₂ concentration suggests that the Ti thin films are etched through a reactive ion etching mechanism, which contains two different etching mechanisms involving physical bombardment by energetic ions and a chemical reaction by radicals[12]. The etch rate increased with increasing Cl₂ concentration due to an increase of chemical reactions between the Ti films and chlorine radicals. The chemical compounds on the film surface can be TiClₓ and can be removed by the desorption from the surface for themselves and/or with the assistance of ion bombardment. The etch rate of the photoresist mask also increased linearly with increasing Cl₂ concentration.

Fig. 2 presents the etch profiles of the Ti films at different Cl₂ concentrations. Fig. 2(a) shows the etch profile in pure Ar. Heavy redeposition on the sidewall of the pattern was observed, which was attributed to the strong bombardment of Ar ions on the films. The etch profile at a 20% Cl₂ concentration showed no redeposition on the pattern sidewall and still a high degree of anisotropy, as shown in Fig. 2(b). As the addition of Cl₂ gas to Ar increased from 20% Cl₂ to 60% Cl₂ concentration, the sidewall slope of the etched patterns (called as etch slope hereafter) became slanted without redeposition on the pattern sidewall. Fig. 2(c) and (d) shows the etch profiles at 40% and 60% Cl₂ concentrations, respectively. No redeposition or residues were observed but the etch slopes were relatively low. This was attributed to the nature of chlorine gas, which is a chemically active species in plasma. In this study, 40% Cl₂ in the Cl₂/Ar gas mix was selected as the standard gas concentration for examining the effect of the etching parameters.

The effect of the etching parameters on the etching of Ti thin films was examined systematically by varying the coil rf power, dc-bias voltage to the substrate and gas pressure. The standard etching conditions were 40% Cl₂ in a Cl₂/Ar gas mix, coil rf power of

**Fig. 1.** Etch rate of Ti thin films as a function of the Cl₂ concentration. Etch condition: coil rf power of 800 W, dc-bias voltage of 300 V and gas pressure of 0.665 Pa.

**Fig. 2.** FESEM micrographs of Ti thin films etched under different Cl₂ concentrations. (a) Pure Ar, (b) 20% Cl₂/Ar, (c) 40% Cl₂/Ar, and (d) 60% Cl₂/Ar.
800 W, dc-bias of 300 V and gas pressure of 0.665 Pa. Fig. 3(a) shows the etch rates as a function of the coil rf power. The coil rf powers were varied from 700 W to 900 W with the other conditions fixed. As the coil rf power increased, the etch rate increased gradually with a significant improvement in etch slope. This was attributed to an increase in the concentration of radicals and ions in the plasma with increasing coil rf power due to the increase in plasma density [2,13]. The etch profile of the Ti films etched at 900 W showed a highly anisotropic etch slope (>80°) without any redeposited material or residue, as shown in Fig. 3(d).

The effect of the dc-bias voltage on the etch properties is presented in Fig. 4. The etch rates increased linearly (Fig. 4(a)) and the etch slope increased gradually with increasing dc-bias voltage from 200 V to 400 V (Fig. 4(b)–(d)). This is because positive ions at high dc-bias voltage of 400 V, which are attracted to the substrate, have higher energy than those at low dc-bias voltage of 200 V. Hence, the sputtering effect by positive ions at high dc-bias voltage is expedited, resulting in an increase in etch rate and a more vertical etch slope in the etch profile. However, redeposition on the sidewall of etched patterns can occur at high dc-bias voltage of 400 V because the strong sputtering effect by ions can be the dominant process over a chemical reaction.

Fig. 5 shows the etch rates of Ti thin films etched at different gas pressure. The etch rates increased slightly as the gas pressure
increased from 0.133 Pa to 1.33 Pa. At 0.133 Pa, a vertical etch slope with a high degree of anisotropy was obtained. However, the etch slope of thin films etched at high gas pressure was slanted compared to that etched at low gas pressure and a small amount of residue was observed on the sidewall of the pattern. The plasma density increased with increasing gas pressure. Therefore, more radicals and ions are created under high gas pressure. However, the mean free paths of those components are reduced by scattering due to the high gas pressure so that the final effect of the gas pressure on the etch rate was minimal but the etch profile can be affected by effective bombardment of energetic ions to the substrate due to low scattering at low pressure. Therefore, the vertical etch slope was achieved at a low pressure of 0.133 Pa.

In order to elucidate the etch mechanism, XPS analysis was performed to examine the Ti film surface after etching in a Cl\textsubscript{2}/Ar gas mix. Bare Ti thin films without photoresist masks were used as specimens for this analysis. All species were pre-sputtered prior to analysis to remove contaminants from the surface due to exposure to the atmosphere. Fig. 6 shows the narrow scan of the Ti 2p peaks for Ti films. The narrow scan of the as-deposited Ti film indicates the chemical state of pure metallic Ti element. However, the Ti peak of the film etched in 40% Cl\textsubscript{2} was shifted to a higher binding energy of 454.3 eV, indicating the existence of Ti compounds, TiCl\textsubscript{X} in this case. This can also explain the increase in etch rate with increasing Cl\textsubscript{2} concentration due to enhanced chemical reactions between Ti and chlorine radicals.

4. Conclusions

Dry etching of Ti thin films patterned with a photoresist was carried out in inductively coupled plasma with Cl\textsubscript{2}/Ar chemistry. The etch rates and etch profiles of the Ti thin films were obtained by varying the Cl\textsubscript{2} concentration and etch parameters. As the Cl\textsubscript{2} concentration increased, the etch rate of the Ti films gradually increased, indicating that the etching process is enhanced by the addition of Cl\textsubscript{2} gas. Both the etch rate and etch slope of the Ti films increased with increasing coil rf power and dc-bias voltage. The etch rate showed a slight increase with increasing pressure but the etch profile was superior at low gas pressure.

XPS analysis confirmed the reaction between Ti metal and chlorine radicals in Cl\textsubscript{2}/Ar plasma during etching, resulting in the formation of TiCl\textsubscript{X} compounds. The etching characteristics and XPS analyses confirmed that the etching of Ti thin films in a Cl\textsubscript{2}/Ar gas mix occurs through a reactive ion etching mechanism.

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References