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## Influence of substrate temperature on the etching of silver films using inductively coupled Cl<sub>2</sub>-based plasmas

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### Abstract

In this study, the influence of substrate temperature on Ag etching is investigated using inductively coupled plasmas. When Cl<sub>2</sub>-based chemistry is used to etch Ag, involatile etch products remaining on the Ag film can be observed after the etching due to the very low vapor pressure of the etch reaction products, therefore, the reaction products thicker than the thickness of Ag are obtained after the etching. Even though these reaction products can be removed in a photoresist stripper, Ag removal rate is generally very low at room temperature. However, when elevated substrate temperatures in the range from 25 to 165 °C are used, due to the enhancement of Cl transport and reaction rate, higher Ag removal rates can be obtained after the photoresist stripping even though these products are not removed in situ during the etch processing. Also, we found that, at the elevated temperatures, the ratio of remaining AgCl layer thickness to the consumed Ag layer thickness is continually decreased with increasing temperature due to the increased vaporization of Ag reaction products.

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**Keywords:** Silver (Ag); Etching; Substrate temperature; Etch product; Cl<sub>2</sub>-based plasma

### 1. Introduction

Silver (Ag) has the lowest resistivity at room temperature (RT) and higher reflectance than aluminum by 10–15%, and thus is an attractive materials, in thin film transistor liquid crystal display (TFT-LCD) and semiconductor industry for interconnect and metal gates. At RT, the resistivity of Ag is 1.57 μΩ cm as compared to 2.67 and 2.0 μΩ cm for Al and Cu, respectively. Also, it is one of the potential candidates for the future integrated circuit to reduce RC delay times [1].

Generally, Ag is wet-etched. However, due to the reduction of critical dimension of the lines, plasma etching is essential and preferable for the next generation TFT-LCD devices. But, several problems must be resolved before Ag plasma etching can be applied to TFT-LCD processing. The main problems are the formation of involatile etch product and low etch rates. For example, many publications on Ag etching reported a thick involatile Ag etch reaction products such as silver chloride, silver fluoride, and silver oxyfluoride remain-

ing during the etch process using O<sub>2</sub> and halogen-based plasmas such as Cl<sub>2</sub> or CF<sub>4</sub> with O<sub>2</sub> [2–6]. These etch products could be removed by the subsequent wet resist-strip process after the plasma etching instead of vaporization or sputtering of the etch reaction products during plasma processing [7]. However, even in this two-step dry–wet method, Ag removal rate is lower than 100 nm/min.

Therefore, in this study, Ag thin films are etched at various elevated substrate temperatures. The influences of substrate temperatures on the Ag thin film etching are studied using inductively coupled chlorine-based plasmas. A possibility of etching Ag at higher rates is investigated by increasing the formation rate of reaction products, which can be removed by the two-step dry–wet processing or by enhancing the vaporization of the reaction products.

### 2. Experimental

To study the Ag etch characteristics, homemade inductively coupled plasma (ICP) equipment was used. To generate ICPs, 13.56 MHz RF power was applied to a 3.5 turn spiral copper coil located on the top of

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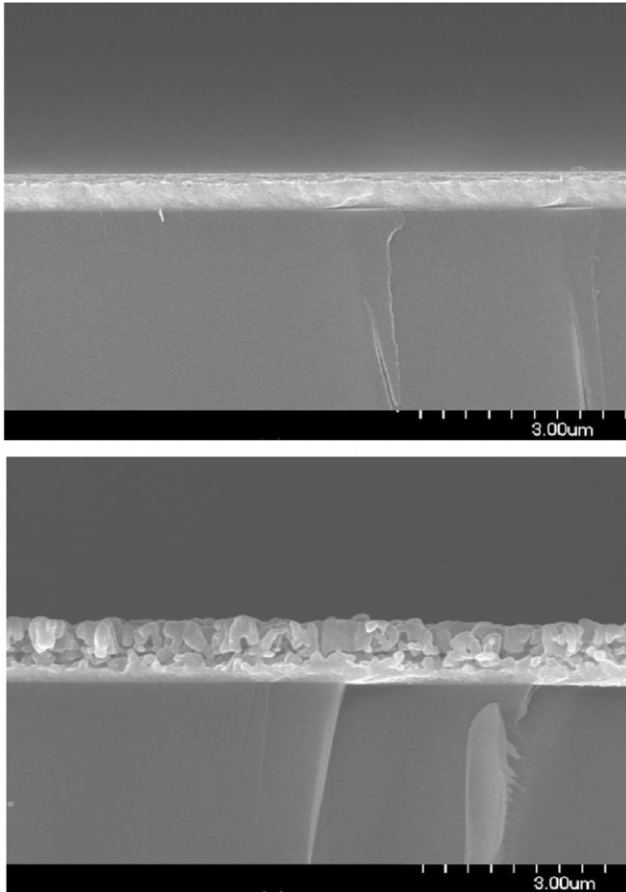


Fig. 1. Cross-sectional SEM micrograph of Ag film before (top) and after (bottom) the etching by  $\text{Cl}_2$  ICPs (process condition: inductive power (500 W), d.c.-bias voltage ( $-150$  V), and operating pressure (2 Pa). Etch time, 1 min).

chamber and separated by a 1-cm thick quartz-window. Separate 13.56 MHz RF power was also applied to the substrate to induce bias voltages on the wafer. The distance between the quartz window and the substrate was 7 cm. Details of the ICP system used in the experiment are described elsewhere [8].

Ag thin films (500 nm) were deposited on LCD-grade glass substrates by RF sputtering. Chlorine gas was used to etch Ag thin films, and other etch parameters such as the inductive power, the d.c.-bias voltage, and the operating pressure were kept at 500 W,  $-150$  V and 2 Pa, respectively. Also, the substrate temperature was varied from 25 to 165 °C using a chiller that can control the substrate temperature from RT to 200 °C.

The step height of the films was measured before and after the etching with stylus profilometry. Changes in the thickness of Ag reaction product layer and Ag layer were determined from the profilometer measurements. A scanning electron microscope (Hitachi, S-2150 SEM) was used to observe Ag surfaces. X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy

(AES, PHI-670) were also used to analyze the reaction product remaining on the etched Ag surface.

### 3. Results and discussions

Fig. 1 shows cross-sectional SEM micrographs of Ag film on the glass substrates observed before and after the etching using a pure  $\text{Cl}_2$  plasma at 500 W of inductive power,  $-150$  V of d.c.-bias voltage and 2 Pa of operational pressure. The etching time was 1 min and the substrate temperature was kept at 25 °C. As shown in Fig. 1, a thick etch product was remaining on the top of the unreacted Ag thin film after the etching. The surface of the etch reaction product became rough and granular while the surface of Ag film before the etching was smooth. The etch product remaining on the top of Ag is from the formation of  $\text{AgCl}$  that has a very low vapor pressure and sputter yield after the exposure to Cl-based plasmas. This involatile etch reaction product could be easily removed by the following wet resist-strip [7].

Fig. 2 shows the XPS narrow scan data of Ag (3d) measured on the Ag thin film before and after the etching using pure  $\text{Cl}_2$  plasma. The process condition was the same as in Fig. 1. As shown in figure, before the etching, pure Ag metal showed the binding energy of Ag (3d) at 368.3 eV, however, after the exposure to the  $\text{Cl}_2$  plasma, the binding energy of Ag (3d) has changed to 368 eV. Therefore, Ag (3d) peak has shifted approximately 0.3 eV compared to that of pure Ag metal suggesting the formation of  $\text{AgCl}$  as the etch reaction product [7].

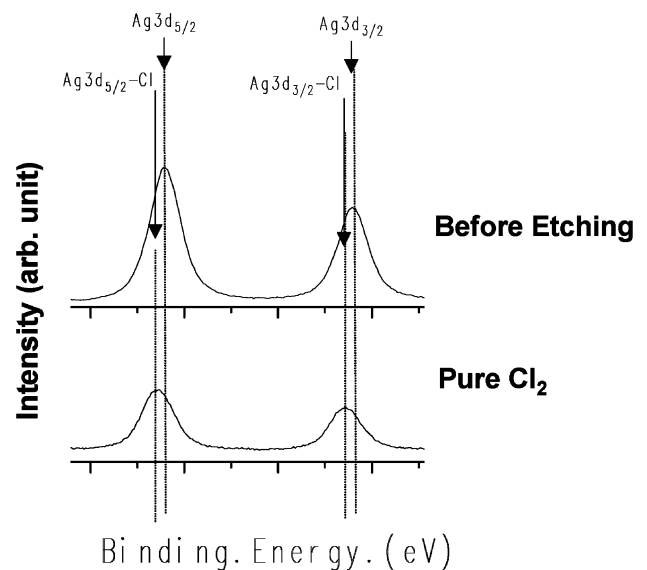


Fig. 2. Ag 3d XPS narrow scan spectra of Ag film surfaces exposed to pure  $\text{Cl}_2$  plasmas (process condition: inductive power (500 W), d.c.-bias voltage ( $-150$  V), and operating pressure (2 Pa).

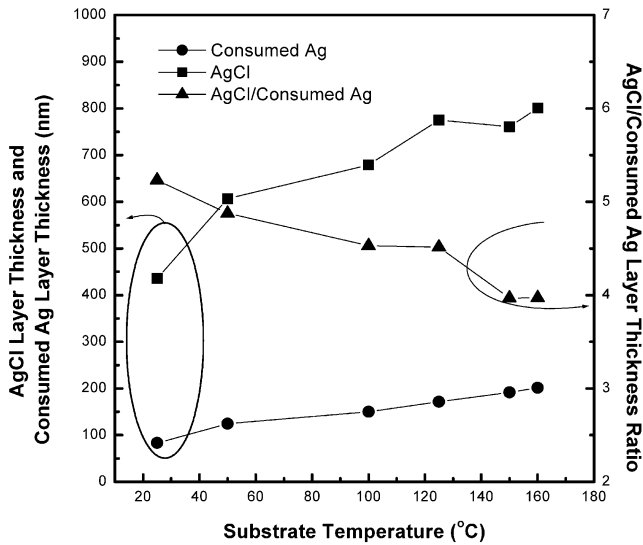


Fig. 3. AgCl growth, Ag consumption, and the ratio of AgCl<sub>x</sub> to consumed Ag layer thickness as a function of substrate temperature during the etching in Cl<sub>2</sub> ICPs (process condition: inductive power (500 W), d.c.-bias voltage (−150 V), and operating pressure (2 Pa). Etch time, 1 min).

The vapor pressures of AgCl is very low at RT because the boiling temperature of AgCl is 1547 °C, therefore, the AgCl formed during the etching of Ag using Cl<sub>2</sub> remains on the surface. Even though the AgCl could be removed using a photoresist stripper during the following wet processing, the formation rate of AgCl at RT was low. Therefore, overall Ag removal rate with Cl<sub>2</sub> at the condition in Fig. 1 was lower than 100 nm/min. To improve the Ag etch rate, the substrate temperature was increased. Change in remaining AgCl and consumed Ag thickness, and the ratio of the thickness of AgCl to consumed Ag were investigated and shown in Fig. 3. The thicknesses of AgCl layer and the consumed Ag layer were calculated after measuring the thickness of the etch step before and after the photoresist stripping of AgCl/Ag bilayer formed during the etching. The substrate temperature was varied from 25 to 165 °C while inductive power, d.c.-bias voltage, operating pressure, etching time were kept at 500 W, −150 V, 2 Pa and 1 min, respectively. As shown in figure, increasing substrate temperature increased the thickness of AgCl layer remaining on the substrate and the consumed Ag layer almost linearly, possibly due to the increase of reaction between Ag and Cl by the increase of Cl diffusion rate and reaction rate [9]. The ratio of AgCl layer to consumed Ag layer was decreased with increasing temperature as shown in figure. The decrease in the ratio suggests that the vaporization of AgCl is increased with increasing substrate temperature, even though the remaining thickness of AgCl is increasing with temperature due to the enhanced reactions.

The surface composition of the etched Ag surface was examined by AES. Fig. 4 shows the composition change of Ag surface etched by Cl<sub>2</sub> as a function of substrate temperature. The operating condition was the same as in Fig. 3. As shown in figure, increasing of substrate temperature from RT to 150 °C decreased the AES intensity ratio of Cl to Ag on the Ag surface. The decrease of the AES intensity ratio of Cl to Ag appears to be related to the vaporization of AgCl on the etched Ag surface as suggested by the ratio of AgCl to consumed Ag in Fig. 3.

Fig. 5 shows AES depth profiles of Cl atomic percentages in the etched Ag film as a function of different substrate temperatures for the condition in Fig. 4. As shown in figure, Cl atomic percentages in the etched Ag film decreases with increasing depth from the surface of Ag film suggesting possible grain boundary diffusion of Cl into the Ag film. Also, increasing the substrate temperature increases the penetration of Cl into Ag film, therefore, the thickness of AgCl is increased. Therefore, not only the vaporization of AgCl formed on the Ag surface is increased, but also the diffusion of Cl into Ag layer through grain boundary with increasing substrate temperature.

Fig. 6 shows cross-sectional SEM micrographs of the Ag film etched at various substrate temperatures. The etch condition is also the same as in Fig. 3. As shown in figure, as the substrate temperature was increased, the thickness of AgCl formed on the Ag surface was increased as discussed in Fig. 3. Also, in addition to the increase in the thickness of AgCl, the size of each grain-like AgCl reaction product and its porosity were increased with the increased substrate temperature. The increased porosity of the etch product at the high substrate temperature appears to be from the increased reactivity and the stress formed on the AgCl due to the

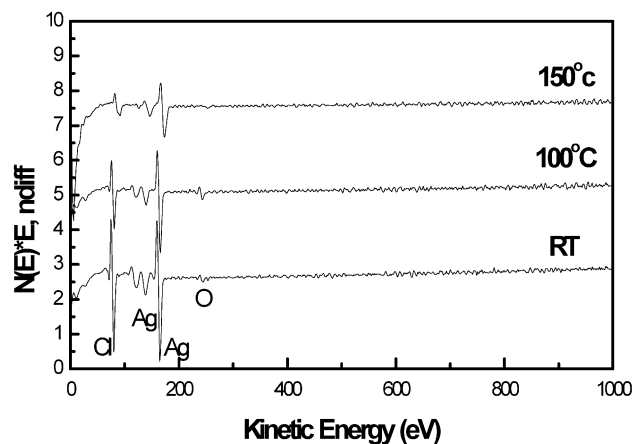


Fig. 4. AES data of the Ag film surface etched in Cl<sub>2</sub> plasmas for various substrate temperatures (process condition: inductive power (500 W), d.c.-bias voltage (−150 V), and operating pressure (2 Pa)).

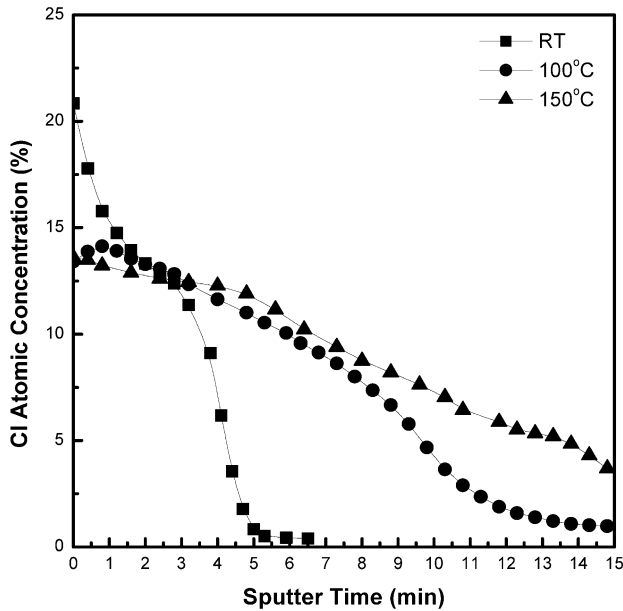


Fig. 5. AES depth profiles on atomic concentration of Cl for the Ag film etched in  $\text{Cl}_2$  plasmas at various substrate temperatures (*process condition*: inductive power (500 W), d.c.-bias voltage ( $-150$  V), and operating pressure (2 Pa). Etch time, 1 min).

expansion of volume during the formation of the product. When the substrate temperature was increased to  $200^\circ\text{C}$ , 500-nm thick Ag was processed within 30 s and only a white particle-like residue was remained (not shown). This residue was so porous and brittle, it could be removed even by blowing  $\text{N}_2$ . Therefore, high Ag removal rate higher than  $1\ \mu\text{m}/\text{min}$  could be obtained by increasing the substrate temperature to  $200^\circ\text{C}$  after the wet stripping by a photoresist stripper.

#### 4. Conclusions

In this study, the effect of elevated substrate temperature were investigated to characterize the etch product formed during the Ag etching using  $\text{Cl}_2$  ICPs and its effect on the Ag etching properties.

Due to the very low vapor pressure of AgCl, a thick etch residue was remained after the etching. This reaction product was easily removed by the following wet processing using a photoresist stripper, however, Ag removal rates were generally very low at RT. Increasing the substrate temperature increases not only the formation of AgCl by diffusion of Cl into Ag film and the reaction of Ag with Cl, but also the vaporization of AgCl on the etched Ag film surface. The AgCl formed at the higher substrate temperature was more granular and more porous compared to that formed at the lower temperature. The increased porosity of the AgCl formed at the high substrate temperature appears to be related to the stress developed by the expansion of the film during the formation of AgCl. By elevating the substrate

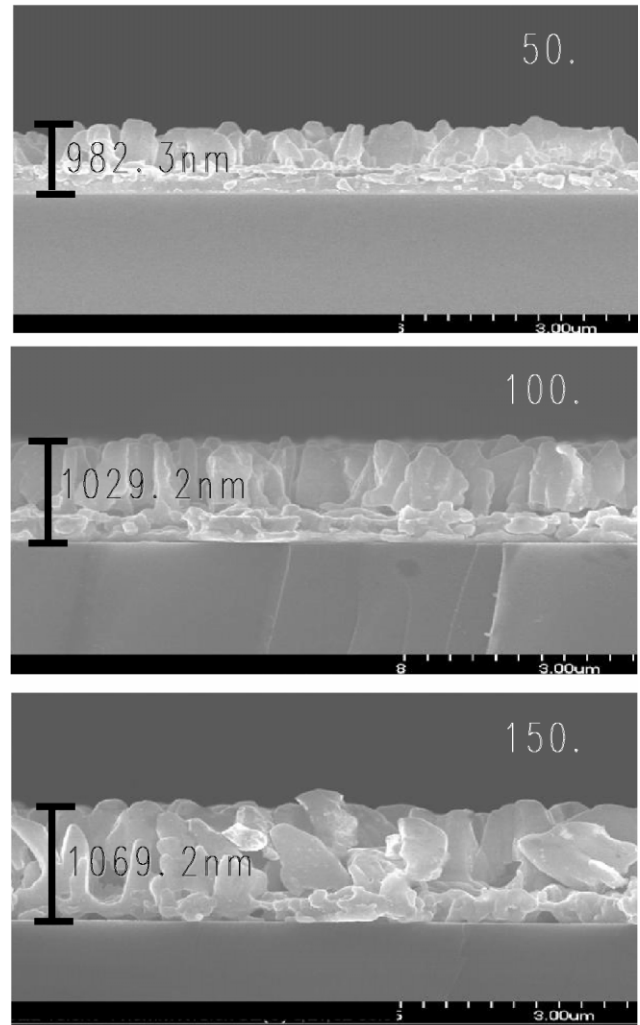


Fig. 6. Cross-sectional SEM micrographs of Ag films etched in  $\text{Cl}_2$  plasmas at various substrate temperatures (*process condition*: inductive power (500 W), d.c.-bias voltage ( $-150$  V), and operating pressure (2 Pa). Etch time, 1 min).

temperature to  $200^\circ\text{C}$ , the Ag removal rate higher than  $1\ \mu\text{m}/\text{min}$  could be obtained after the wet stripping of the etch product.

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