

Effects of Additive Gases on Ag Etching Using Inductively Coupled Cl₂-Based Plasmas

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In this study, the effects of additive gases on the Ag etching were investigated using Cl₂-based inductively coupled plasmas. When Cl₂-based gases were used to etch Ag films, due to the formation of involatile etch by-products, thick etch reaction products were remained. However, these etch by-products could be removed during the photoreist wet stripping process, therefore, various Ag removal rates could be obtained depending on the process conditions. When Cl₂ was used with N₂ and O₂, higher Ag removal rates than those by pure Cl₂ could be obtained. These results are interpreted as the increase of Cl radical due to the enhancement of the dissociation of Cl₂ gas when N₂ was added to Cl₂ and the formations of more porous and reactive etch reaction products when O₂ was added to Cl₂. Therefore, Ag films removal rates showed the maximum at 50 %Cl₂/50 %N₂ for Cl₂/N₂ and also at 50 %Cl₂/50 %O₂ for Cl₂/O₂. However, when Cl₂ was used with Ar, Ag removal rates was not increased with the addition of Ar possibly due to the formation of a dense etch by-product and a low sputter yield of the formed etch by-product.

PACS numbers: 55.77.Bn

Keywords: Silver(Ag), Etching, Additive gas, Etch by-product, Cl₂-based plasma

I. INTRODUCTION

Since Silver (Ag) has the lowest resistivity among metals at room temperature and has higher reflectance than aluminum (Al) by 10~15 %, it is known to be one of the ideal candidates as interconnects and gate metals for semiconductor integrated circuits and flat panel display such as thin film transistor liquid crystal display (TFT-LCD) [1]. To apply to those devices successfully, Ag has to be patterned and etched successfully.

Generally, Ag etching is performed using wet etching methods. However, wet etching is incapable of etching high-resolution features. Ag films also have to be patterned into fine lines with a tapered profile to apply Ag to TFT-LCDs. For these reasons, plasma etching has been investigated for producing feature sizes compatible to the next generation TFT-LCD devices. However, there are some problems to be solved before Ag plasma etching to be applied to TFT-LCDs processing. The main problems are the formation of involatile etch by-products and low etch rates [2-6]. The reaction of Ag with a halogen containing gas and the following removal of resulting by-products have been one of the most popular methods. For example, additional energy sources such as high substrate temperature and high ion bombardment energy have been used to remove the by-products [7-9]. However, these methods may cause a problem in pro-

cessing large area substrates due to the potentially poor etch uniformity. Also, the equipment design and operation become complicated. Therefore, a two-step dry-wet method has been studied for Ag patterning, where involatile etch by-products formed during the plasma processing are removed by the subsequent resist wet strip process after the plasma processing instead of vaporization or sputtering of the etch reaction products during the plasma processing [10]. However, even in this two-step dry-wet method, the Ag removal rates investigated are still very low.

Therefore, in this study, plasma processing of Ag for the dry-wet method was carried out using inductively coupled Cl₂-based plasmas and the effects of various additive gases such as Ar, O₂, and N₂ were investigated to obtain higher Ag removal rates by the formation of more reactive etch by-products of Ag.

II. EXPERIMENTAL

500 nm-thick silver (Ag) thin films were deposited on LCD-grade glass substrates by rf-sputtering and 2.0 μm-thick photoresist with the tapered angle about 30 degree was used as the mask layer. The plasma exposure experiment was performed in a homemade inductively coupled plasma (ICP) equipment. This equipment was

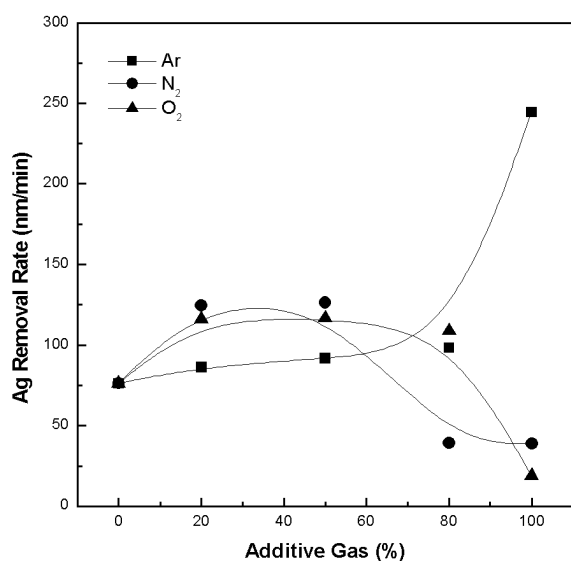


Fig. 1. Removal rates of Ag films as a function of mixtures such as Cl₂/Ar, Cl₂/N₂, and Cl₂/O₂ using inductive power of 500 Watts, dc-bias voltage of -150 Volts, and operating pressure of 15 mTorr.

composed of a 3.5 turn and 0.6 cm diameter spiral copper coil located on the top of anodized Al chamber and separated by a 1 cm-thick quartz window. A rf power of 13.56 MHz was applied to the coil to generate inductively coupled plasmas and a separate 13.56 MHz rf power was also applied to the substrate to generate dc-bias voltages to the wafer. The distance between the quartz window and the substrate was 7 cm. More details of the system used in the experiment can be found elsewhere [11].

Chlorine (Cl₂) gas was used as the main etch gas to etch Ag thin films and Ar, O₂, and N₂ were used as additive gases. Other etch parameters such as inductive power, dc-bias voltage, operating pressure, and substrate temperature were kept at 500 Watts, -150 Volts, 15 mTorr, and room temperature, respectively.

Removal rates of Ag thin films were determined using by stylus profilometry of the Ag step height formed after the removal of the photoresist using a wet stripper which also removes the etch by-product formed during the plasma processing. A scanning electron microscope (Hitachi, S-2150 SEM) was used to observe the as-etched Ag surfaces before the wet stripping. X-ray diffraction (XRD, D8 Discover) and Auger electron spectroscopy (AES, PHI-670) were also used to analyze the reaction products remaining on the etched Ag surface.

III. RESULTS AND DISCUSSION

Figure 1 shows the Ag removal rates as a function of additive gases such as Ar, N₂, O₂ to Cl₂ measured after the wet stripping using a photoresist wet stripper. The

operational conditions of the inductively coupled plasmas were 500 Watts of inductive power, -150 Volts of dc bias voltage, 15 mTorr of operational pressure, and 25 °C of substrate temperature. As shown in the figure, when Ar was added to Cl₂, the Ag removal rate did not show a significant change with Ar except for the case with pure Ar. With pure Ar, the Ag etch rate showed the highest Ag etch rate of about 250 nm/min and no reaction product was observed. However, when Cl₂ was mixed with Ar, an involatile etch by-product layer was observed on the top of the etched Ag surface before the photoresist wet stripping. Therefore, the low Ag removal rates of

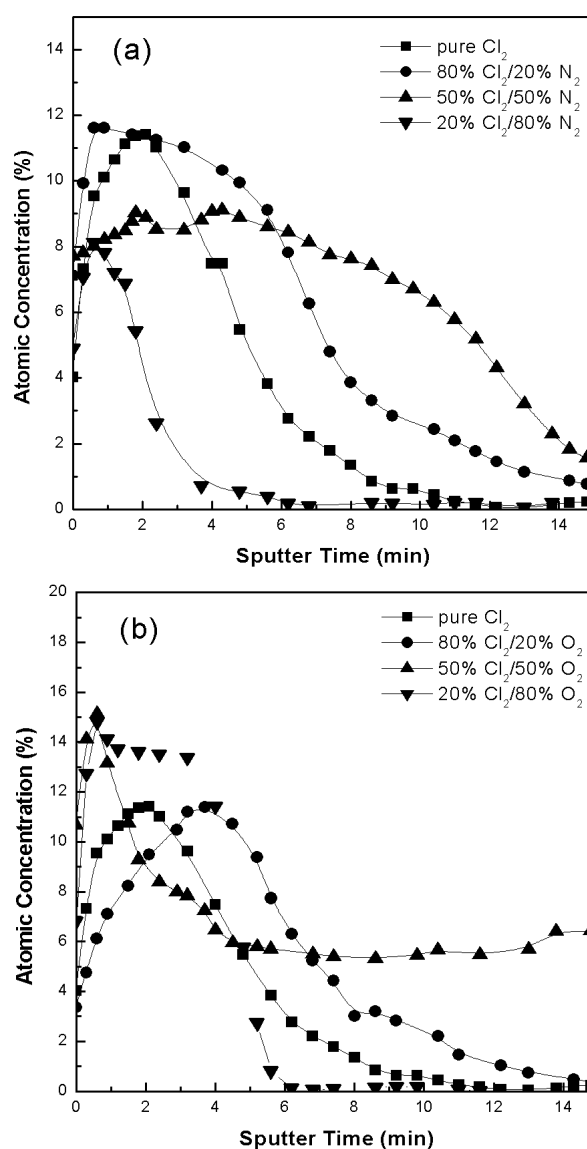


Fig. 2. AES depth profiles on the concentration of Cl for the Ag film etched in (a) Cl₂/N₂ plasma and (b) Cl₂/O₂ plasma using inductive power of 500 Watts, dc-bias voltage of -150 Volts, and operating pressure of 15 mTorr for the etch time of 1.5 minutes.

Cl₂/Ar mixtures compared to that of pure Ar appear to be from the formation of the etch by-products such as AgCl_x which have low sputter yields and very low vapor pressures.

The high Ag etch rate with pure Ar is related to the high sputter yield of Ag by Ar⁺ ion (3.4 atom/ion, by Ar⁺ ion, 400eV) [12]. Even though Ag etching with pure Ar shows the highest etch rates, Ag sputtering by pure Ar deposits a thin Ag layer around the chamber wall and the dielectric window on the top of chamber. Especially, the formation of Ag layer on the dielectric window prevents the delivery of inductive power to the plasmas through the dielectric window, therefore, makes it difficult to operate the inductively coupled plasma source

after a few minutes. Therefore, pure Ar can not be used for Ag etching when high density plasma sources such as inductively coupled plasmas are used. However, when halogen-based gases are used to etch Ag, the deposition of Ag halide on the dielectric window did not show any problem in transmitting the rf electromagnetic field to the plasmas [7,10]. Figure 1 also shows the effect of N₂ and O₂ to Cl₂ on the Ag removal rate estimated after the photoresist wet stripping. As shown in the figure, the mixture of N₂ or O₂ to Cl₂ increased the Ag removal rate, therefore, showed higher etch rates than that with pure Cl₂ or Cl₂/Ar, and the addition of 50 % N₂ or 50 % O₂ to Cl₂ showed the highest Ag removal rate.

Figure 2 shows the AES depth profile of Cl in the Ag thin films etched using (a) Cl₂/N₂ and (b) Cl₂/O₂. The etch conditions were the same as that in Figure 1 and the etch time was 1.5 minutes. As the reference, the AES depth profile of Cl in the Ag thin film etched using pure Cl₂ was included in both figures. As shown in Figure 2(a), the mixture of N₂ to Cl₂ increased the depth of Cl in the etched Ag thin film and the penetration depth of Cl was maximum at 50 % N₂. Therefore, the mixture of N₂ to Cl₂ up to 50 % increased the Cl penetration depth in the etched Ag thin film. The low Cl penetration depth at 80 % N₂ appears to be from the low Cl concentration in the plasma due to the insufficient supply of Cl₂ gas. When O₂ was mixed to Cl₂, the Cl penetration depth showed the similar trend as that of Cl₂/N₂ as shown in Figure 2(b), therefore, the maximum Cl penetration depth was observed at 50 % O₂. However, a long steady tail of Cl atomic percentage was observed especially for 50 % O₂ possibly indicating enhanced grain boundary diffusion of Cl into Ag thin film. The comparison of the results on the Ag removal rate in Figure 1 with the results on the Cl penetration depth in Figure 2 shows that the Ag removal rate is related to the Cl penetration.

Figure 3 shows the XRD data of the etched Ag thin films for the conditions shown in Figure 2. Figure 3(a) shows XRD data of the Ag thin films etched with Cl₂/N₂ and Figure 3(b) shows those etched with Cl₂/O₂. As references, X-ray diffraction data of Ag film itself and that etched in pure Cl₂ were included in both figures. As shown in Figure 3(a) and (b), the peaks related to only AgCl (200) and Ag were found and the mixture of N₂ or O₂ increased the relative intensity of AgCl (200) peak when N₂ or O₂ was mixed up to 50 % and the further increase of N₂ or O₂ decreased the intensity of AgCl (200) peak. Higher intensity of AgCl peak indicates more AgCl amount in the etched Ag thin film, which results in higher Ag removal rate. In the case of Ag etching with Cl₂/O₂, in addition to AgCl, it is known to form AgO and the X-ray diffraction angle of AgO ($\bar{1}11$) peak is similar to that of AgCl (200) (the diffraction angle 2θ of AgCl (200) is 32.243 while that of AgO ($\bar{1}11$) is 32.279). Therefore, the AgCl (200) observed with Cl₂/O₂ may be mixed with AgO peak.

Figure 4 shows the SEM pictures of the Ag thin films

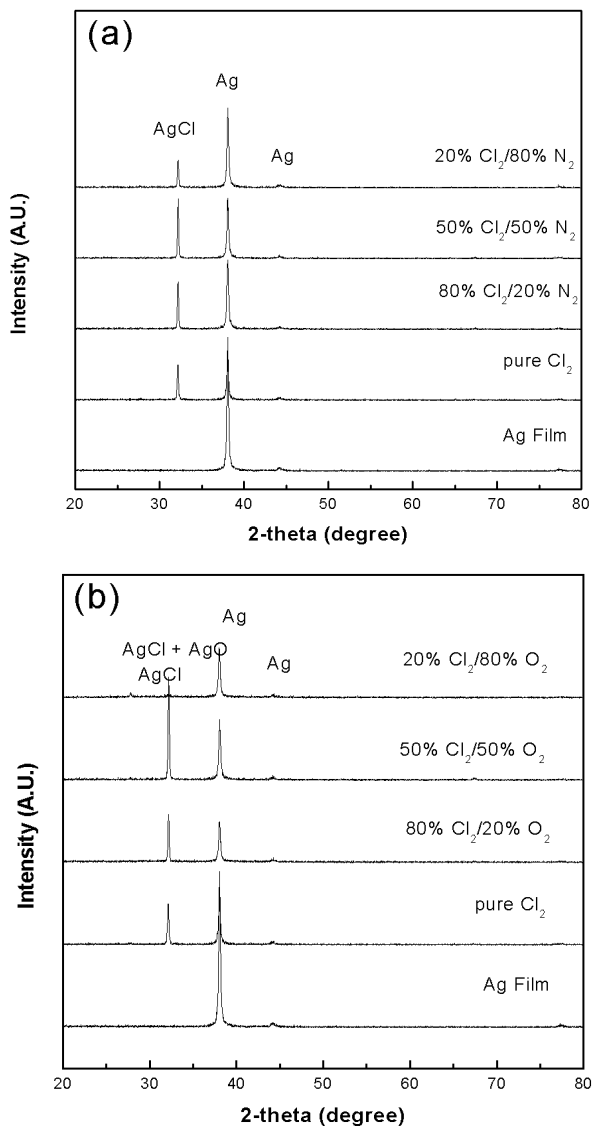


Fig. 3. XRD patterns of the Ag film etched in (a) Cl₂/N₂ plasma and (b) Cl₂/O₂ plasma using inductive power of 500 Watts, dc-bias voltage of -150 Volts, and operating pressure of 15 mTorr for the etch time of 1.5 minutes.

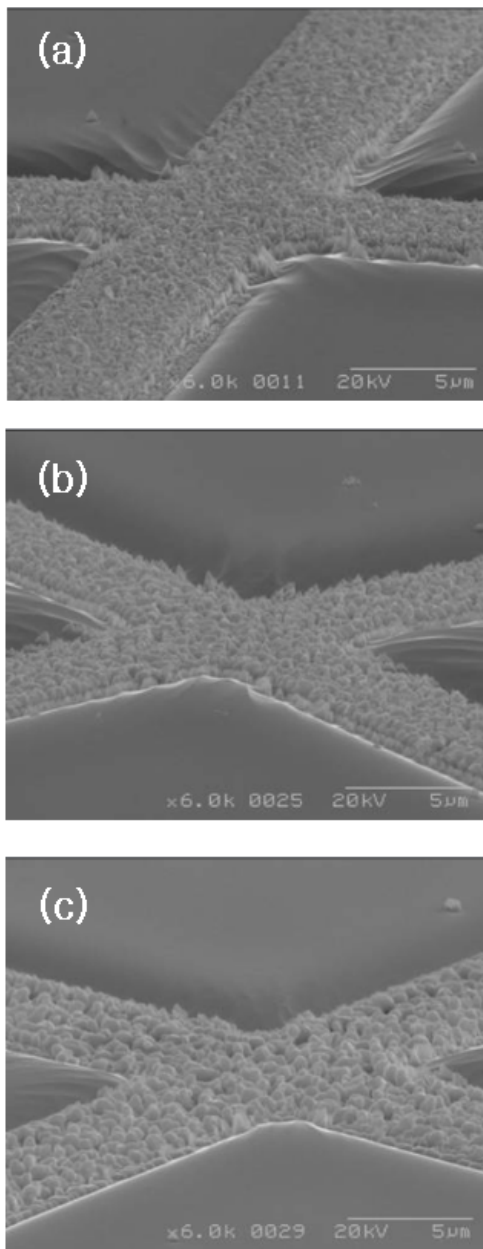


Fig. 4. SEM micrographs of Ag film surfaces exposed to (a) pure Cl_2 , (b) 80 % Cl_2 /20 % N_2 , and (c) 80 % Cl_2 /20 % O_2 plasma using inductive power of 500 Watts, dc-bias voltage of -150 Volts, and operating pressure of 15 mTorr for the etch time of 3 minutes.

etched by (a) pure Cl_2 , (b) 80 % Cl_2 /20 % N_2 , and (c) 80 % Cl_2 /20 % O_2 . The operational conditions were the same as those in Figure 1 and the etch time (or plasma exposure time) was 3 minutes. As shown in the figures, the etch by-products observed after the etching by Cl_2/O_2 and Cl_2/N_2 were thicker than those observed after the etching by pure Cl_2 due to the formation of thicker AgCl on Ag thin film. However, the shape of the etch by-products formed after the etching by 80 % Cl_2 /20

% N_2 was similar to those formed after the etching by pure Cl_2 . In the case of the etch by-products formed after the etching by 80 % Cl_2 /20 % O_2 , more porous and granular type etch by-products were observed as shown in the figure. The porous and granular shape of the etch by-product by Cl_2/O_2 appears to be related to the long steady tail of Cl concentration observed by AES depth profile in Figure 2(b). More porous and granular shape of the etch by-products by Cl_2/O_2 might be related to the volume expansion by formation of the mixed AgCl and AgO in the Ag thin film.

From the above results, it is believed that the increase of Ag removal rate by the mixture of N_2 to Cl_2 is related to the increase of Cl radicals to react with Ag thin films by the increased dissociation of Cl_2 in Cl_2/N_2 . The increase of Cl concentration by mixing N_2 to Cl_2 in Cl_2/N_2 plasmas was studied by other researchers [13]. However, the increase of Ag removal rate by the mixture of O_2 to Cl_2 appears to be more related to the enhanced diffusion of Cl through the grain boundaries of the Ag thin films formed by the porous and granular etch by-products.

IV. CONCLUSIONS

In this study, the effect of additive gases such as Ar, N_2 , and O_2 to Cl_2 on the Ag removal (or etching) rate was investigated using an inductively coupled plasma etching system and its etching mechanism was studied by analyzing the etch by-products formed on the etched Ag film surfaces.

When Cl_2 -based gases were used to etch Ag thin film, involatile etch by-products were formed on the Ag film surface. However, these etch by-products were removed easily by a photoresist stripper during the following wet processing, therefore, various Ag removal rates could be obtained after the photoresist wet stripping depending on the gas combinations. When pure Cl_2 was used to etch Ag thin film, the Ag removal rate estimated after the photoresist stripping was low as 76 nm/min and the mixture of Ar to Cl_2 did not change the Ag removal rate significantly possibly due to the low sputter yield of the etch by-product. However, when N_2 or O_2 was mixed with Cl_2 , the Ag removal rates were increased and 120 nm/min of Ag removal rate could be obtained by mixing 50 % N_2 or 50 % O_2 . The increase of Ag removal rate by the mixture of N_2 to Cl_2 appears to be related to the increase of Cl radicals by the increased dissociation of Cl_2 in Cl_2/N_2 . However, the increase of Ag removal rate by the mixture of O_2 to Cl_2 appears to be more related to the enhanced diffusion of Cl through the grain boundaries of the Ag thin films formed by the more porous and granular etch by-products.

ACKNOWLEDGMENTS

This work was supported by the Samsung Electronics Co. and the National Research Laboratory Program (NRL) by the Korea Ministry of Science and Technology.

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