

Characteristics of Ag Etching using Inductively Coupled Cl₂-based Plasmas

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In this study, Ag thin films deposited on glass were etched using inductively coupled Cl₂-based plasmas and the effects of various Cl₂-based gas mixtures on the formation of reactive byproducts affecting Ag etching were investigated. When Cl₂-based gas mixtures were used with Ar and O₂, due to the very low vapor pressure of the etch products, thick etch products remaining on the substrate could be observed after the etching. However, these etch products were easily removed during the photoresist stripping by a photoresist stripper. In particular, when O₂ was added to Cl₂, higher Ag removal rates during the photoresist stripping than those by pure Cl₂ or O₂ could be obtained. These results are interpreted as the formations of more porous and reactive etch reaction products when O₂ was added to Cl₂. The Ag removal rates by Cl₂/O₂/50%N₂ estimated after the photoresist stripping were higher than those by Cl₂/O₂/50%Ar and the use of Cl₂/O₂/50%Ar resulted in higher Ag etch rates than those by Cl₂/50%Ar. Therefore, the physical and chemical properties of the etch products formed by the specific gas mixture appear to be important in removing Ag for Cl₂-based plasmas. [DOI: 10.1143/JJAP.42.286]

KEYWORDS: silver (Ag), etching, removal rate, etch product, Cl₂-based plasma

1. Introduction

Silver (Ag) is a very attractive material in thin film transistor liquid crystal display (TFT-LCD) due to its lowest bulk resistivity of all metals at room temperature and high reflectivity. The resistivity of Ag is 1.47 μΩ·cm lower than that of Al (2.67 μΩ·cm), Al alloys (5.0–7.0 μΩ·cm), or Cu (2.0 μΩ·cm) is currently employed as the conductor in semiconductor integrated circuits and the reflectance of Ag is higher than that of Al by 10–15%. Large area and high quality TFT-LCD requires low electrically resistive gate materials such as Ag for the next-generation devices. Also, it is one of the potential candidates for the future interconnect metallization in integrated circuit (IC) manufacturing even though it has a low mechanical and highly corrosion sensitive property.^{1–5)}

To apply Ag as conductors easily to TFT-LCD or semiconductor metallization, Ag has to be patterned by dry etching methods, however, only a few studies on dry etching of Ag have been conducted. O₂ plasmas have been applied to etch Ag,^{6–8)} however, a slow etch rate and postetch surface roughness are the drawbacks of O₂ etching. Very recently, mixtures of halogen gases such as Cl₂ and CF₄ with O₂ have also been investigated for Ag patterning using conventional reactive ion etchers.^{9–12)} Nguyen *et al.*¹²⁾ reported that the etch products remaining after Ag etching by CF₄ or CF₄/O₂ chemistries were easily removed through the reaction of the products with a photoresist stripper during the photoresist stripping process. In this process, the dry process is employed to form reactive byproducts of Ag, and the subsequent resist wet strip process removes these byproducts. In this two-step process, the Ag removal rate is determined by the reactivity of the plasma itself with Ag to form byproducts easily soluble in the following wet processing.

Even though the two-step process could pattern Ag, the Ag removal rates are still very low and more study is required to understand the removal mechanism. Therefore, in this study, using an inductively coupled plasma etcher, the

effects of various Cl₂-based gas mixture plasmas were investigated to obtain higher Ag removal rates by the formation of more reactive byproducts of Ag.

2. Experimental

Ag thin films were etched using inductively coupled plasma (ICP) equipment. To generate inductively coupled plasmas, 13.56 MHz rf inductive power was applied to a planar spiral Cu coil separated by a 1-cm-thick quartz window on the top of the process chamber after the introduction of process gas combinations. Separate 13.56 MHz rf power was also applied to the bottom electrode, where the substrates were located to generate dc-bias voltages. The details of the ICP equipment used in our experiment are described elsewhere.¹³⁾

5,000-Å-thick Ag films were deposited by sputtering on LCD-grade glass substrates and 1.8-μm-thick photoresist with the taper angle of about 30° was used as the mask layer. Chlorine gas was used as the main etching gas to etch Ag thin films and Ar and O₂ were used as additive gases while keeping the pressure, inductive power, and dc-bias voltage at 15 mTorr, 500 W, and –150 V respectively. The influence of noble additives themselves such as He, Ar, and Kr on the etching of Ag thin films in addition to the mixture with Cl₂ or Cl₂/O₂ was also investigated.

Etch rate was determined using stylus profilometry of the feature depth after removal of the photoresist. Photoresist and involatile reaction products in the halogen gas-based plasma processes used in our experiments were removed simultaneously by dipping in a photoresist stripper at room temperature. A scanning electron microscope (Hitachi, S-2150 SEM) was used to observe as-etched and photoresist-stripped Ag surfaces. X-ray photoelectron spectroscopy (XPS) was also used to analyze the nonvolatile residues remaining on the etched Ag surface for different gas chemistries.

3. Results and Discussion

3.1 He, Ar, and Kr plasmas

Before studying the effects of Cl₂-based gases on the etching of Ag, the effects of pure sputtering by inert gases on

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the Ag etching were investigated as a possible etching method of Ag for TFT-LCD process applications. The results on Ag and photoresist etch rates are shown in Fig. 1 for He, Ar, and Kr. The Ag removal result by pure Cl_2 is also shown in the figure as a comparison. The process conditions were 500 W of inductive power, -150 V of bias voltage, 15 mTorr of operational pressure, and 25°C of substrate temperature. As shown in the figure, the Ag etch rates by noble gases were generally high due to the high sputter yield of Ag film (Ag: 3.4 atoms/ion, Al: 1.2 atoms/ion, Si: 0.5 atoms/ion and so forth by Ar^+ ion, 400 eV)¹⁴ and the etch rate increased with the increase of the mass of the noble gas in the order of He, Ar, and Kr. The etch rate of the photoresist also showed a similar trend. However, in the case of Cl_2 , due to the formation of an involatile compound during the exposure to Cl_2 plasma, a thick reaction product was formed on Ag film and this was removed during the photoresist wet stripping while the Ag film was not. Therefore, the etch rate shown in the figure is the removal rate after the photoresist stripping. Even though this reaction product could be removed by the following wet stripping, the overall etch rate estimated after the wet stripping was generally lower than sputter etch rates by noble gases. On the contrary, the photoresist etch rate was the highest due to the formation of volatile compounds of photoresist with Cl_2 .

Figure 2 shows the etch profile of Ag thin film masked with a $1.8\text{-}\mu\text{m}$ -thick photoresist by Kr plasma for the operational condition in Fig. 1. About 300 nm of the 500-nm-thick Ag film was etched and, as shown in the figure, the etched Ag bottom area was very clean and no residue could be observed, however, the sidewall of the etched profile showed a thick and tall Ag residue possibly due to the redeposition of the sputtered Ag. This remaining Ag residue was not easily removed even after the wet stripping of the photoresist, therefore, it will cause a problem during the subsequent process steps. In addition, the use of pure sputter etching in high-density plasmas will coat the sputtered metal on the dielectric window, which delivers an electromagnetic

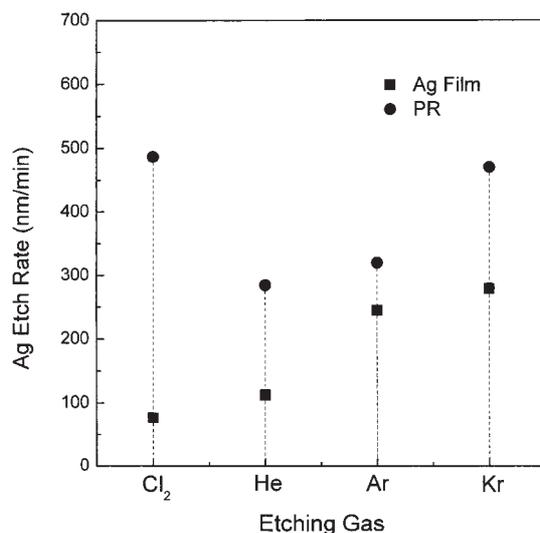


Fig. 1. Removal rates of Ag films estimated after the photoresist stripping and the etch rates of photoresist as a function of pure He, Ar, Kr, and Cl_2 [process condition: inductive power (500 W), dc-bias voltage (-150 V), and operational pressure (15 mTorr)].

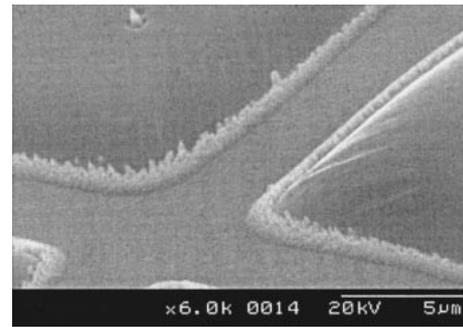


Fig. 2. SEM micrograph of the etched Ag film (under-etching, 300 nm in thickness) patterned by $1.8\text{-}\mu\text{m}$ of photoresist using pure Kr gas [process condition: inductive power (500 W), dc-bias voltage (-150 V), and operational pressure (15 mTorr)].

field to the plasmas, and it will prevent rf power from being delivered to the plasmas. Therefore, for use with high-density plasmas, reactive plasmas that do not interfere with rf power delivery by the formation of nonconductive compounds with Ag as the reaction products are required.

3.2 Cl_2 plasmas

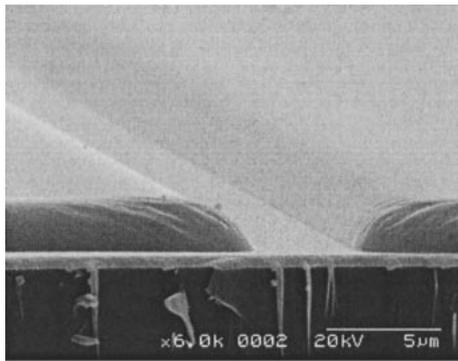
Table I shows boiling points and melting points of some of the possible halogen compounds of Ag that could be formed during the exposure of Ag to halogen plasmas.¹⁵ From the table, the formation of involatile reaction products is expected due to the high boiling points or melting points of these compounds.

Figure 3 shows the SEM micrographs of Ag (a) before etching with photoresist mask, (b) after the exposure to Cl_2 plasma with the same conditions as in Fig. 1, and (c) after the photoresist stripping. The thickness of the Ag thin film was about 500 nm as shown in Fig. 3(a). As shown in Fig. 3(b), the unmasked area changed to a rough one and porous granular reaction products were formed after the Cl_2 plasma exposure due to the formation of involatile compounds. The reaction products remaining on the unmasked area, however, were completely removed during the wet photoresist stripping by a photoresist stripper while the masked Ag area remained unattacked as shown in Fig. 3(c). However, the sidewall Ag profile was not smooth enough and was also difficult to control, therefore, more study is required for controlling the sidewall Ag profile and smoothness.

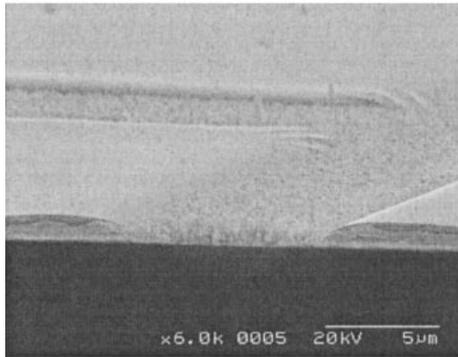
Cl_2 enables use of high-density plasmas without blocking electromagnetic waves passing through the dielectric win-

Table I. Boiling points and melting points of halogen compounds of Ag.

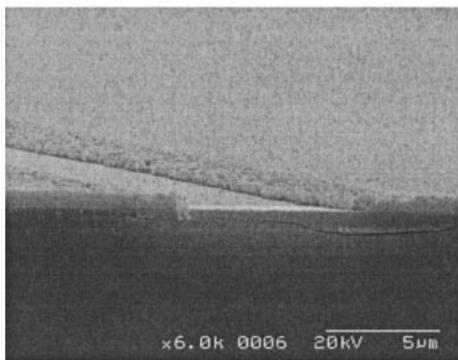
Compound	Melting point	Boiling point	Solubility	
Ag_2F	decomposes	100	—	reacts with H_2O
AgBr	432	1502	—	insoluble in H_2O , acid
Ag_2CO_3	218	—	—	slightly soluble in H_2O , soluble in acid
AgClO_3	230	decomposes	270	soluble in H_2O , slightly soluble in ethanol
AgCl	455	1547	—	insoluble in H_2O
AgF	435	1159	—	soluble in H_2O
AgNO_3	212	decomposes	440	very soluble in H_2O , slightly soluble in ethanol, acetone



(a)



(b)



(c)

Fig. 3. SEM micrographs of Ag films before (a) and after (b) etching by Cl_2 and (c) after the etching followed by photoresist wet stripping [process condition: inductive power (500 W), dc-bias voltage (-150 V), and operational pressure (15 mTorr)].

dow, however, a higher Ag removal rate is required, and therefore, the use of a gas mixture with Cl_2 has been investigated. Figure 4 shows the effect of Ar, and O_2 mixed with Cl_2 on Ag removal rate. Other operational conditions were kept the same as those shown for Fig. 1. When Cl_2 was mixed with Ar, due to the formation of involatile reaction products, the Ag etch rate estimated after the photoresist stripping decreased monotonically from 250 nm/min to 76.3 nm/min with the increase of Cl_2 to Ar. However, when O_2 was mixed with Cl_2 , higher Ag removal rates close to 130 nm/min could be obtained by mixing 20–50% of O_2 with Cl_2 . Nguyen *et al.* showed that the exposure of Cl_2/O_2 plasma to Ag using the reactive ion etching method leads to the formation of thermodynamically unfavorable oxychloride Ag compounds such as AgClO_x , by analyzing the Ag

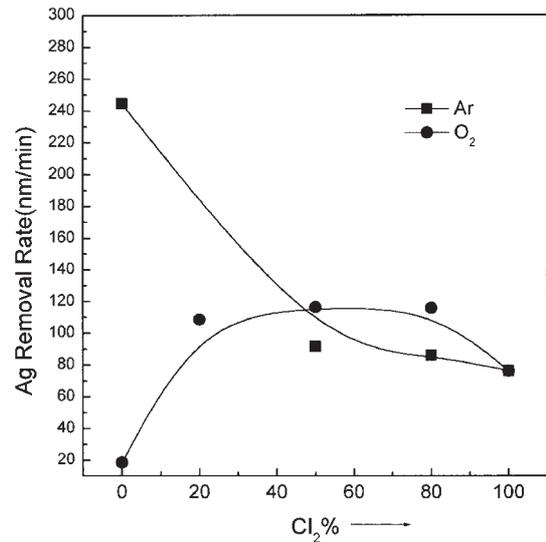
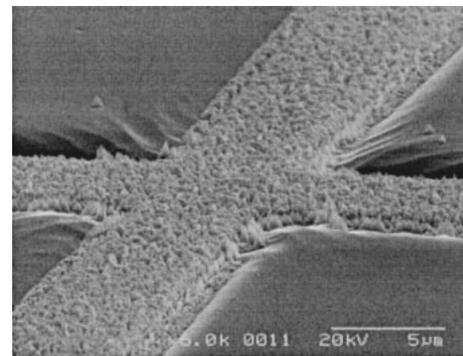


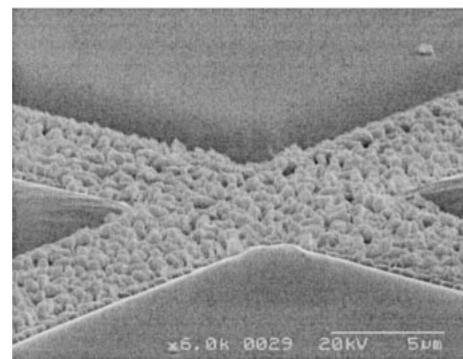
Fig. 4. Removal rates of Ag films estimated after the photoresist stripping as a function of gas mixtures such as Cl_2/Ar and Cl_2/O_2 [process condition: inductive power (500 W), dc-bias voltage (-150 V), and operational pressure (15 mTorr)].

reaction products using X-ray diffraction.⁹⁾ Therefore, the increased Ag etch rate estimated after the wet stripping could be related to the formation of AgClO_x which might be more reactive or volatile compared to AgCl_x .

Figure 5 shows the scanning electron micrographs of the Ag surface exposed to (a) Cl_2 plasma, and (b) $\text{Cl}_2/20\%\text{O}_2$



(a)



(b)

Fig. 5. SEM micrographs of Ag film surfaces exposed to (a) pure Cl_2 plasma and (b) $\text{Cl}_2/20\%\text{O}_2$ plasma for the time required to remove the same Ag thickness [process condition: inductive power (500 W), dc-bias voltage (-150 V), and operational pressure (15 mTorr)].

plasma for the time required to remove the same Ag thickness after photoresist stripping. As shown in the figure, the exposure to these gas mixtures revealed involatile granular Ag reaction products for all of the conditions. However, more porous or less dense reaction products appeared to be formed for the mixture of O₂ with Cl₂ compared to the case of Cl₂ only. The Ag removal rates estimated after the photoresist stripping were higher when 20–50% O₂ was mixed with Cl₂ as shown in Fig. 4. Therefore, the increase of Ag removal rate for the mixture of O₂ with Cl₂ could be related to the formation of more porous or less dense reaction products, which enables easier diffusion of the reactants diffuse into Ag, and helps to form thicker Ag reaction products during the same plasma exposure time.

The characteristics of the reaction products were investigated using XPS narrow scan and the results are shown in Fig. 6. 500-nm-thick blank Ag thin films were exposed to pure Cl₂ and Cl₂/O₂ plasmas for the same time. In the case of pure Ag metal, a photoelectron peak with the binding energy of 368.3 eV corresponding to Ag3d_{5/2} could be seen. However, Ag exposed to pure Cl₂ and Cl₂/20%O₂ showed the peaks at 368 eV and 367.7 eV possibly related to Ag3d_{5/2}-Cl and Ag3d_{5/2}-Cl-O, respectively. Also, in the case of Cl₂/20%O₂, the peak could be deconvoluted into two peaks related to Ag3d_{5/2}-O, and Ag3d_{5/2}-Cl-O. Therefore, these reaction products exposed to Cl₂ and Cl₂/O₂ appeared to be related to the AgCl_x and the mixture of AgO and AgCl_xO_y, respectively.

Using Cl₂/20%O₂ gas chemistry, the effect of additional gas mixture such as N₂, He, Ar, and Kr on the Ag removal rate was investigated for the same operational conditions shown in Fig. 4. Due to the involatile product formation, the

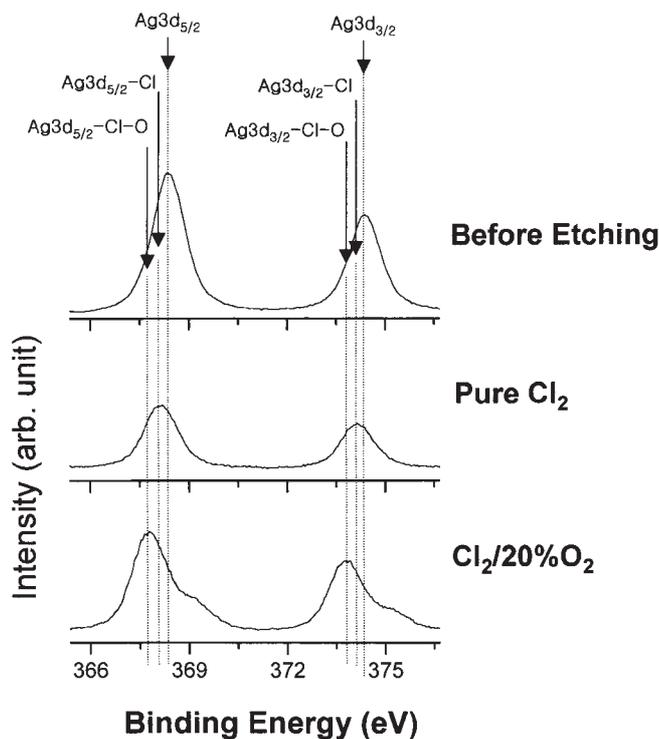


Fig. 6. Ag 3d XPS narrow scan spectra of Ag film surfaces exposed to pure Cl₂ and Cl₂/O₂ plasmas [process condition: inductive power (500 W), dc-bias voltage (−150 V), and operation pressure (15 mTorr)].

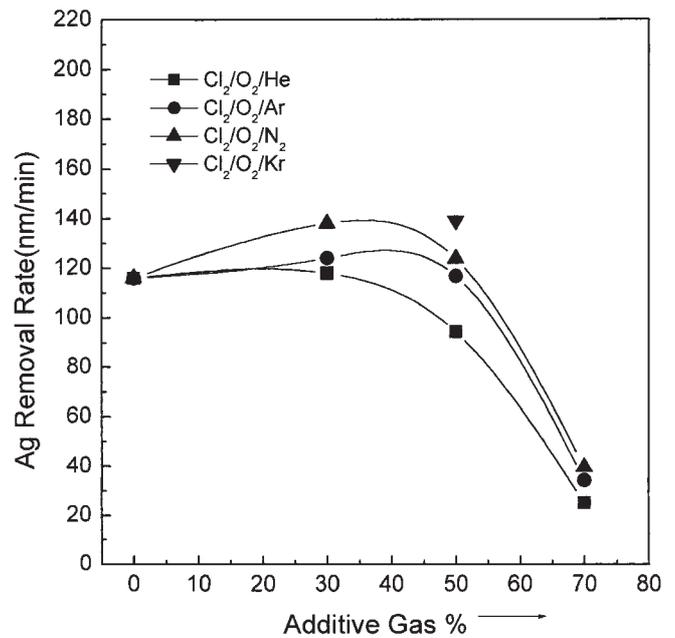


Fig. 7. Ag removal rates estimated after the photoresist stripping as a function of additional additive gases such as He, Ar, Kr, and N₂ to Cl₂/20%O₂ gas mixture [process condition: inductive power (500 W), dc-bias voltage (−150 V), and operation pressure (15 mTorr)].

removal rates were also estimated after the removal of the reaction products with the photoresist stripper. As shown in the figure, the mixture with a small additional additive gases showed a higher Ag removal rate and a higher atomic mass of the additive gas resulted in a higher removal rate in general possibly due to the increased sputtering of the Ag reaction products. However, the use of N₂ as the additional additive gas resulted in a higher Ag removal rate compared to the use of Ar even though the atomic mass of N₂ is smaller than Ar. The increase of Ag removal rate was also observed when Cl₂/N₂ gas mixtures were used. (not shown) The mechanism of higher Ag removal rate on using N₂ as an additive gas in Cl₂ or Cl₂/O₂ is currently under investigation, however, it appears to be related to the increase of AgCl or AgClO etch products by the increase of Cl radicals in the plasmas not by forming N-related etch products such as AgCl_xN_y, AgN_xO_y, and so forth. The use of more than 50% additional additive gas generally decreased the Ag removal rate drastically possibly by the combined effect of the formation of a thinner reaction product by the low concentration of reactants and the low sputter yield of the formed reaction products by the additive gases.

4. Conclusion

In this study, etching of Ag thin films applied to TFT-LCD metal layers was attempted using Cl₂-based high-density plasmas and the effects of various gas mixtures on the Ag removal characteristics were investigated.

The use of Cl₂-based inductively coupled plasmas in the etching of Ag led to the formation of a thick reaction layer due to the low vapor pressure of the reaction products, however, a photoresist stripper easily removed the reaction products during the wet stripping of the photoresist. The use of inert gases such as He, Ar, and Kr resulted in higher Ag etch rates by sputter etching compared to the Ag removal

rate by Cl_2 estimated after the wet stripping. However, the use of pure sputter etching by noble gases caused problems such as the sidewall residue and the deposition of metal layers on the dielectric window.

The use of Cl_2/O_2 instead of pure Cl_2 yielded similar involatile reaction products, however, it yielded higher Ag removal rate when estimated after the wet stripping. When the reaction products were observed using scanning electron microscopy, more porous or less dense reaction products appeared to be formed by Cl_2/O_2 compared to those formed by pure Cl_2 . Also, when these products were analyzed by XPS, the formation Ag compounds such as AgCl_x by Cl_2 and the mixture of AgO and AgCl_xO_y by $\text{Cl}_2/20\%\text{O}_2$ could be identified from $\text{Ag}3d_{5/2}$ peaks. These different reaction compounds appear to be related to the increased Ag removal rates by the formation of a thicker and more porous reaction compound for Cl_2/O_2 . The small additive gases such as He, Ar, Kr, and N_2 to $\text{Cl}_2/20\%\text{O}_2$ showed an increased Ag removal rate possibly due to the increased sputter effect for inert gases and due to the formation of more reaction products for N_2 . However, the addition of more than 50% drastically decreased the Ag removal rate estimated after the wet stripping due to the low sputter yield of the formed Ag reaction products in addition to the formation of thinner reaction products.

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