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Dry etch characteristics of Al-Nd films for TFT-LCD

H.R. Han[a,*], Y.J. Lee[a], G.Y. Yeom[a], K.H. Oh[b], M.P. Hong[c]

[a] *Department of Materials Engineering, Sungkyunkwan University, Suwon 440-746, South Korea*
[b] *Agency for Technology and Standards, Kwachon 427-010, South Korea*
[c] *Samsung Semiconductor, Suwon 440-600, South Korea*

Abstract

In this study, Al-Nd thin films deposited on glass were etched using magnetized inductively coupled plasmas and their etch characteristics were investigated as a function of gas combination of Cl_2/BCl_3 and HBr/BCl_3, inductive power, bias voltage and pressure. When Cl_2/BCl_3 gas mixtures were used to etch Al-Nd films, low etch rates close to 1/3 of that of pure Al and etch selectivities over photoresist less than 0.9 were obtained due to the non-volatile Nd in Al-Nd thin films. Also, some residues originating from the remaining Nd were observed on the surface of glass and side wall of the Al-Nd lines after the etching of Al-Nd. However, the use of HBr/BCl_3 gas mixtures increased Al-Nd etch rates and etch selectivities over photoresist, and the highest Al-Nd etch rate close to 140 nm/min and etch selectivity close to 1.1 could be obtained with 50% HBr/50% BCl_3. In addition, barely no residues and no critical dimensional loss could be found with this etch condition. X-Ray photoelectron spectrometry (XPS) showed preferential removal of Nd by HBr during the Al-Nd etching and preferential removal of Al by Cl_2 and BCl_3. Therefore, the highest Al-Nd etch rate at 50% HBr/50% BCl_3 appears to be related to the optimal combination of Nd etching with HBr and Al etching with BCl_3. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Al-Nd; Thin film transistor-liquid crystal display (TFT-LCD); Dry etch; BCl_3; HBr

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1. Introduction

For advanced thin film transistor-liquid crystal display (TFT-LCD) manufacturing processes, dry etching of thin-film layers (a-Si, SiN_x, source/drain and gate electrodes, indium–tin–oxide (ITO), etc.) is increasingly preferred instead of conventional wet etching processes. For the gate electrode, aluminum (Al) is generally used, and some metals such as Ti and Nd are added to Al to prevent the formation of hillocks during post-annealing processes in addition to maintaining low-resistivity ($< 10\ \mu\Omega$ cm) and enhancing corrosion resistance of Al thin films [1,2]. Specifically, Al-Nd alloy films have been recently applied for the interconnections of TFT-LCDs. However, Al-Nd alloy film remains one of the most challenging types of film to be etched successfully. In the case of wet etching, low etch rate, the reduction of line width and the presence of post-etch residues are observed [3]. Therefore, dry etching techniques are actively investigated for gate electrode etching of the next generation TFT-LCDs. However, in the dry etching of Al-Nd alloys, a common problem is the difficulty in making the process aggressive enough to remove any residue while maintaining high selectivity over photoresist. Obtaining required etch uniformity over the large substrate is another problem in developing the next generation of process equipment [4,5].

For the next generation plasma etching equipment for TFT-LCD, among the many high density plasma sources, planar inductively coupled plasma (ICP) sources are actively studied due to their possibility to extend to large area easily. However, due to the huge

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[*] Corresponding author. Tel.: +82-331-290-7418; fax: +82-331-290-7410.

E-mail address: hhyerhee@mail.skku.ac.kr (H.R. Han).

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size of the substrate, the plasma uniformity, and, therefore, etch uniformity, still pose a problem. To improve the etch uniformity of the ICP, various techniques are under investigation, and among these, multidipole magnet buckets have been applied to the side wall of the chamber and reasonably good plasma uniformities were obtained for some of the configurations. In addition to the multidipole magnets, to increase the plasma density further, Helmholtz type axial magnetic field has been applied to ICP and, with optimized combinations of axial magnetic field and multidipole magnetic bucket, higher plasma densities with good uniformities ($< 5\%$) could be obtained in the previous study [6].

In this study, etch characteristics of Al-Nd alloy used for TFT-LCD gate electrode have been investigated using the magnetized ICP with two different gas combinations, Cl_2/BCl_3 generally used for Al alloy etching and HBr/BCl_3 to improve etch selectivity over photoresist.

2. Experiment

Al-Nd thin films were etched using magnetized ICP equipment with a Helmholtz axial electromagnet and a permanent magnet bucket. To form optimized magnetic cusping, eight pairs of permanent magnets were arranged along the inside of the chamber wall in a specially designed anodized aluminum housing, and the Helmholtz type axial electromagnet was located outside of the chamber. The chamber was designed as a square, mainly for the FPD applications, and was made of anodized aluminum also. The details of the magnetized ICP equipment are described elsewhere [6].

Al-Nd (1 at.%) films (300 nm thick) were deposited by sputtering on LCD-grade glass substrates. Nd addition of only $1 \sim 2$ at.% results in a low hillock density and the film resistivity below 6 $\mu\Omega$ cm. Fig. 1 shows a schematic of a TFT-LCD. As can be seen in the figure, the Al-Nd gate needs to be tapered for better step coverage. Therefore, Al-Nd films were patterned using 2.0 μm thickness photoresist with the tapered angle of 30°.

Al-Nd thin films were dry etched with various Cl_2/BCl_3 [7,8] and BCl_3/HBr combinations while keeping the pressure at 0.67 Pa, inductive power at 600 W, and self-bias voltage at -150 V. To study the effect of etch parameters such as inductive power, bias voltage, and operational pressure on the etch properties of Al-Nd thin films, operational pressures were varied from 0.67 to 4.0 Pa, dc self-bias voltages from -50 to -200 V, and inductive powers from 400 to 800 W, while maintaining the same gas composition of 50% HBr/50% BCl_3 at 30 sccm. To compare with wet etching, some of the patterned Al-Nd films were wet etched in a H_3PO_4–HNO_3–H_2O solution [9]. The solution contained 74.1% phosphoric acid, 7.3% nitric acid and 18.5% water.

Etch rates were determined using a stylus profilometer of the feature depth after removal of the photoresist. A scanning electron microscope (Hitachi, S-2150 SEM) was used to observe side wall roughness, surface residue, and to measure the critical dimension loss. X-Ray photoelectron spectroscopy (XPS) was used to observe the composition of etched Al-Nd surfaces.

3. Results and discussion

Al-Nd thin films were etched in Cl_2/BCl_3 and their etch rates and etch selectivites over photoresist are

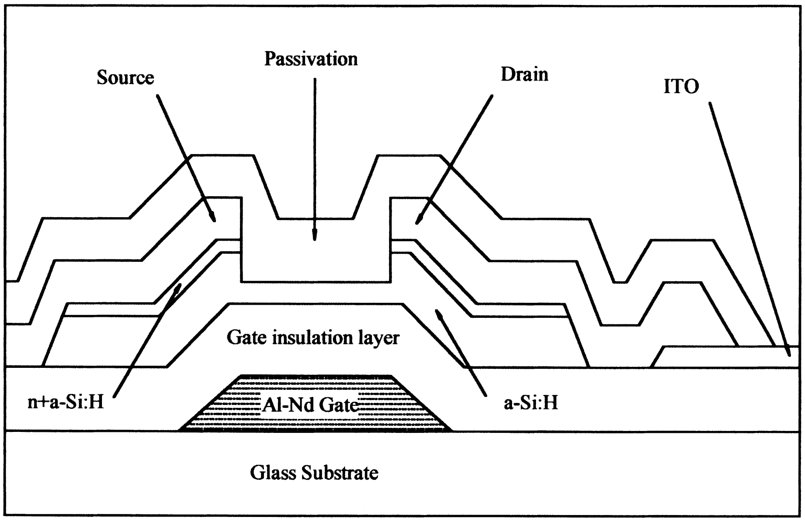

Fig. 1. Cross-section of thin-films transistor containing Al-Nd gate electrode.

Table 1
Etch characteristics of Al and Al-Nd films for Cl_2/BCl_3 chemistry

Etching condition	Al–Nd etch rate (nm/min)	Al etch rate (nm/min)	Photoresist etch rate (nm/min)	Etch selectivity (Al-Nd/ photoresist)
Wet etching	50	60	–	–
100% Cl_2	40	113	413	0.09
75% Cl_2/25% BCl_3	92	267	380	0.24
50% Cl_2/50% BCl_3	123	327	347	0.35
25% Cl_2/75% BCl_3	121	307	186	0.65
10% Cl_2/90% BCl_3	112	256	153	0.73
100% BCl_3	106	211	123	0.86

shown in Table 1. The etch condition was 0.67 Pa, 600 W of inductive power, −150 V of bias voltage. Pure Al thin films were also etched in the same etch conditions to compare with Al-Nd thin films. Wet etch rates of pure Al and Al-Nd were also measured. As shown in the table, dry etching of Al and Al-Nd with Cl_2/BCl_3 gas mixtures showed higher etch rates compared with the etching in pure Cl_2 or pure BCl_3. The highest etch rates of Al (327 nm/min) and Al-Nd (123 nm/min) were observed with 50% Cl_2/50% BCl_3. However, the Al-Nd etch rates were generally approximately 1/3 of Al etch rates and the etch selectivities were lower than 0.9 even though there were no significant differences in wet etch rates between Al and Al-Nd. The difference in the dry etch rates between Al and Al-Nd appears to results from the 1 at.% of Nd in Al which is not easily removed from the surface during the etching. Therefore, different gas chemistries which can increase Nd etch rate from the Al-Nd surface need to be used to improve etch rates and etch selectivities of Al-Nd.

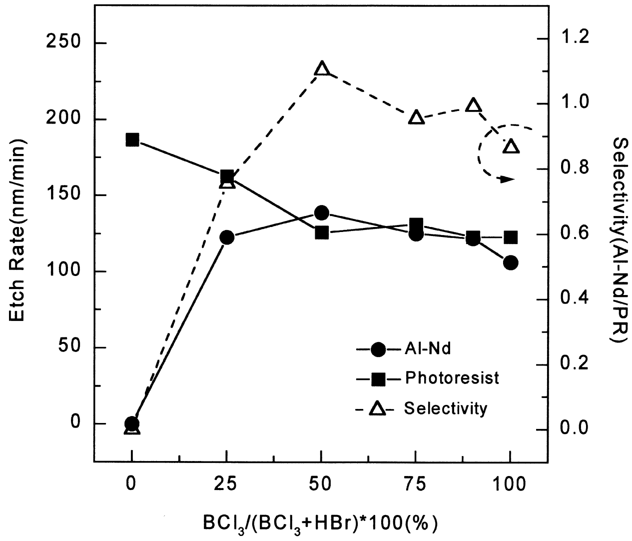

Fig. 2. Etch rates of Al-Nd and photoresist, and Al-Nd etch selectivities over photoresist as a function of HBr/BCl_3 gas mixture. Process condition: 0.67 Pa of operational pressure, 600 W of inductive power and −150 V of bias voltage.

To increase the etch selectivities over photoresist in addition to increasing the etch rates, Al-Nd thin films were etched using HBr/BCl_3 gas mixtures. The results are shown in Fig. 2. The other etch conditions such as power, pressure, bias voltage, etc., were kept the same as the conditions in Table 1. As shown in the figure, Al-Nd etch rates increased with the increase of BCl_3 in HBr/BCl_3 mixtures until 50% HBr/50% BCl_3; the further increase of BCl_3 decreased the Al-Nd etch rates slowly. In the case of photoresist, the etch rate decreased with the increase of BCl_3 in HBr/BCl_3 mixtures until 50% HBr/50% BCl_3;the further increase of BCl_3 did not change the photoresist etch rates significantly. Therefore, at 50% HBr/50% BCl_3, the highest Al-Nd etch rate of 139 nm/min and the highest etch selectivity of 1.1 could be obtained.

The surface compositions of Al-Nd during the dry etching with Cl_2/BCl_3 and HBr/BCl_3 were investigated using XPS, and the results are shown in Table 2 for pure Cl_2, pure BCl_3, pure HBr, 50% Cl_2/50% BCl_3, and 50% HBr/50% BCl_3. The surface composition ratio (Nd/Al) of non-etched Al-Nd (control) was also included as a reference. As shown in the table, the surface composition ratio of Al-Nd during the etching with pure Cl_2, 50% Cl_2/50% BCl_3, and pure BCl_3 changed to from 0.01 (control) to 0.019 ~ 0.025. Therefore, Nd-richer surfaces were obtained during the etching with Cl_2 and BCl_3 based gases indicating the difficulty in removing Nd from the Al-Nd thin films.

Table 2
Variation of Al-Nd surface composition ratio (Nd/Al) during the etching with Cl_2, HBr, BCl_3, 50% Cl_2/50% BCl_3 and 50% HBr/50% BCl_3 measured by XPS[a]

Sample condition	Nd/Al ratio
Control	0.010
100% Cl_2	0.019
50% Cl_2/50% BCl_3	0.024
100% BCl_3	0.025
50% HBr/50% BCl_3	0.011
100% HBr	0.006

[a] The surface composition ratio of non-etched Al-Nd (control) was included.

However, when 50% HBr/50% BCl_3 was used, the composition ratio changed close to that of control sample and, in the case of pure HBr, the ratio became 0.006 which is Al-richer, therefore, Nd was removed easier with HBr-based gases. The low etch rate of Al-Nd at 100%HBr, however, appears to be from the low Al etch rate by HBr. Therefore, gas combinations having reasonably high etch rates of both Al and Nd are required to obtain high etch rates of Al-Nd. The highest Al-Nd etch rate with 50% HBr/50% BCl_3 compared to that with Cl_2/BCl_3 mixtures appear to be related to the easier removal of both Al and Nd with the HBr/BCl_3 gas mixture. The preferential removal of Al by Cl_2 or BCl_3 appears to be from the formation of $AlCl_x$ which has high vapor pressure, however, the preferential removal of Nd by HBr is not clear whether it is from the formation of NdH_x or $NdBr_x$. The use of HBr/BCl_3 instead of Cl_2/BCl_3 decreased photoresist etch rates especially in the high HBr content region possibly due to the enhanced absorption of HBr on the photoresist, which prevents the etching of photoresist by halogen radicals as reported by other researchers [10,11]. However, the decrease of the photoresist etch rate with the increase of BCl_3 in the high HBr content region also might suggest the effect of BCl_x in addition to HBr in decreasing the photoresist etch rate. It is because BCl_x is known to react and form thermodynamically more stable B_xO_y with oxygen radicals possibly remaining in the chamber by the sputter etching of the quartz windows during the ICP processing [12–14]. Therefore, in general, higher Al-Nd etch selectivities were obtained with HBr/BCl_3 compared to those with Cl_2/BCl_3.

To study the effects of other etch parameters on the Al-Nd etch rates and etch selectivities over photoresist, Al-Nd thin films were etched as functions of inductive power, bias voltage, and pressure using 50% HBr/50% BCl_3, and the results are shown in Fig. 3 for inductive power (a), bias voltage (b) and pressure (c). The other etch parameters were kept the same as before. As shown in Fig. 3a, the increase of inductive power from 400 to 800 W generally increased the etch rates of Al-Nd and photoresist, therefore, the etch selectivity remained similar in the range from 0.9 to 1.1. Also, as shown in Fig. 3b, the increase of bias voltage from −50 to −200 V increased the etch rates of Al-Nd and photoresist, however, the rate increased more for Al-Nd; therefore, with the increase of bias voltage, the etch selectivity over photoresist increased from 0.3 at −50 V to 1.1 at −150 V. However, as shown in Fig. 3c, the increase of operational pressure from 0.67 to 4.0 Pa generally decreased the etch rates of Al-Nd and photoresist. The Al-Nd etch rate decreased faster, and, therefore, the etch selectivity decreased from 1.1 to 0.3.

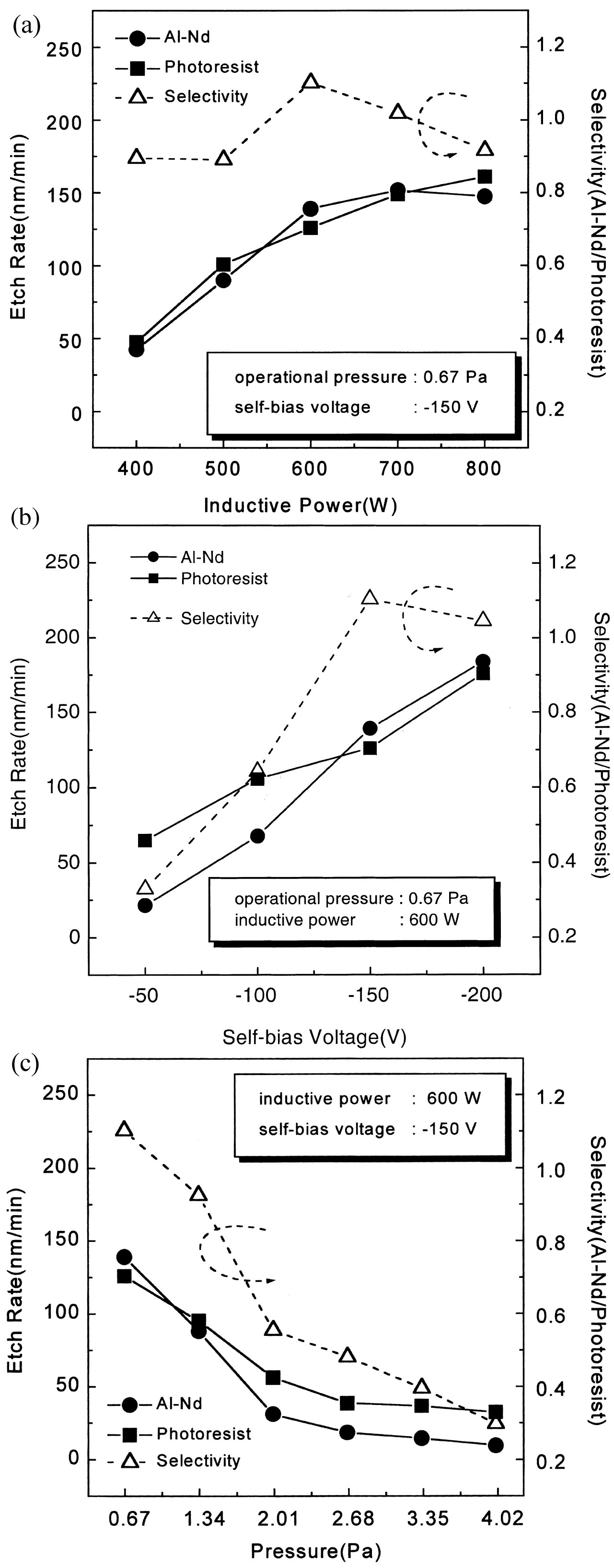

Fig. 3. Etch rates of Al-Nd and photoresist, and Al-Nd etch selectivities over photoresist as a function of (a) inductive power, (b) dc self-bias voltage and (c) operational pressure.

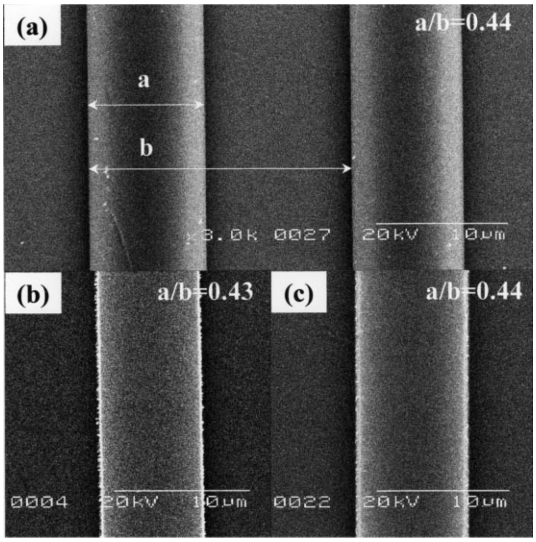

Fig. 4. Critical dimension (CD) of gate line observed by SEM (a) control (before etching), (b) wet etching and (c) dry etching by 50% HBr/50% BCl_3. 30% overetchings were used.

The increase of inductive power generally increases the number of reactive ions and radicals; therefore, the increase of etch rates of Al-Nd and photoresist with increasing inductive power appears to result from the increased number of reactive ions and radicals. The increase of bias voltage increases only the energy of the ions; therefore, the increase in the etch rates of Al-Nd and photoresist with increasing bias voltage is caused by the increased sputter removal of the reaction products. The increase of operational pressure generally increases the number of reactive radicals more than the number of reactive ions. Also, it increases the residence time of etch products and etch gases, redeposition of non-volatile etch product, and scattering of ions incident to the substrates, and these can decrease the etch rate. In our experimental conditions, the effect of residence time on the etch rate appears to be negligible due to the high gas flow rate used in the experiment, and the redeposition of non-volatile etch product and the scattering of the incident ions appear to affect the etch rate. Therefore, the decrease of etch rates of Al-Nd and photoresist with increasing pressure is caused by the decreased sputter removal of the reaction products. The increase of etch selectivity with the increase of bias voltage and the increase of etch selectivity with the decrease of pressure suggest more ion-enhanced etching of Al-Nd compared with photoresist, possibly due to the non-volatile Nd in Al-Nd thin films.

Using SEM, the surface roughness, critical dimension loss, etch residue, etc., were examined after etching of Al-Nd by wet chemicals, 50% Cl_2/50% BCl_3, and 50% HBr/50% BCl_3. Thirty percent overetchings were performed for each etching condition and the photoresist was removed before the SEM examination. Fig. 4 shows the SEM micrographs of critical dimension lines before the etching (a), after the wet etching (b), and after the dry etching using 50% HBr/50% BCl_3 (c). As shown in Fig. 4a, the ratio of linewidth/pitch (a/b) was 0.44 before the etching. However, after the wet etching, the ratio decreased to 0.43, therefore, a critical dimension loss was observed for the wet etching. In the case of the dry etching of Al-Nd with 50% HBr/50% BCl_3, the ratio of linewidth/pitch remained the same as that of the photoresist pattern and the irregularity of the edge of the line was smaller than that by wet etching. Fig. 5 also shows the etch profiles of Al-Nd for wet etching(a), dry etching with 50% Cl_2/50% BCl_3 (b), and dry etching with 50% HBr/50% BCl_3 (c). Due to the difficulty in the etching of Nd in Al-Nd using 50% Cl_2/50% BCl_3, the etch residues visible on the glass and the side wall of the Al-Nd lines in Fig. 5b are possibly related to Nd compounds. In the case of wet etching, as shown in Fig. 5a, some residues possibly related to Nd, were also observed on the glass surface. The cleanest etching could be observed on both glass surface and the side wall of Al-Nd line with 50% HBr/50% BCl_3 as shown in Fig. 5c.

4. Conclusions

In this study, Al-Nd (1 at.%) thin films used for the

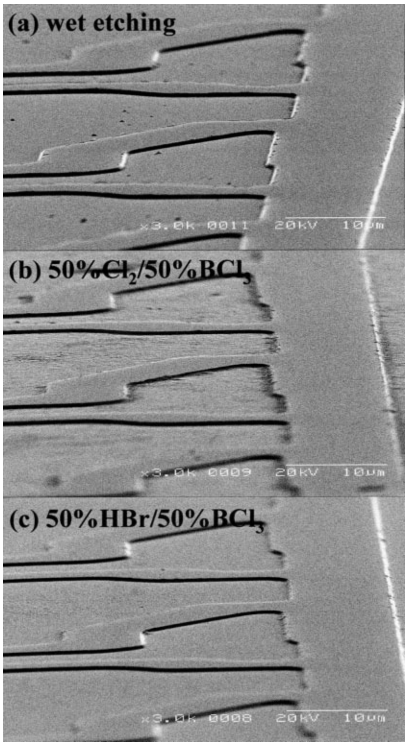

Fig. 5. Surface residue observed by SEM (a) wet etching, (b) dry etching by 50% Cl_2/50% BCl_3 and (c) dry etching by 50% HBr/50% BCl_3 plasma. 30% over etching were used.

gate electrode of TFT-LCD have been etched by a magnetized ICP using Cl_2/BCl_3 and HBr/BCl_3 gas mixtures. Effects of gas combination, inductive power, bias voltage, and pressure on the etch rates and etch selectivities of Al-Nd were investigated. XPS was used to examine the change of surface compositions of Al-Nd during the etching and SEM was used to compare etch profiles and remaining etch residues.

The etch rates of Al-Nd (1 at.%) were approximately 1/3 of those of pure Al when conventional Cl_2/BCl_3 gas mixtures were used, and the etch selectivities were less than 0.9. To improve the Al-Nd etch rates and etch selectivities over photoresist, HBr/BCl_3 gas mixtures were used, and with 50% HBr/50% BCl_3, the highest Al-Nd etch rates of 139 nm/min with etch selectivities over photoresist of 1.1 could be obtained. XPS showed that HBr removes Nd preferentially during the etching of Al-Nd while Cl_2 and BCl_3 remove Al preferentially. Therefore, the highest Al-Nd etch rate at 50% HBr/50% BCl_3 appears to be related to the optimal combination of Nd etching with HBr and Al etching with BCl_3. The increased etch selectivity with HBr/BCl_3 gas mixtures appears to result not only from the decreased photoresist etch rate by HBr but also from the oxygen removal effect of BCl_x from BCl_3 by the formation of B_xO_y. The Al-Nd etch rates increased with increasing inductive power, increasing bias voltage, and decreasing operational pressure. The Al-Nd etch selectivity over photoresist increased with increasing bias voltage and with decreasing operational pressure while the increase of inductive power did not change the selectivity significantly. SEM micrographs showed some residues on the glass surface and side wall of Al-Nd line possibly originating from the non-volatile Nd compounds for the dry etching with 50% Cl_2/50% BCl_3. Wet etching of Al-Nd showed the critical dimension loss, some residue on the glass surface, and irregular side wall of Al-Nd line, however, dry etching with 50% HBr/50% BCl_3 showed the least irregular Al-Nd line, no critical dimensional loss and a clean etched glass surface.

References

[1] K. Kato, J.T. Wada, N. Kakuda, IEICE Trans. Electron. E80-C (1997) 320.

[2] H. Takatsuji, E.G. Colgar, C. Cabal Jr., J.M.E. Harper, IBM J. Res. Dev. 42 (1998) 501.

[3] S. Wolf, R.N. Tauber, Silicon Processing for the VLSI Era, 1, 1st ed, Lattice Press, California, 1986, p. 534.

[4] E. Iwamura, T. Ohnishi, K. Yoshikawa, Thin Solid Films 270 (1995) 450.

[5] T. Arai, H. Iilori, Y. Hiromasu, M. Atsumi, S. Ioku, K. Furuta, IBM J. Res. Dev. 42 (1998) 491.

[6] S.W. Hwang, Y.J. Lee, H.R. Han, J.B. Yoo, G.Y. Yeom, J. Vac. Sci. Technol. A 14 (1999) 1211.

[7] H. Kazumi, R. Hamasaki, K. Tago, Jpn. J. Appl. Phys. 36 (1997) 4829.

[8] J.H. Ha, M. Yim, J. Kim, Jpn. J. Appl. Phys. 37 (1998) 6928.

[9] T. Onishi, E. Iwamura, K. Takagi, Thin Solid Films 340 (1999) 306.

[10] M. Puttock, Surf. Coat. Technol. 97 (1997) 10.

[11] Y. Kuo, Electrochem. Soc. Proc. 98(4)

[12] J.H. Lee, G.Y. Yeom, J.W. Lee, J.Y. Lee, J. Vac. Sci. Technol. A 15 (1997) 573.

[13] J.F. Pieson, T. Czerwiec, T. Belmonte, H. Michel, Surf. Coat. Technol. 97 (1997) 749.

[14] T. Banjo, M. Tsuchihashi, M. Hanazaki, M. Tuda, K. Ono, Jpn. Appl Phys. 36 (1997) 4824.