# Etching Characteristics of Au Thin Films using Inductively Coupled $CF_4$ / $Cl_2$ /Ar Plasma

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The etching of Au thin films has been performed in an inductively coupled $CF_4/Cl_2/Ar$ plasma. The etch properties including etch rate and selectivity were examined as $CF_4$ content adds from 0 to 30 % to $Cl_2$/Ar plasma. The $Cl_2/(Cl_2 + Ar)$ gas mixing ratio was fixed at 20%. Other parameters were fixed at an rf power of 700 W, a dc bias voltage of −150 V, a chamber pressure of 15 mTorr, and a substrate temperature of 30℃. The highest etch rate of the Au thin film was 370 nm/min at a 10 % additive $CF_4$ into $Cl_2$/Ar gas mixture. The surface reaction of the etched Au thin films was investigated using x-ray photoelectron spectroscopy (XPS) analysis. The XPS analysis shows that the intensities of Au peaks are changed, indicating that there is a chemical reaction between Cl and Au. Au-Cl is hard to remove on the surface because of its high melting point. However, etching products can be sputtered by Ar ion bombardment.

*Keywords* : Au, ICP, $Cl_2/CF_4/Ar$, XPS.

## 1. INTRODUCTION

Aluminum and its alloys, tungsten, copper, platinum, and gold (Au) have been employed as thin-film electrodes in the semiconductor industry. The choice of one material over another for specific applications is determined by considering performance results, which need to be optimized for any conductor layer. The conductor should satisfy the properties including electrical resistance of film, mechanical and chemical stability, adhesion characteristics, considerations for deposition, and the easy for pattern transfer. Au offers several notable performance features: Au has a lower resistivity (2.21 μΩ-cm ) than aluminum (2.65 μΩ-cm), high chemical stability, a low surface work function allowing good ohmic contact with other metals, a high electro migration resistance because of its large atomic mass, and a higher melting point (1064℃) compared with Al (660℃)[1]. Therefore, Au thin films are currently being investigated as a substitute for Al for the interconnections in semiconductor devices. Au is also employed extensively in the electrodes of high dielectric capacitors or in compound semiconductor[2,3].

As the feature size of device become below sub-micron, it is important to develop fine pattern transfer process using high-density plasma etch processes, which show fine CD control and high etch rate. In our previous experiment[4], Au thin films were etched in $Cl_2$/Ar plasma. We obtained that the physical sputtering was the dominant mechanism in Au etch. The reason is that Au chlorides are very low volatile compounds. For $Cl_2$/Ar plasma, we obtained a maximum etch rate at 20% $Cl_2$. At the same time, D. P. Kim et al.[5] reported that the addition of small amount of $CF_4$ in $Cl_2$/Ar plasma helps to increase the etch rate of $SrBi_2Ta_2O_9$ (SBT). Considering the SBT components form low volatile chlorides, we expect the same effect for Au thin films. Moreover, we expect also that for the Au thin films, the addition of $CF_4$ will improve the etch selectivity and etch profile through the deposition of polymer layer on the photoresist and side walls. However, there is no report on the etch rate and etch mechanism in literature using $CF_4/Cl_2/Ar$ plasma.

In this study, the etch rates of Au thin films were investigated with various $CF_4$ contents in $Cl_2$/Ar plasma. The mixing ratio $Cl_2$/Ar was fixed at 20%. The diagnostics of the $CF_4/Cl_2/Ar$ plasma were performed using optical emission spectroscopy (OES). The chemical states on the surface of the etched Au thin films were investigated with X-ray photoelectron spectroscopy (XPS).

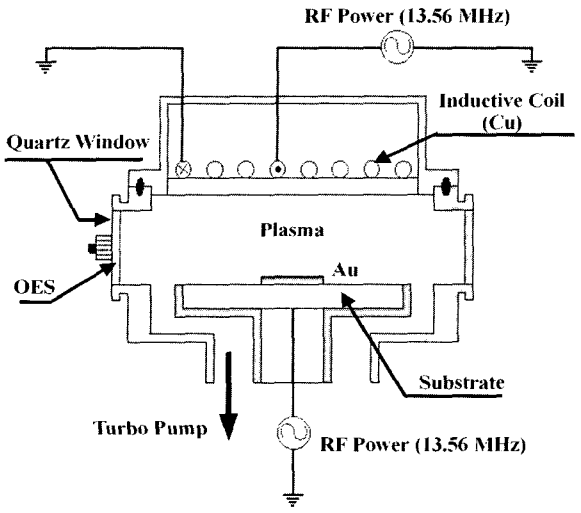


Fig. 1. A schematic of the inductively coupled plasma (ICP) system.

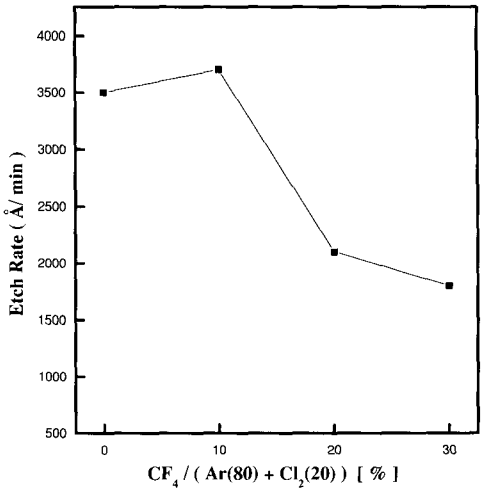


Fig. 2. Etch rate of Au as a function of additive $CF_4$ into $Cl_2/(Cl_2 + Ar)$ gas mixing ratio of 0.8.

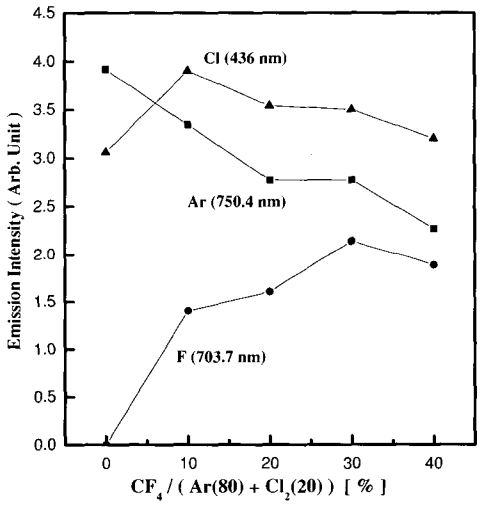


Fig. 3. Optical emission intensities of Cl, F, and Ar as a function of additive $CF_4$ into $Cl_2/(Cl_2+Ar)$ gas mixing ratio of 0.8.

## 2. EXPERIMENTAL DETAILS

Si substrates used for this study were doped with B (0.85-1.15 Ω cm) and oriented (100). The substrates were chemically etched for 7 min using 10 % HF:$H_2O$ prior to Au deposition. Au thin films were deposited on the Si substrate directly by rf sputtering using a Au target (purity = 99.99 %). An rf sputtering system equipped with a 4 inch conical magnetron-sputtering source were used for the deposition of Au thin films. The rf power density, chamber pressure, and distance from source to substrate were fixed at 1.85 W/cm$^2$, 5 × $10^{-7}$ Torr, and about 6 cm, respectively. During the deposition, the substrate was grounded and the substrate temperature was held at room temperature (27℃) using water cooling. These conditions resulted in a nominal deposition rate of 2 Å/min and the final thickness of the sputtered Au thin films was about 4000 Å.

Plasma etching of the Au thin films was performed using an ICP etching system. Figure 1 shows a schematic diagram of the experimental apparatus. A planar ICP etching equipment having a 3.5 turn spiral copper coil on the top of the chamber separated by a 24-mm-thick quartz window was used in this experiment. To generate inductively coupled plasmas, an rf generator with 13.56 MHz was connected to the planar spiral copper coil. Another rf generator was applied to the bottom electrode to induce bias voltage to the substrate. The gas inlet located under 1cm from upper cover. The samples were placed on a bottom electrode. The temperature of substrate during the Au etching was held at 30℃ using the circulation of cooling water. The gas outlet connects to a mechanical pump and a turbomolecular pump.

The Au thin films were etched with $CF_4$ addition from 0% to 30% to $Cl_2/(Cl_2+Ar)$ ratio of 0.2. Other parameters were fixed at an rf power of 700 W, a dc bias voltage of −150 V, a chamber pressure of 15 mTorr, and a substrate temperature of 30℃. Etch rates were measured using a α-step 500 surface profiler [Tencor]. The volume density of atoms (Cl and F) and Ar ions as a function of the additive $CF_4$ into the $Cl_2$/Ar gas mixture was measured with OES [NANOTEK NTS-U101]. The etched surface region was examined by XPS

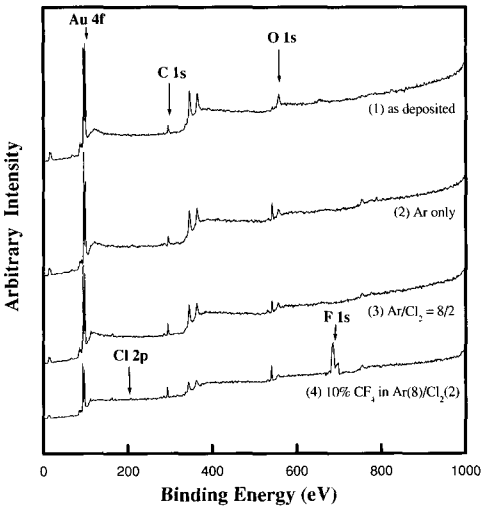


Fig. 4. XPS wide scan spectra of the Au thin film surfaces etched with different gas mixture.

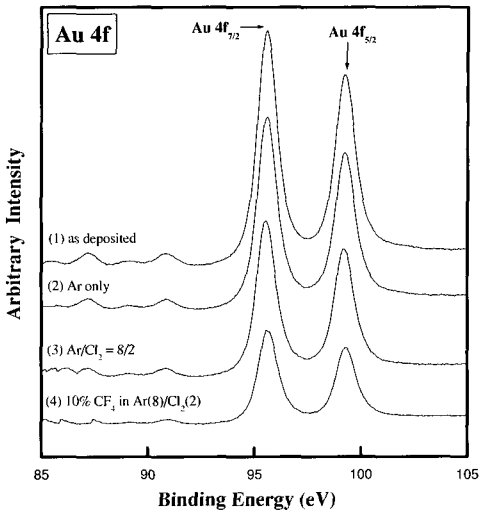


Fig. 5. Au 4f XPS narrow scan spectra of the Au thin film surfaces etched with different gas mixture.

(ESCALAB 220-IXL). The XPS Al kα source provides chromatic x ray at 1486 eV. Narrow scan spectra of all interested regions were recorded with 20 eV pass energy in order to quantify the surface composition and identify the chemical binding state. The etch profile of Au thin films was examined with scanning electron microscope (SEM).

## 3. RESULTS AND DISCUSSION

Au thin films were etched as a function of the additive $CF_4$ to $Cl_2$/Ar gas mixture, which was fixed at 20% $Cl_2$/Ar. The process parameters were fixed at an rf power of 700W, a dc-bias voltage of -150 V, a chamber pressure of 15 mTorr, and a substrate temperature of 30℃. Figure 2 shows the etch rates of Au as a function of the additive $CF_4$ into $Cl_2$ /Ar gas mixture. The highest etch rate of the Au thin film is 370 nm/min at a 10 % additive $CF_4$ to $Cl_2$/Ar gas mixture. As $CF_4$ content increases over 10% addition, the etch rate of Au thin films decreases. This result suggests that Au thin films are dominantly etched by Ar ion bombardment and also assisted by the chemical reaction with Cl and F atoms [6]. Au reacts with Cl and F, and thus forms non-volatile etch-by products. These nonvolatile etch byproducts can be removed only by the Ar ion sputtering.

To understand the effects of the gas combination on the etch rate of Au thin films, we estimated the volume densities of Cl and F atoms and Ar ions by using OES.

Figure 3 shows the variations of Cl (436 nm), F (703.7 nm), and Ar (750.4 nm) associated peaks in $CF_4/Cl_2/Ar$

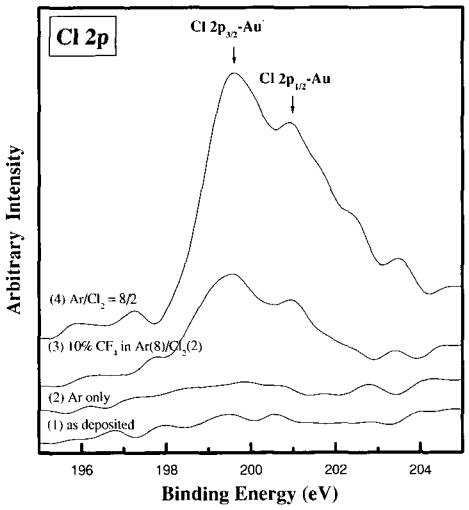


Fig. 6. Cl 2p XPS narrow scan spectra of the Au thin film surfaces etched with different gas mixture.

plasma. As the addition of $CF_4$ to $Cl_2$ /Ar gas mixture, which is fixed at 20%, increases up to 10 %, the emission intensities of $Cl_2$ (436 nm) and F (703.7 nm) reached a maximum, while Ar ions (750.4 nm) decreases rapidly. These results suggest that the emission intensities of the Cl radical increase due to increasing dissociation of $Cl_2$ molecules [8]. As the additive $Cl_2$ into the $CF_4/(CF_4+Ar)$ exceeds 10%, Cl radical intensity decreased due to the possible recombination with $CF_4$[7-10].

Figure 4 shows the XPS wide scan analysis of the etched Au thin films in $CF_4/Cl_2/Ar$ plasma. The

photoelectron peaks of Cl 2p, F 1s, Au 4f, and C 1s peaks were observed from the surface. Carbon was not considered because the carbon peak was resulted from the exposure to air after etching process. The existence of Cl and F peaks suggests that chlorine and fluorine compounds are formed on the Au thin films during the $CF_4/Cl_2/Ar$ plasma etching.

Figure 5 shows Au 4f XPS narrow scan spectra on the surface of the etched Au thin films with different gas mixtures. In Fig. 5, the peaks of Au $4f_{7/2}$ and Au $4f_{5/2}$ are presented at 95.6 and 99.3 eV, respectively. In the spectrum (2) of Fig. 5, the intensity of Au is decreased compared with spectrum in (1) of Fig. 5 because Au bond was broken by Ar sputtering. In the spectra (3) and (4) of Fig. 5, the peak intensity of Au decreases because it formed AuCl, which can be removed by Ar ion sputtering.

Figure 6 shows Cl 2p XPS narrow scan spectra on the surface of the etched Au thin films with different gas mixtures. In spectra (1) and (2) of Figure 6, the Cl 2p without a chemical reaction in the narrow scan spectrum can be resolved into two sharp peaks, which are associated with Cl $2p_{3/2}$ (206.1 eV) and Cl $2p_{1/2}$ (207.6 eV), respectively. However, in the spectra (3) and (4) of Fig. 6, there are new peaks on the etched Au samples. These peaks can be resolved into two chemical components as Cl-Cl and Au-Cl. The peaks at 200.2 and 201.6 eV binding energies correspond to Au-Cl.

Figure 7 shows SEM photograph of Au thin film surfaces etched at a 10% additive $CF_4$ into $Cl_2/Ar$ gas mixing ratio of 0.2. We obtained clean surface and the etch slope of over 65°. We cannot obtained steep etch profile because we used photoresist for mask.

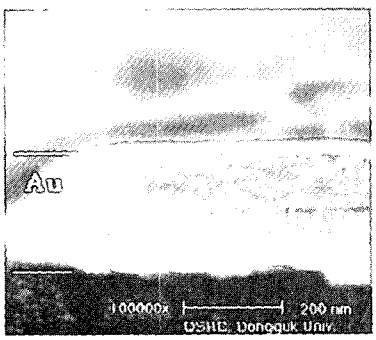


Fig. 7. SEM photograph of Au thin film surfaces etched with 10 % additive $CF_4$ into $Cl_2/(Cl_2 + Ar)$ gas mixing ratio of 0.2.

## 4. CONCLUSIONS

The effects of an additive $CF_4$ into $Cl_2/Ar$ gas mixture in the Au etch were studied by using ICP. The maximum etch rate of the Au thin films is 370 nm/min at a 10 % additive $CF_4$ to into $Cl_2/Ar$ gas mixture, which was fixed at 20%. XPS analysis shows the existence of Au-Cl bonding by the chemical reaction between Cl and Au. The Au atoms of the Au thin films react with chlorine and fluorine, therefore compounds such as Au-Cl and Au-F bonds remained on the surface of the etched Au thin films due to their low volatility. These products can be removed by Ar ion bombardment. These results confirmed the maximum etch rate of Au at the 10 % additive $CF_4$ into $Cl_2/Ar$ gas mixture owing to the predominant etch of Ar ion bombardment as well as the assistance of the chemical reaction of Cl atoms.

## REFERENCES

[1] H. Ohtake, S. Samukawa, H. Oikawa, and Y. Nashimoto, "Enhancement of reactivity in Au etching by pulse-time-modulated $Cl_2$ plasma", Jpn. J. Appl. Phys., Vol. 37, No. 4B, p. 2311, 1998.

[2] R. M. Ranade, S. S. Ang, and W. D. Brown, "Reactive ion etching of thin gold films", J. Electrochem. Soc., Vol. 140, No. 12, p. 3676, 1993.

[3] F. T. Aldridge, "Highspeed anisotropic reactive ion etching of gold films", J. Electrochem. Soc., Vol. 142, No. 5, p. 1563, 1995.

[4] Y. S. Chang, D. P. Kim, C. I. Kim, E. G. Chang, and S. J. Lee, "Etching characteristics of gold thin films using inductively coupled $Cl_2/Ar$ Plasma", J. of KIEEME(in Korean), Vol. 15, No. 12, p. 1011, 2002.

[5] D. P. Kim, C. I. Kim, W. J. Lee, B. G. Yu, T. H. Kim, and E. G. Chang, "Etching characteristics of $SrBi_2Ta_2O_9$ thin film with adding $Cl_2$ into $CF_4/Ar$ plasma", J. of KIEEME(in Korean), Vol. 14, No. 9, p. 714, 2001.

[6] T. Kanashima and M. Okuyama, "Analyses of high frequency capacitance-voltage characteristics of Metal-Ferroelectrics-Insulator-Silicon structure", Jpn. J. Appl. Phys., Vol. 38, No. 4A, p. 2044, 1999.

[7] J. K. Jung and W. J. Lee, "Dry etching characteristics of $Pb(Zr,Ti)O_3$ films in $CF_4$ and $Cl_2/CF_4$ inductively coupled plasmas", Jpn. J. Appl. Phys., Vol. 40, No. 3A, p. 1408 , 2001.

[8] N. C. M. Fuller, V. M. Donnelly, and I. P. Herman, "Electron temperatures of inductively coupled $Cl_2$–Ar plasmas", J. Vac. Sci. Technol. A, Vol. 20, Issue 1, p. 170, 2002.

[9] N. C. M. Fuller, V. M. Donnelly, and I. P. Herman, "Optical actinometry of $Cl_2$, Cl, $Cl^+$, and $Ar^+$ densities in inductively coupled $Cl_2$–Ar plasmas", J. Appl. Phys., Vol. 90, Issue 7, p. 3182, 2001.

[10] S. W. Shin, C. I. Kim, and E. G. Chang, "The study of etching Characteristic in $SrBi_2Ta_2O_9$ thin film by optical emission spectroscopy", J. of KIEEME(in Korean), Vol. 14, No. 3, p. 185, 2001.