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Etching of Copper Films for Thin Film Transistor Liquid Crystal Display using Inductively Coupled Chlorine-Based Plasmas

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In this study, using inductively coupled Cl_2/Ar plasmas (ICP), the effects of various process conditions such as source power, bias power, Cl_2/Ar gas ratio, and ultraviolet (UV) ray were investigated to obtain high Cu etch rates without remaining any nonvolatile etch products. Due to the formation of nonvolatile copper chloride, copper film was not etched and, instead, a thick copper chloride residue was formed on the copper surface when Cl_2/Ar ICP plasma was used. However, the residue could be removed and the copper film could be etched when high ICP source power was used with high intensity of ultraviolet rays and high bias power. Especially, when the ICP source power higher than 300 W and the bias power higher than 70 W were used, no UV irradiation was required to etch copper films, and which is more desirable for the etching of thin film transistor liquid crystal display (TFT-LCD) substrates. The maximum copper etch rate obtained was 300 nm/min with inductive power of 600 W, bias power of 75 W, and 0.5 of Cl_2/Ar gas ratio at the pressure of 7 mTorr without applying UV. [DOI: 10.1143/JJAP.43.8300]

KEYWORDS: Copper (Cu), Etching, Cl_2/Ar plasma, Inductively-coupled plasma, etch product

1. Introduction

Due to the low electrical resistivity at room temperature and low material cost, copper (Cu) is actively considered as a candidate for the metal electrode of high quality and large area TFT-LCD. In fact, the development of a metal electrode process with low electrical resistivities is a core technology in the next generation high quality and large area TFT-LCD. It is due to the fact that the increase of electrode length and the reduction of electrode width for the higher aperture ratio increases the resistance and capacitance of the circuit and results in flickering and crosstalk phenomena of the TFT-LCD devices.[1,2)]

Currently, the Cu etch process applied to the next generation TFT-LCD is being developed using a wet etching method. During the wet etching of Cu, due to the galvanic effect between the Cu and the interlayer such as Mo, Al, Ti, etc. which is required to improve adhesion between Cu and α-silicon or SiN_x, severe corrosion of the interlayer is occurred in addition to the grainboundary etching of Cu metal line sidewall. Therefore, a dry plasma etching process can be more adequate to acquire better etch profile and high etch selectivity over various inter-layers. However, present problems of Cu dry etching are known to be the low etch rate, sidewall roughness, and substrate roughness due to etch products remaining during the etching using halogen compound gases.[3,4)]

Dry etching of Cu thin films has been studied by many researchers for the application to semiconductor processing using chlorine-based plasmas and it is known that the ratio of ion to neutral, ion energy, and ion flux are main factors on the successful Cu dry etching.[5–10)] For example, in the case of Cu etching conducted using electron cyclotron resonance (ECR) plasma, Cu could be successfully etched at the etch rate of 600 nm/min using Cl_2/Ar when the ECR power was 1000 W, however, thick chlorine halides were formed when the ECR power was lower than 300 W.[8)] Therefore, enough ion flux can prohibit the formation of $CuCl_x$ on the Cu surface during the etching. In the case of reactive ion etching (RIE), ion flux is generally lower than the ECR plasma, therefore, a thick copper chloride layer was formed during the etching. To achieve Cu etching in the RIE, substrate heating higher than 200°C or ultraviolet radiation in addition to a high ion bombardment energy has been used.

For the application of Cu dry etching to large area TFT-LCD manufacturing, the ECR plasma system can not be used due to the problems in the scalability. However, for some of the high density plasma sources such as inductively coupled plasma (ICP), large area sources that can be applied to TFT-LCD substrates are being developed,[11)] and these sources can be applied to Cu dry etch processing for TFT-LCD. Therefore, in this study, as one of the scaleable high density plasma sources, inductively coupled plasma (ICP) was used and its Cu dry etching characteristics were investigated using a smaller ICP source as a function of intensity of ultraviolet rays, source and bias power, and Cl_2/Ar ratio and its possible application to large area TFT-LCD processing was studied.

2. Experimental

In this experiment, a planar inductively coupled plasma (ICP) source operated at 13.56 MHz RF power was used and the rf power up to 650 W was applied to the source. The ICP source was consisted of 12 cm diameter and 3.5 spiral turn water cooled Cu coil and 1.5 cm thick quartz plate was used to transfer inductive power to the plasma and to separate the vacuum chamber from the ICP source. On the top of quartz plate, a UV lamp with a peak wavelength of 365 nm and 10 mW/cm^2 was located to investigate the effect of UV irradiation. The distance between the quartz plate and the substrate was 6.5 cm. The substrate was connected to 13.56 MHz power to generate dc bias voltages. The applied bias power was from 0 to 100 W. The substrate was maintained at room temperature using a chiller. Due to the etch product problem, the sidewall of the chamber was heated about 70°C using a heating jacket. More details of the system used in the study can be found elsewhere.[12)]

As the sample, 300–400 nm thick Cu film sputtered on the corning 1737 LCD glass having 2.0 μm·cm resistivity was used. To study the Cu etch rate and etch profile, 25 μm thick photoresist was patterned on the Cu film and its step and profile after the Cu etching were measured using a step profilometer (alpha step 500, Tencor) and using a field emission scanning electron microscope (FE-SEM; S-4700, Hitachi), respectively. The characteristics of Cu etching were investigated as functions of Cl_2/Ar gas ratio, inductive power, bias power, and UV intensity. The surface roughness of the etched Cu and glass substrate was measured using an atomic force microscope (AFM, CP Research, THERO-MICROSCOPE) and the surface chemistry of the Cu film after the exposure to Cl_2/Ar plasma with/without UV irradiation was investigated using a X-ray photoelectron spectrometer (XPS; ESCALAB 220i).

3. Results and Discussion

Figure 1 shows the effect of UV and ICP source power on the copper etch rates for the source power in the range from 200 to 400 W and UV intensity from 0 to 10 mW/cm^2. No bias power was applied and the Cl_2/Ar ratio was 0.5 at 7 mTorr of operational pressure. The substrate temperature was maintained at room temperature. As shown in the figure, when UV ray was not applied, swelling of Cu film was observed by the formation of nonvolatile etch products such as copper chlorides. With the increase of UV intensity, the swelling was decreased at the same ICP power and, in the case of ICP source power higher than 300 W, etching of Cu film instead of swelling was observed at the UV intensity higher than 3 mW/cm^2. The wavelength of UV ray used in the experiment was 365 nm where the photon energy related to the wavelength is 3.4 eV. The energies required to vaporize the copper chlorides are as follows.[13)]

$$\begin{aligned} CuCl\ (s) &\rightarrow CuCl\ (g) &&:\ 2.2\,eV \\ Cu_3Cl_3\ (s) &\rightarrow Cu_3Cl_3\ (g) &&:\ 1.6\,eV \end{aligned}$$

Therefore, the decrease of swelling of Cu film with increasing the UV intensity at a given power appears related to the vaporization of copper chlorides. When ICP source power was higher than 300 W, etching instead of swelling was observed and it appears related to the formation of more volatile copper chlorides such as Cu_3Cl_3 instead of CuCl at the higher power by the increased dissociation of chlorine molecules in the plasma.

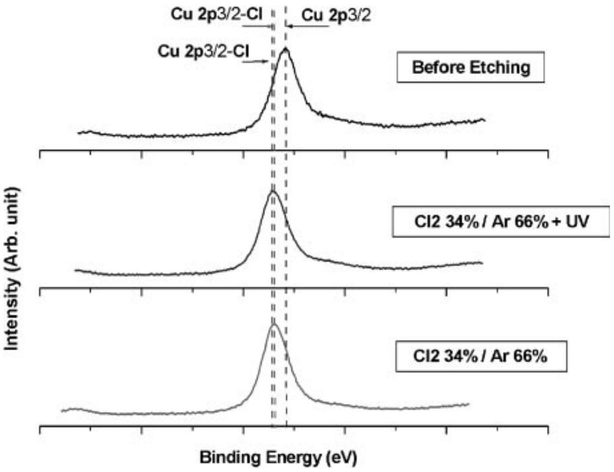

Fig. 2. Cu 2p XPS narrow scan spectra of Cu film surfaces exposed to Cl_2/Ar plasma + UV and Cl_2/Ar plasma. Cl_2/Ar ratio was 0.5. As a reference, Cu $2p_{3/2}$ peak from pure Cu metal was also measured.

The formation of copper chloride on the Cu film surface during the etching of Cu using Cl_2/Ar ICP plasma could be observed using XPS and some of the results are shown in Fig. 2 for the conditions etched with UV and without UV. Cl_2/Ar ratio was 0.5. As a reference, the Cu $2p_{3/2}$ peak from the pure Cu metal was also measured. As shown in the figure, the Cu $2p_{3/2}$ peak from the pure Cu metal could be observed at 933 eV, however, the Cu $2p_{3/2}$ observed after the exposure to Cl_2/Ar plasma was moved to 932.5 eV indicating the formation of copper chlorides. Also, the surface of the Cu film exposed to Cl_2/Ar plasma and UV showed the Cu $2p_{3/2}$ peak at 932.5 eV similar to the case with the Cu film exposed to Cl_2/Ar plasma only.

Figure 3 shows the effect of bias power and the addition of UV to the bias power on the Cu etch rates. The bias power

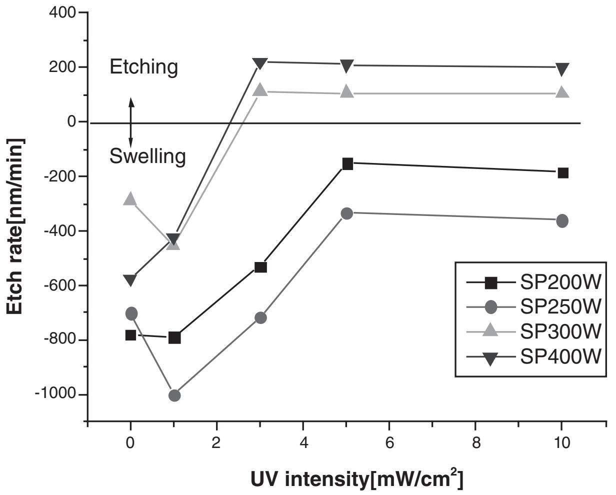

Fig. 1. Effect of UV irradiation and ICP source power on the copper etch rates for the source power in the range from 200 to 400 W and UV intensity from 0 to 10 mW/cm^2. No bias power was applied and the Cl_2/Ar ratio was 0.5 at 7 mTorr of operational pressure. The substrate temperature was maintained at room temperature.

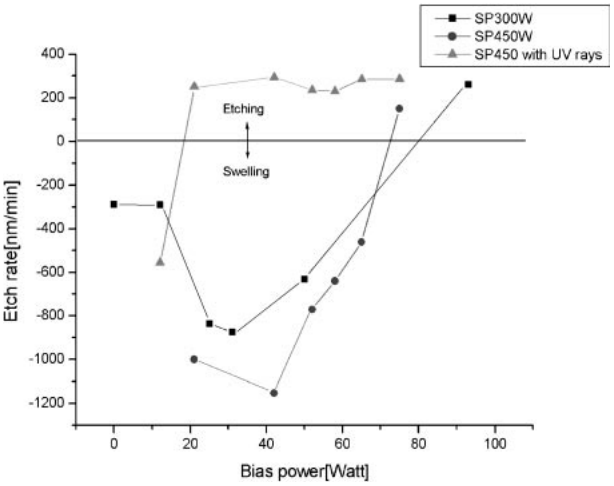

Fig. 3. Effect of bias power and the addition of UV to the bias power on the Cu etch rates. The bias power was varied from 0 to 100 W for the source power of 300 and 450 W and 5 mW/cm^2 of UV was added to the 450 W of source power. Cl_2/Ar ratio was 0.5 and operational pressure was 7 mTorr.

was varied from 0 to 100 W for the source power of 300 to 450 W and 5 mW/cm^2 of UV was added to the 450 W of source power. The other operational conditions such as Cl_2/Ar ratio, operational pressure, and substrate temperature were kept the same as before. As shown in the figure, the application of bias power smaller than 40 W to the substrate increased the swelling of the Cu film, however, the further increase of bias power decreased the swelling of the film and finally etched the Cu film. The addition of UV in addition to the bias power decreased the bias power required to etch the film. The increased swelling of Cu film with the application of small bias power appears related to the increased formation of copper chloride by increased chlorine ion flux to the substrate without enhancing the sputtering of the etch products formed on the surface due to the low energy of the ion flux. By applying higher bias power enough to sputter the copper chlorides formed on the surface, the swelling was decreased and the etching of the Cu films was observed. As shown in the figure, by applying the bias power enough to sputter the etch products, Cu film could be etched at the rate of 200 nm/min without applying UV to the substrate. In fact, it is very difficult to apply uniform UV radiation to the substrate especially for the large area substrate such as TFT-LCD. Therefore, the successful etching of Cu film with high density plasmas by applying bias power high enough to sputter the etch products is very important for the application to the TFT-LCD processing.

Figure 4 shows the effect of Cl_2/Ar ratio on the Cu etch rate for 600 W of inductive power and 75 W of bias power. No UV ray was applied and the operational pressure was maintained at 7 mTorr. As shown in the figure, when the Cl_2/Ar ratio was higher than 0.5, swelling instead of etching was occurred possibly due to the faster formation of copper chlorides than the removal of them. Therefore, to etch Cu film, appropriate combinations of the process parameters were required. The roughness of the etched Cu surface was investigated after the etching of 300 nm thick copper film for 1 minute with the Cl_2/Ar ratio of 0.5 in Fig. 4 and the result is shown in Fig. 5. Because the etch rate at the condition was about 300 nm/min, the Cu film on the glass substrate was just etched and some copper residue could be remaining on the glass surface due to nonuniformity in the deposition and etching. However, as shown in the figure, the RMS surface roughness of the glass surface was about 0.5 nm and similar results could be obtained when the surface of the Cu film was measured after the removal of 300 nm for the 400 nm thick copper film at the same etching condition. Therefore, smooth Cu etched surface or smooth glass surface could be obtained after the Cu etching with bias power without applying UV.

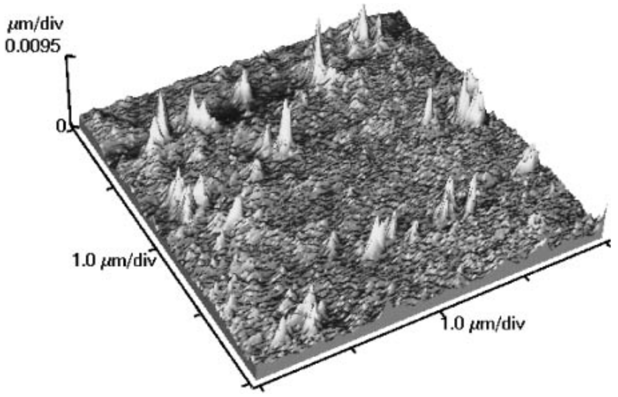

Fig. 5. Surface roughness of the etched Cu measured by AFM after the etching of 300 nm thick copper film for 1 minute with the Cl_2/Ar ratio of 0.5 in Fig. 4. At this condition Cu film etch rate was about 300 nm/min.

The Cu etch profile was observed after the etching of a photoresist patterned Cu film. 400 nm thick Cu film on the 1737 corning glass and patterned with 25 µm thick photoresist was used as the sample. The process conditions were 600 W of inductive power, 70 W of bias power without applying UV, and Cl_2/Ar was 0.5 at 7 mTorr and the result is shown in Fig. 6 after the removal of photoreist. As shown in the figure, no residue could be observed on the glass surface after the removal of photoresist, however, the sidewall of the Cu etched feature was not smooth enough even though it has a sloped profile required for the following TFT-LCD processing. The sidewall roughness is partially originated from the irregular surface line of the developed 25 µm thick

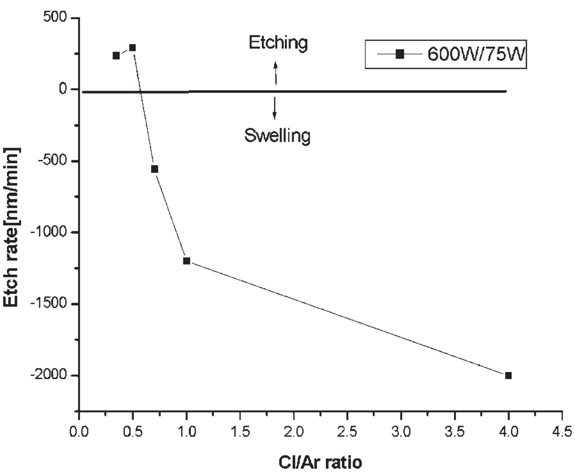

Fig. 4. Effect of Cl_2/Ar ratio on the Cu etch rate for 600 W of inductive power and 75 W of bias power. No UV ray was applied and the operational pressure was 7 mTorr.

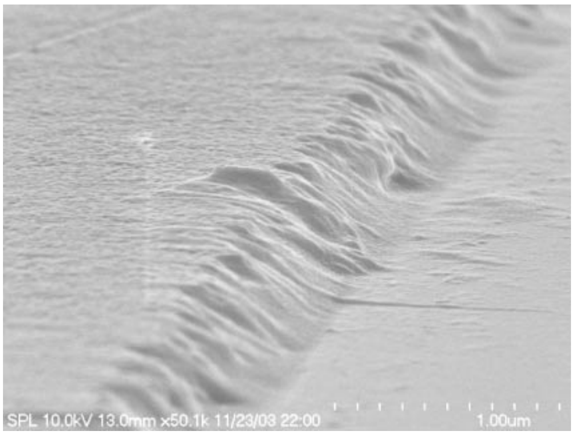

Fig. 6. Etch profile of Cu film observed after the etching of a photoresist patterned Cu film. 400 nm thick Cu film on the 1737 corning glass and patterned with 25 µm thick photoresist was used as the sample. The process conditions were 600 W of inductive power, 70 W of bias power without applying UV, and Cl_2/Ar was 0.5 at 7 mTorr.

photoreist, but it appears more related to the preferential attack of Cu grain boundaries by chlorine radicals. It is believed that the sidewall roughness of the etched Cu film could be reduced by using lower Cl_2/Ar ratio and by applying higher bias power, therefore, by increasing ion bombardment effect without increasing sidewall attack by chlorine radicals.

4. Conclusions

In this study, using inductively coupled Cl_2/Ar plasmas, the effects of source power, bias power, Cl_2/Ar gas ratio, and ultraviolet rays on the Cu film etching were investigated for the application to TFT-LCD processing.

Cu thin film could be successfully etching by using inductive power higher than 300 W together with 365 nm UV higher than $3\,mW/cm^2$. The irradiation of 365 nm UV to the Cu film appears to remove copper chloride formed on the surface during the exposure to high density Cl_2/Ar plasma. The formation of copper chloride on the Cu film surface during the exposure to high density Cl_2/Ar plasma could be observed using XPS. Even though Cu film could be etched by the application of UV during the exposure to Cl_2/Ar plasmas, it is difficult to obtain uniform UV intensity on a large area required for TFT-LCD processing. Fortunately, by the application of bias power in addition to inductively coupled plasma, Cu film could be successfully etched and, in this experiment, the etch rate close to 300 nm/min could obtained at 600 W of inductive power, 75 W of bias power, 7 mTorr of operational pressure, and 0.5 of Cl_2/Ar gas ratio without UV. At this condition, even though the sidewall etch profile was a little rough, a sloped Cu etch profile required for TFT-LCD processing could be obtained without remaining any residue on the etched glass surface.

Acknowledgments

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