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Characteristics on the Gate Insulator of Metal Tip Field Emitter Arrays after Wet Etching Process

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The effect of wet-etching process on the gate insulator for fabrication of field emitter arrays (FEAs) was examined. Three types of wet-etching process have been performed to fabricate metal tip FEAs, they are Mo (gate metal), oxide (gate insulator) and Al (release layer) etching, respectively. We examined the effect of gate insulator after wet etching through breakdown field strength and rms surface roughness. And the effect by residual ions or atoms was also examined. The breakdown field strength of gate insulator by the measurement of current-voltage for immersing in oxide etchant was rapidly lowered at the expense of large etching time. However in case of Al etchant, the breakdown field strength was lowered slowly. In all cases, it has been validated through Auger electron spectroscopy (AES) analysis that the residual atom was phosphor after wet-etching process when compared cleaned with non-cleaned samples. Also, we obtained excellent result when aluminum etchant was substituted for 3% tetra-methyl ammonium hydroxide (TMAH). In case of TMAH, decrease of the breakdown field strength was the slowest, surface roughness was smoother, and it did not attack gate and tip material.

KEYWORDS: FEAs, gate, release layer, breakdown field strength, TMAH

1. Introduction

Many research workers have studied the field emission display (FED) with particular emphasis on emitter tips. The performance of gate insulator has been treated with a less interest.

In general, in fabricating a metal tip field emitter arrays (FEAs) three types of wet-etching process have been used. These are molybdenum and oxide etching to form the gate hole and, aluminum etching to remove the release layer. Such wet-etching processes are known to affect the gate oxide and subsequently, it is necessary to investigate the characeristics of gate insulator after wet-etching process.

In operation of FED, the characteristics of the gate insulator has significant contribution to the distribution of the field once a voltage is applied to the gate.[1)]

In this study, breakdown field strength of silicon dioxide was calculated by measurement of current-voltage in order to investigate the characteristics of gate insulator before and after wet-etching processes. Besides breakdown field strength, through atomic force microscopy (AFM) display and Auger electron spectroscopy (AES) analyses the effect on the gate insulator by residual ions (or atoms) was investigated.

2. Experimental

Heavilly doped n-type, resistivity 0.005 Ω·cm, and (100) Si wafer was used. Firstly, 1 μm thick thermal silicon dioxide was grown by wet oxidation at 1100°C in furnace for gate insulator. Secondly, molybdenum was deposited by RF magnetron sputtering for gate electrode. Figure 1 shows the Spindt type metal tip FEAs fabrication process and molybdenum dot-gate structure which formed on the thermal oxide. The diameter and the thickness of Mo dot-gate was about 0.7 mm and 4000 Å, respectively.

In our experiments, Mo etchant was a mixed solution of H_3PO_4:HNO_3:H_2O (5:3:2), oxide etchant was a 7:1 BHF, Al etchant was a mixed solution of H_3PO_4:CH_3COOH:HNO_3:H_2O (4:4:1:1), and new Al etchant was a 3% water diluted tetra-methyl ammonium hydroxide ($[(CH_3)_4N]OH$). Every etching process was performed at room temperature in atmospheric ambient. The etch rate of SiO_2 layer by oxide etchant was about 800 Å/min. In case of oxide etching, dot-gate metal acted as an etch mask. Though we considered the undercut etching, the difference of current density between original dot-gate and etched dot-gate was so small as 0.2 nA/cm^2. So we could disregard undercut etching.

Authors have studied on the characteristics of gate oxide with various etching time. Also, the characteristics of gate oxide of cleaned sample was compared with that of non-cleaned sample. Table I shows the etching time for every etchants in this experiment. The samples were ultrasonic cleaned for 15 min. in acetone and followed by deionized water rinsing. The samples were ultrasonic cleaned for 15 min. in methanol again. After final rinse in deionized water the cleaned samples were dried by the nitrogen blower.

Current-voltage characteristics were measured in atmospheric ambient by Keithley high voltage Source Measure Unit (SMU 237) and then breakdown field strength of oxide was calculated. In our experiments, breakdown field strength of oxide was determined when leakage current density was 1×10^{-6} A/cm^2. Surface roughness was measured by Park Scientific Instrument (PSI)

Table I. Etching time with various step of etching process.

	Mo etchant	Oxide etchaat	Al etchant
Etching time	0, 30, 60, 90, 120, **150** (s)	0, 5, 10, **13.5** (min)	0, 10, 15, 20, 25, **30** (min)
Cleaned sample	**150** (s)	**13.5** (min)	**30** (min)

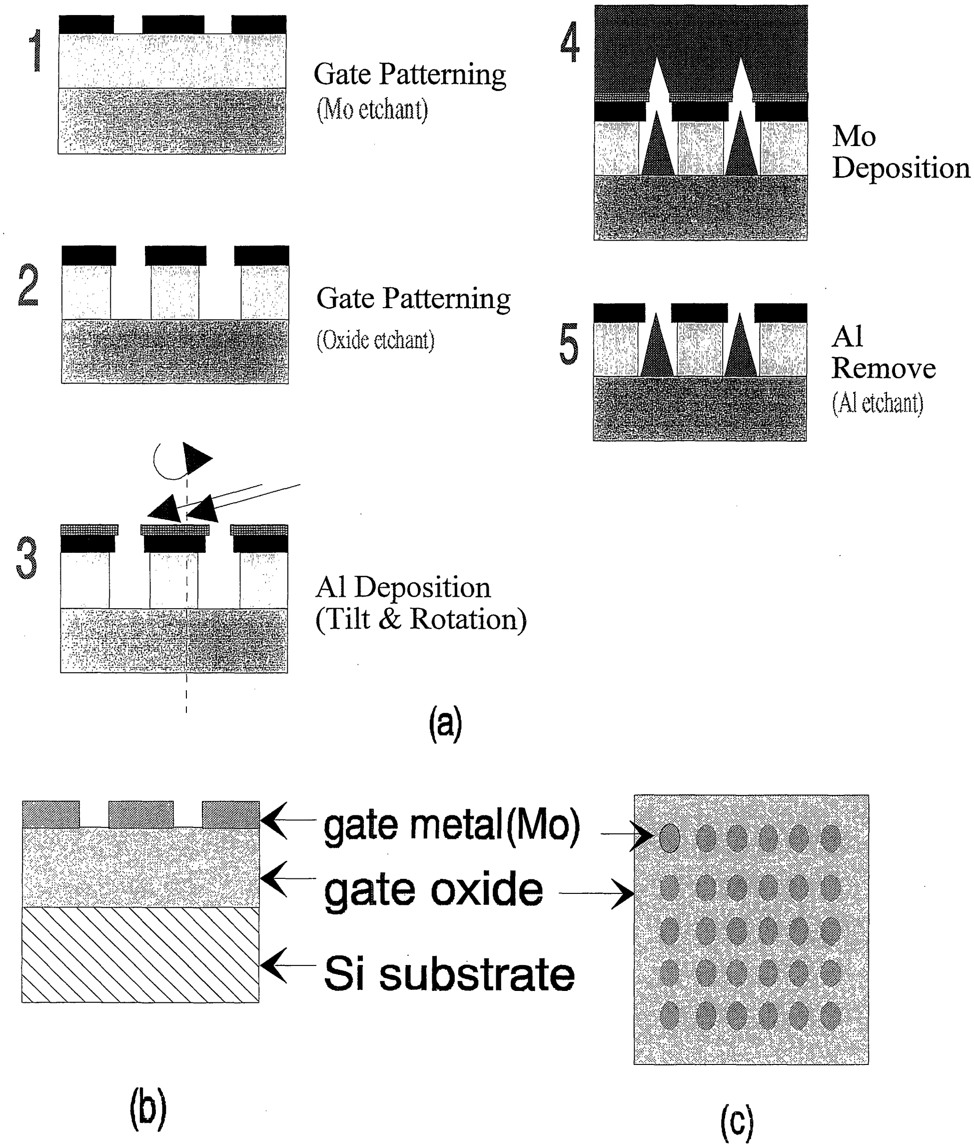

Fig. 1. (a) Spindt type metal tip FEA fabrication process and sample structure of this study of (b) cross-sectional view, (c) top view.

AFM. Residual ions or atoms after wet-etching process was measured by AES.

3. Result and Discussion

Figure 2 shows the breakdown field strength of oxide for molybdenum etchant with etching time. In this study, breakdown field strength of thermal silicon dioxide is 8 MV/cm, which is general characteristics of thermal silicon dioxide. It is shown that as the time of immersing in etchant is increased, the breakdown field strength is rapidly decreased. Molybdenum dot-gate electrode was deposited after the sample's being immersed in molybdenum etchant. The main factor affecting the decrease of breakdown field strength of oxide may be attributed to the oxide caused by residual ions or atoms. Breakdown field strength of non-cleaned sample (about 5.6 MV/cm) is decreased continuously whereas the case of cleaned sample (about 7.3 MV/cm), the breakdown field strength is increased. It can be shown that residual ions or atoms are removed after cleaning, a fact validated by AFM display. RMS surface roughness of thermal oxide is 1.7 Å

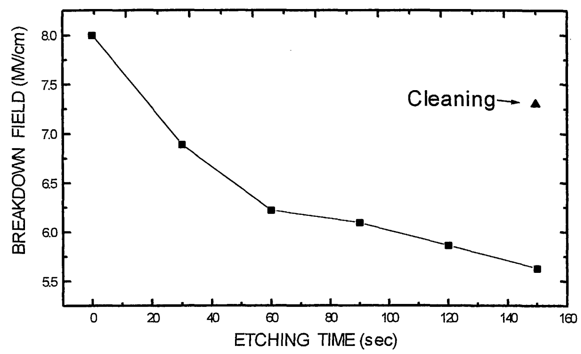

Fig. 2. Breakdown field of oxide with various etching time for Mo etchant.

and that of etched thermal oxide with Mo etchant is 2.5 Å. But the roughness of cleaned sample is 1.8 Å. Due to wet etching electrical breakdown of the rough surface occurs at lower voltage because of breakdown through short path or existence of residual ions or atoms. In contrast, in case of the cleaned sample, because residual ions

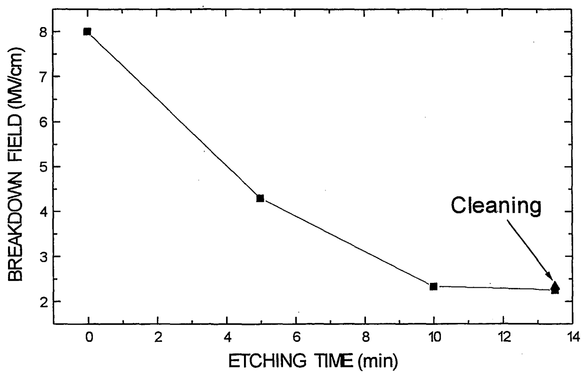

Fig. 3. Breakdown field of oxide with various etching time for oxide etchant.

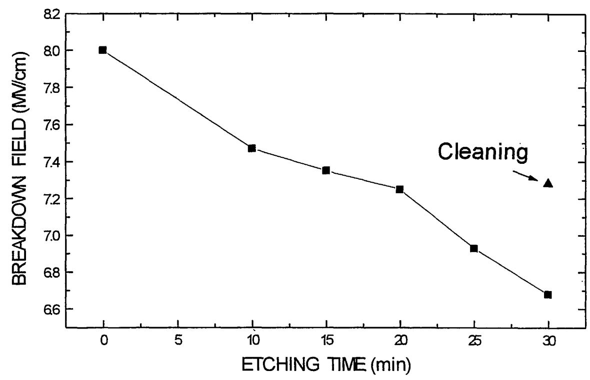

Fig. 4. Breakdown field of oxide with various etching time for Al etchant.

or atoms are removed at the surface of sample, roughness is less than etched sample.

Figure 3 shows the breakdown field strength of oxide for oxide etchant with etching time. Similar to the trend shown in Fig. 2, the slope of graph decreases with etching time. But unlikely Fig. 2, the slope in Fig. 3 is more steep than that in Fig. 2 and the change of breakdown field strength is not observed before and after cleaning. It is explained that the main factor contributing to the decrease of breakdown field strength of oxide is mainly the defect of surface caused by damage of oxide rather than residual ions or atoms. Also this fact matched with AFM result. The change of RMS roughness of sample is from 4.2 Å to 4.0 Å before and after cleaning, respectively.

The etching mechanism of oxide was come out as towards. Fluoric ion of fluoric acid takes part in etching of oxide and hydrogen ion occurred from the etching change the pH value of reagent and that influence on the etch rate. So in order to maintain the pH value ammonium fluoride must be added.[2)]

The reaction equation of etching is following.

$$SiO_2 + 6HF \rightarrow H_2 + SiF_6 + 2H_2O,$$

$$HF \rightarrow H^+ + F^-,$$

$$NH_4F \rightarrow NH_4^+ + F^-$$

There is an opinion that the role of ammonium fluoride is not a buffer, it is evident that a complexing agent of precipitating a formed $(NH_4)_2SiF_6$.[3)] Therefore precipitant of $(NH_4)_2SiF_6$ and HF and ions of HF_2^-, F^-, and etc affect breakdown field of oxide.[4–6)]

Figure 4 shows the breakdown field strength of oxide for aluminum etchant with etching time. The slope of this figure is less steep than that in Figs. 2 and 3, but the breakdown field strength of oxide is lessened continuously. Unlike Fig. 2, breakdown field strength of cleaned sample is similar to that of thermal silicon dioxide. So it is thought that residual ions or atoms are removed by cleaning. This fact is confirmed by AFM display, also.

A problem of aluminum etching is that the aluminum etchant is similar to molybdenum etchant, where aluminum etchant etched molybdenum tip and gate electrode. Therefore we changed aluminum etchant to 3% tetra-methyl ammonium hydroxide (TMAH). In this

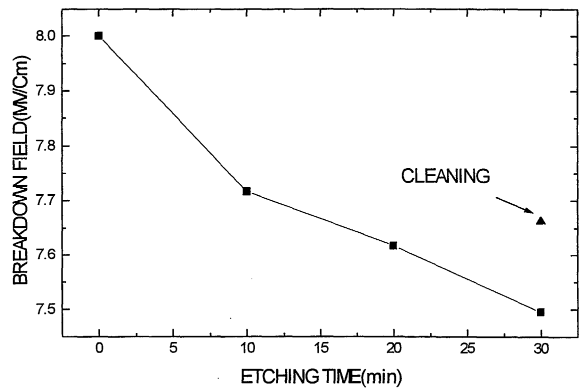

Fig. 5. Breakdown field of oxide with various etching time for 3% TMAH.

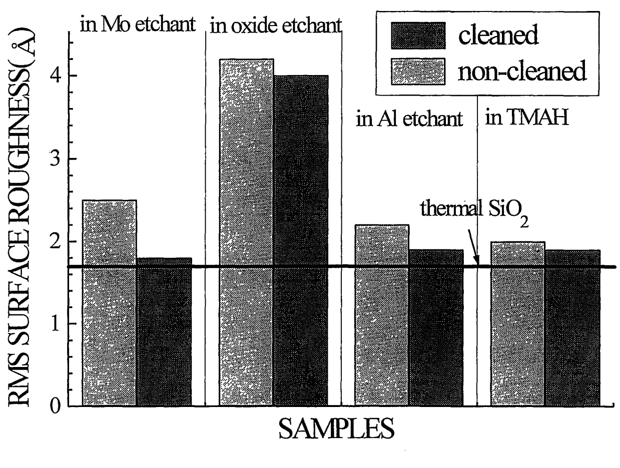

Fig. 6. Comparison of RMS surface roughness by AFM for various etchant.

case, the slope of breakdown field strength is the most gentle (Fig. 5) and RMS roughness of etched sample is the least shown in Fig. 6.

Figure 7 shows AES photograph and Fig. 8 shows AES spectroscopy of etched surface. In this study, phosphorous atom was detected in #2 and #3, whereas in thermal oxide and #1 phosphorous atom was not detected. It is thought that phosphorous atom is originated in phosphoric acid.

Through this study, we could demonstrate that residual ions or atoms bonded with weak bond, so breakdown

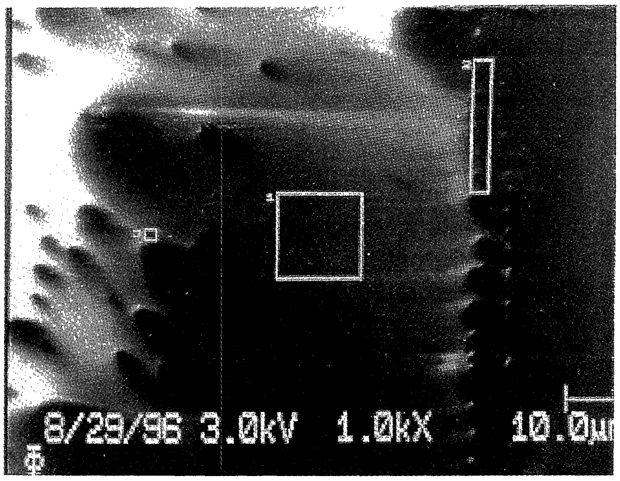

Fig. 7. AES photograph of species.

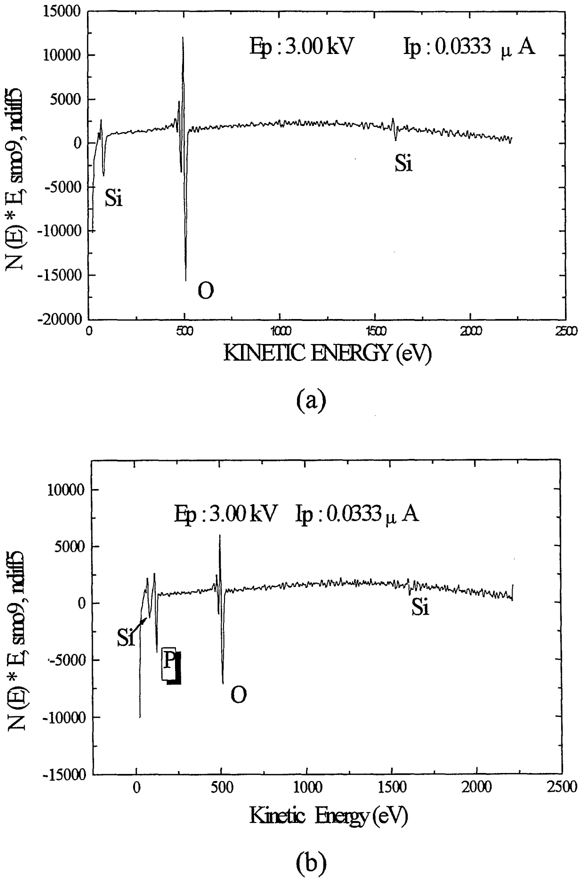

Fig. 8. AES spectroscopy of (a) SiO_2 and #1 and (b) #2 and #3.

occurred easily.

4. Conclusion

In order to examine the effect to the gate insulator when fabricating a metal tip FEAs breakdown field strength of oxide, RMS surface roughness and AES spectroscopy were investigated.

After immersing in molybdenum and aluminum etchant, it was found that the breakdown field strength is affected by residual ions or atoms.

In the case of oxide etchant, the decrease of breakdown field strength is most severe and the effect by residual ions or atoms can be ignored because there is no difference in breakdown field strength, before and after cleaning.

After changing aluminum etchant to 3% TMAH, the slope of breakdown field strength is less steep and RMS roughness is minimal.

Subsequently deteriorating the characteristics of gate insulator was avoided by substituting molybdenum etchant for anisotropic dry etching and by substituting aluminum etchant for 3% TMAH.

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