Development of Blackening Materials for Cu Wiring TFTs with H₂O₂ Based Etchant

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ABSTRACT

We've developed blackening materials with high durability for TFTs wiring by using Nb based materials in IDW'19. However, the Nb based materials could not dissolve to H_2O_2 based etchant. In this paper, we improved the H_2O_2 etching properties of the blackening material remaining high durability.

1 INTRODUCTION

The development trends of FPD used in TVs have been towards increased screen size and enhanced resolution. In the large size screen display, the Cu gate electrode is widely adapted by substitution for Al, owing to its high conductivity to reduce the resistance-capacitance propagation delay as well as its higher stress-migration and electro-migration resistance [1][2]. However, Cu have serious issues, one of which is well-known to exhibit poor adhesion to glass substrate [3]. Several methods are proposed to resolve this problem, by inserting an extra layer between the interface of copper and substrate such as Ti [1], Mo [3], MoW [4] and so on. The use of Cu alloy is also researched to improve the adhesion of Cu and glass substrate [5]. In the Cu and buffer layer etching process, H₂O₂ based etchant is basically used in substitution for oxone [3]. The TFT wiring is located in the visual side such as bottom emission type OLED [2] and the front side TFT structured display [6], the metal based film between the glass and Cu bottom gate is likely visible. We have developed the Nb based blackening materials with high durability for TFTs wiring to reduce the reflectivity on the surface of wiring metal in the previous IDW'19. However, the Nb based materials couldn't be etched by H₂O₂ based etchant. In this study, we improved the H₂O₂ etching properties of the blackening film by using high durability materials remaining high durability.

2 EXPERIMENT

2.1 Optical Simulation

Firstly, the optical constant of the blackening film for Cu bottom gate was optimized by optical simulation. We created the ideal model to check the reflectivity on glass/blackening film/Cu structure. The reflectivity with different optical constant in the blackening film was calculated by simulation.

2.2 Sputtering Deposition and Analysis

The sputtering target for the blackening film was obtained by sintering of several kinds of powder mixture. The composition of the sputtering target was designed to get the optimal optical constant of the film, DC sputtering availability, non-reactive sputtering (without reactive gas). High durability of the film was ensured by using high durability materials. The blackening film was deposited on EAGLE XG (Corning Inc.) glass substrate. Pure Cu was deposited on the blackening film by Cu sputtering target. Then the reflectivity and sheet resistance of the glass/blackening film/Cu stacked film was observed by spectrophotometer and 4 probe method respectively. In order to evaluate the durability, the reflectivity and sheet resistance ware measured again after the heat treatment in nitrogen gas at 500 °C. The GHP-3 (Kanto Chemical Co., Inc.) etchant was used as a H₂O₂ based etchant. The etching process was performed by dipping method at 40 °C. The etching speed of the blackening film was calculated from the film thickness divided by the etching time. The glass/ blackening film/Cu stacked film was patterned by using photolithography. The stacked film was etched by one step process. The photoresist was removed by TOK104 (Tokyo Ohka Kogyo Co., Ltd.) stripper. The crosssection of the etching profile was observed by FE-SEM.

3 RESULTS

3.1 Optical Simulation

Fig. 1 shows the reflectivity simulation results of a) Cu/blackening film/glass and b) blackening film/Cu/glass. The refractive index (n) of the blackening film was fixed at 2.5, while the extinction coefficient (k) was changed from 0 to 1.25. When the blackening film thickness increased, the reflectivity decreased, and then increased again. This tendency is caused by optical interference effect on the blackening film surface and Cu surface. The reflectivity from bottom side in Cu/blackening film/glass, the lowest value can be obtained when the k is 0.75 to 1.0. On the other hand, the reflectivity from top side in blackening film/Cu/glass, the lowest value can be obtained when the k is 0.75, the lower reflectivity can be obtained in both structures. In this experiment, in order to focus on the bottom gate

structure, we set the target value of k to 0.75-1 and proceeded with the material design.



Fig. 1 Reflectivity simulation of blackening films (n= 2.5, k=0-1.25) stacked a) below Cu b) above Cu.

3.2 Reflectivity and Durability of Blackening Film

The blackening film was deposited by high durability material target. We call this material "MMCB29-2". The refractive index is 2.67 and extinction coefficient is 0.85 at 550 nm. The reflectivity from bottom side of Cu/MMCB29-2/glass is shown in Fig. 2. The extinction coefficient is adjusted to optimal value, the reflectivity of Cu decreased from 73.4 % to 8.1 % in average value of visible light (380nm-780nm). In is noted that the value including the reflection (around 4 %) on the surface of glass. Which means the reflectivity without glass reflection is below 5 %. The low reflectivity was kept after 500 °C annealing in N₂ gas. The average value shows 8.2 % in visible range. The sheet resistivity of stacked film was 0.034 Ω /sq. in as deposited film. The value after annealing at 500 °C was 0.035 Ω /sq. Those results shows MMCB29-2 has high durability.



Fig. 2 Reflectivity from bottom side of Cu/MMCB29-2/glass.

3.3 Etching Properties of Blackening Film

The MMCB29-2 could be dissolved to H₂O₂ etchant by selecting high durability materials. The etching speed is 0.4 nm/sec while Cu is 5.8 nm/sec. We made the test pattern shown in Fig. 3 to check the patterning availability. The number in Fig.3 a) and c) means the width of line & space in µm unit. The Cu(600nm)/ MMCB29-2(40nm) stacked film was etched by one step process. The bottom side appearance c) shows low reflectivity even if after patterning process. Fig. 3 b) and d) show microscope images of line/space=30/30 µm position. There is no residue in the edge of wiring. Fig. 4 shows the cross-section of edge position in Cu(600nm)/ MMCB29-2(40nm) stacked film. Since MMCB29-2 surface is flat, the Cu surface showed also smooth surface. In addition, there was no peeling between MMCB29-2/glass interface. Which means MMCB29-2 has higher adhesion to glass substrate. MMCB29-2 could be etched by one batch with Cu layer without step in interface. The angle of the edge was around 40 degree.



Fig. 3 Appearances and microscope images of Cu/ MMCB29-2/glass stacked film after etching. a), b) is Cu side while c), d) is glass side.



Fig. 4 Cross-section of Cu/MMCB29-2/glass stacked film after etching

4 CONCLUSIONS

The blackening material for Cu bottom gate TFT wiring was developed. We succeeded in adjusting optical constant with durability by selecting high durability materials. The Cu/MMCB29-2/glass stacked film shows low reflectivity and almost no change after durability test. MMCB29-2 shows high adhesion to glass substrate. MMCB29-2 could be etched by one batch process with Cu layer. We believe this material is useful for designing high performance displays such as high resolution, transparent and so on.

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