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Etchant for dissolving thin layer of Ag-Cu-Au alloy

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Abstract. As to the reflection electrode of LCD (liquid crystal displays), silver-copper-gold alloy (hereafter, it is called as ACA (Ag98%, Cu1%, Au1%)) is an effective material of which weathering resistance can be improved more compared with pure silver. However, there is a problem that gold remains on the substrate as residues when ACA is etched in cerium ammonium nitrate solution or phosphoric acid. Gold can not be etched in these etchants as readily as the other two alloying elements. Gold residue has actually been removed physically by brushing etc. This procedure causes damage to the display elements. Another etchant of iodine/potassium iodide generally known as one of the gold etchants can not give precise etch pattern because of remarkable difference in etching rates among silver, copper and gold. The purpose of this research is to obtain a practical etchant for ACA alloy.

The results are as follows. The cyanogen complex salt of gold generates when cyanide is used as the etchant, in which gold dissolves considerably. Oxygen reduction is important as the cathodic reaction in the dissolution of gold. A new etchant of sodium cyanide / potassium ferricyanide whose cathodic reduction is stronger than oxygen, can give precise etch patterns in ACA alloy swiftly at room temperature.

Keywords: liquid crystal displays (LCD), ACA, silver, copper, gold, alloy, etchant, cyanogen complex salt, cerium ammonium nitrate, phosphoric acid, sodium cyanide, potassium ferricyanide

1. INTRODUCTION

As for LCD installed in personal digital assistants such as mobile, usage of the LCD using an external light source for power saving has been increasing, and the quality demand of the reflection electrode used for this type has been rising in recent years, too. ACA is an effective material of which weathering resistance can be improved more compared with pure silver. However, there is a problem that gold remains on the substrate as residues when ACA is etched in cerium ammonium nitrate solution or phosphoric acid. Gold can not be etched in these etchants as readily as the other two alloying elements. Gold residue has actually been removed physically by brushing etc. This procedure causes damage to the display elements. Another etchant of iodine/potassium iodide generally known as one of gold etchants can not give precise etch pattern because of remarkable difference of etching rates among silver, copper and gold. The purpose of this research is to obtain a practical etchant for ACA alloy.

2. EXPERIMENTAL

2.1 Polarization curve measurement

2.1.1 Electrode plate

Each constituent of ACA was put into polarization measurement in various kinds of etchants.

They were Ag plate of 99.98%, purity Cu plate of 99.96% purity and Au plate of 99.95% in the size of 20 x 10 x 0.1mm. (The Nilaco corporation).

2.1.2 Test conditions

The etchant was composed of ceric ammonium nitrate system ($Ce(NO_3)_4 \cdot 2NH_4NO_3$ 17%, $HClO_4$ 5%, H_2O 78%) and 1% Sodium cyanide(aq). It was poured into the cell. The cell was made of glass and its volume was 500cm^2. Counter electrode was platinum plate and working electrodes were above-mentioned plates. The saturated calomel electrode (SCE) was used as an external reference electrode via salt bridge. The polarization curves were measured with the potentiostat (Hokuto denko co. ltd. Model HBA-151). Potential was shifted from the spontaneous potential (E_{sp}), first to the less noble potential direction and then noble potential one. The sweep rate was 1000mV/min.

2.2 Etching-rate measurement

2.2.1 Test pieces

ACA layer (thickness of 3000Å) which was vapor-deposited on the glass plate with the size of 20 x 20 mm square was put into etching test.

2.2.2 Test conditions

Etching rates tests were conducted in 300ml of etchant stirred at room temperature.

3. RESULTS AND DISCUSSION

Gold remained on the substrate as residue when ACA was etched in cerium ammonium nitrate solution or phosphoric acid. Fig. 1 shows polarization curves for copper (Cu), silver (Ag) and gold (Au) in the etchant of ceric ammonium nitrate solution ($Ce(NO_3)_4 \cdot 2NH_4NO_3$ 17%, $HClO_4$ 5%, H_2O 78%).

The corrosion current of gold is 0.01 mA/cm^2, and about 1/100 of that of Ag or Cu. This shows that the dissolving power of this liquid is considerably weaker to gold than to silver and copper. Fig. 2 shows the polarization curves for Ag, Cu and Au. The corrosion current of Au is measured 0.8mA/cm^2. The chemical formulas of Au dissolution are shown in formulas (1) to (3). It is the dissolution mechanism of Ag so-called cyaniding method.[1)-2)]

Stirring speed was actually changed and the etching rates of the ACA layers were measured. The result is shown in Table 1. Etching rates are increased with stirring speed.

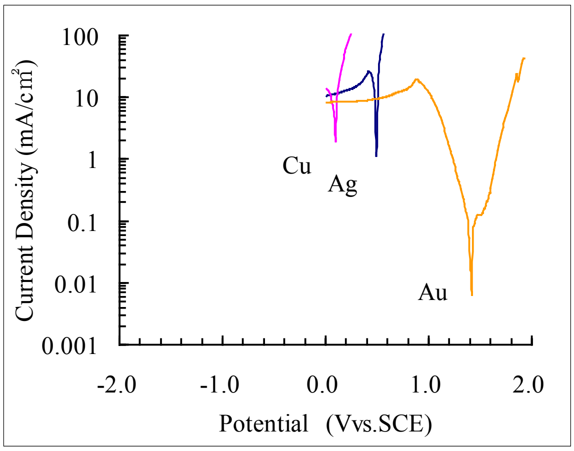


Fig.1 Polarization curves for Ag, Cu and Au in ceric ammonium nitrate solution ($Ce(NO_3)_4 \cdot 2NH_4NO_3$ 17%, $HClO_4$ 5%, H_2O 78%) at room temperature.

Table 1. The relation between stirring speed and etching rate at room temperature.

Stirring speed	Etching rate
m/s	Å/sec.
0	33
1	150
2	200

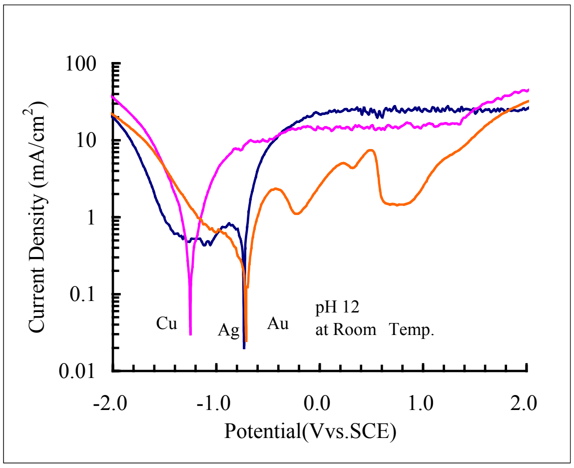


Fig.2 Polarization curves for Ag, Cu and Au in 1% Sodium cyanide solution at room temperature.

Increase in the amount of oxygen to an electrode increases the cathodic reaction of Au (formula (2)). Churning speed increase results in accelerating dissolution of Au.

Anodic reaction	$4Au + 8NaCN$	$\rightarrow 4Au(CN)_2^- + 8H^+ + 4e^-$	(1)
Cathodic reaction	$O_2 + 2H_2O + 4e^-$	$\rightarrow 4OH^-$	(2)
All over reaction	$8NaCN + 4Au + O_2 + 2H_2O$	$\rightarrow 4Na[Au(CN)_2] + 4NaOH$	(3)

Table. 2 The relation between oxidizers and etching rates in the 1% sodium cyanide solution

Oxidizers	Chemical formula	Amount of addition %	Etching rate Å/sec
-	-	-	3
Hydrogen peroxide(30%)	H_2O_2	1	100
Potassium ferricyanide	$K_3[Fe(CN)_6]$	1	100
Ammonium peroxodisulfate	$(NH_4)_2S_2O_8$	1	20
Potassium nitrate	KNO_3	1	3
Ferro potassium cyanide	$K_4[Fe(CN)_6]$	1	3

in the 1% sodium cyanide solution at room temperature

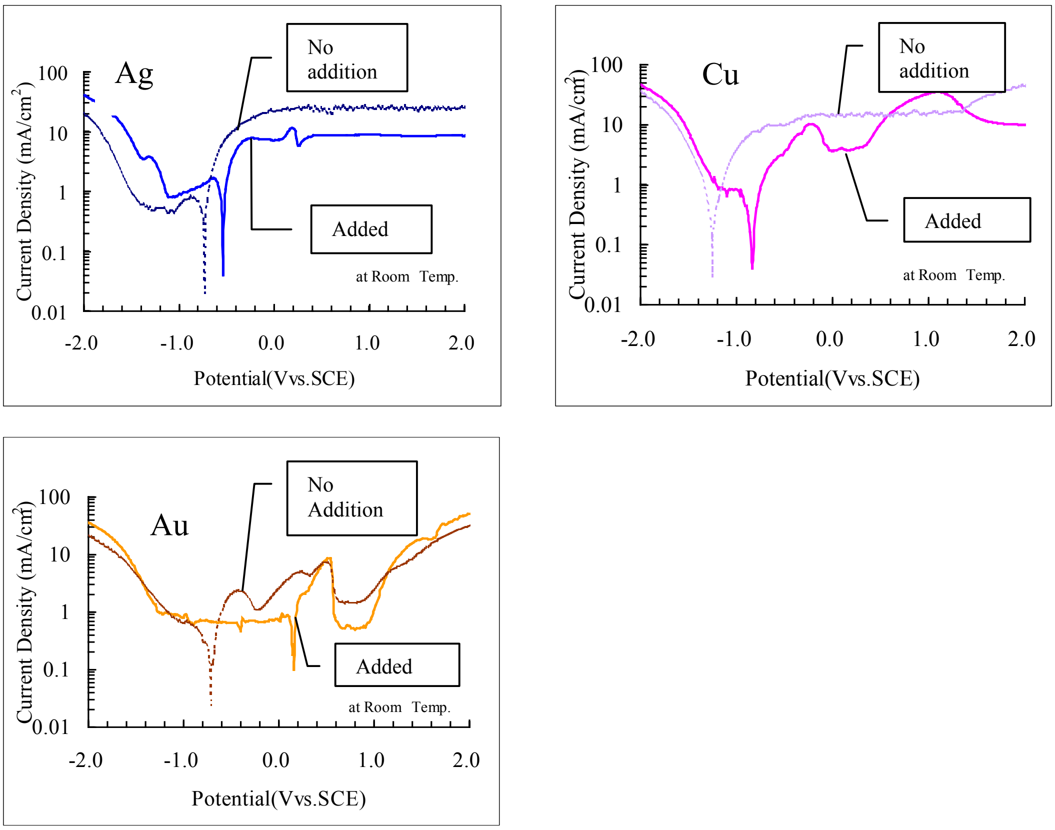


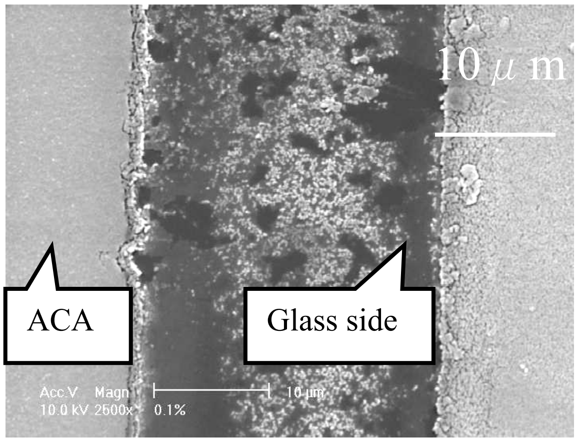
Fig.3 Polarization curves for Au in 1% sodium cyanide solution with or without 1% potassium ferricyanide.

It is summarized that oxygen shortens overall reaction etching time as an oxidizer.
When the ACA substance is etched in the 1% sodium cyanide solution, no reside of Au is found.

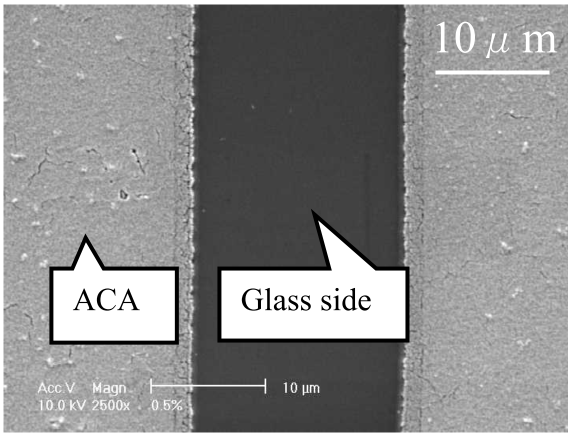
However, since etching rate is very slow, it won't be a practical etchant. Therefore, various oxidizers were tested in the point view of cathodic reactions for the purpose of powerful improvement in the rate.
Consequently, addition of potassium ferricyanide in 1% sodium cyanide solution turns out that etching rate is improved about 20 times. (Table. 2)
The polarization curves in Fig. 3 show the effect of potassium ferricyanide on the dissolution of Ag, Cu and Au in 1% sodium cyanide solution. In general, the corrosion potentials and corrosion currents for gold, silver, and copper increase respectably as shown in Fig. 3. In the sodium cyanide solution with potassium ferricyanide enables gold, silver, and copper to dissolve almost at the same high speed. The corrosion potential of ACA in the solution rises near to the corrosion potential of purity gold.

ACA substrates with a resist pattern were dipped in the solution of sodium cyanide, sodium cyanide + potassium ferricyanide or iodine/potassium iodine at room temperature for 60sec.

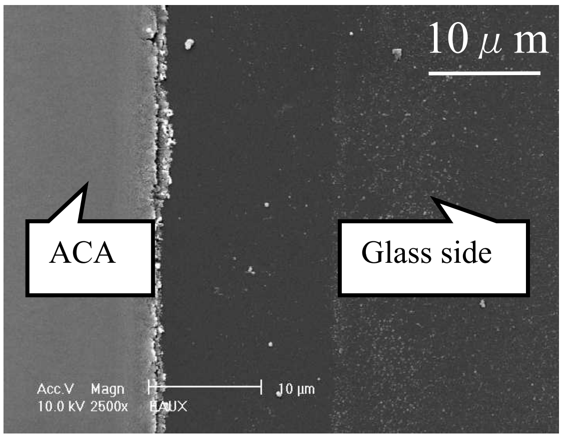
Fig. 4 is the result of exfoliating resist pattern observed by SEM after etching.
The place of black is the portion in which the ACA layer was completely dissolved.
When etched in iodine/potassium iodide solution golden residual substance still can be seen. On the other hand, etched in 1% sodium cyanide solution with addition of potassium ferricyanide, the residual substance was not detected on glass. Thus, since gold in ACA dissolves quickly, this etchant makes a minute patterning is possible without gold residue.



(a) 1% sodium cyanide (aq)



(b) 1% potassium ferricyanide was added



(c) iodine/potassium iodide

Fig. 4 The result of exfoliating resist pattern after etching by SEM.

4. SUMMARY

1. Gold in Ag-Cu-Au alloy can not be etched away in conventional etchants as readily as the other two alloying elements of copper and silver.
2. The cyanogen complex salt of gold generates when cyanide is used for the etchant, in which gold dissolves. However, dissolution rate of gold is still considerably slow.
3. Oxygen reduction is important as the cathodic reaction in the dissolution of gold. A new etchant[3)] of sodium cyanide and potassium ferricyanide of which cathodic reduction is stronger than oxygen, can give precise etch patterns on ACA alloy swiftly at room temperature.

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