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A New Eco-Friendly Photo Resist Stripping Technology Using "Ethylene Carbonate"

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SUMMARY Recently, it is demanded to form a high performance pattern on an enlarged circuit board in a low cost in the process to produce LCD devices. In the part of upgrading the performance, the materials are reexamined such as Al or Mo to Cu. Furthermore, in the process of reexamining the materials, it is demanded that such materials are low in environmental load. Therefore, we examined if it is possible to reuse Ethylene Carbonate, a photo resist stripper, with low environmental load by decomposing dissolved photo resist using ozone gas. Furthermore, we examined if it is possible to apply Ethylene Carbonate without damaging the next generation wiring materials. As a result, we were able to identify the most efficient condition for ozone gas to recycle Ethylene Carbonate used as a photo resist stripper. Ethylene Carbonate was not only suitable for Al · Mo wiring, but was also suitable for the next generation Cu wiring. Therefore by using Ethylene Carbonate for the new and old process for stripping photo resists, it is able to reduce the environmental load and also reduce the cost for stripping.

key words: *eco-friendly new resist stripper*

1. Outline of Technology

1.1 Past Technology

Recently, Amine system (will be abbreviated as "Amine") strippers, such as "monoethanolamine" (will be abbreviated as "MEA"), "N-methylpyrrolidone" (will be abbreviated as "NMP"), were used as strippers to strip photo resist in the progress of manufacturing array for FPD's [1]. Amine is very dangerous and highly toxic. Furthermore, used Amine will be disposed as waste. There is a report that disposing Amine will pollute the environment. To prevent this, it is said that Amine needs to be distilled to remove impurities before disposing [2]. Even when distilled, the impurities from the used Amine must be disposed and will be a great environmental load. Therefore, from the point of view of global warming, which is an international issue, the reexamined material for the enlarged LCD device should be one that is not only safe but also low in environmental load.

1.2 EC Technology

This time we focused on an aprotic polar solvent, Ethylene Carbonate (will be abbreviated as "EC"), an ethylene glycol with a cyclic carbonate ester which has a high polarity and has a high dissolution ability against water, organic solvents, and high-molecular substance [3]. (See Fig. 1) EC is being introduced to the array producing process of FPD for it is compatible structurally with positive photo resist and for it has a characteristic that the photo resist stripping rate is very high.

The basic physical properties of EC and Amine were compared. EC has a high boiling point, melting point and flash point, the vapor pressure is low and is non toxic. (See Table 1)

Furthermore, to see the environmental load, the output of CO_2 to produce 1 kg was calculated from the heat of formation. Comparing EC and Amine (MEA: dimethyl sulfoxide (will be abbreviated as "DMSO") = 7:3), the CO_2 output of EC is 1/3 of that of Amine. (See Fig. 2) From this, it can be said that EC is safer and environmentally friendly compare to Amine.

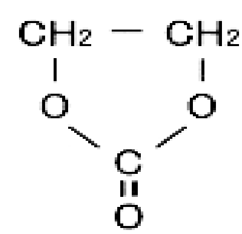

Fig. 1 Structure of molecule.

Table 1 Comparison between photo resist strippers for LCD.

PR Stripper	NMP	MEA	EC
b.p. (℃)	202	171	246
m.p. (℃)	-24	10.5	36
f.p. (℃)	95	93	152
v.p. (hPa)	5.3 (60℃)	0.7 (20℃)	0.03 (36.4℃)
Acute toxicity Rat LD_{50} (Oral)	4.2g/kg	3.3 g/kg	10g/kg
Odor	Amine	Amine	No Odor
Fire protection law of Japan	The 4th Kind of Petroleum 3	The 4th Kind of Petroleum 3	Don't apply

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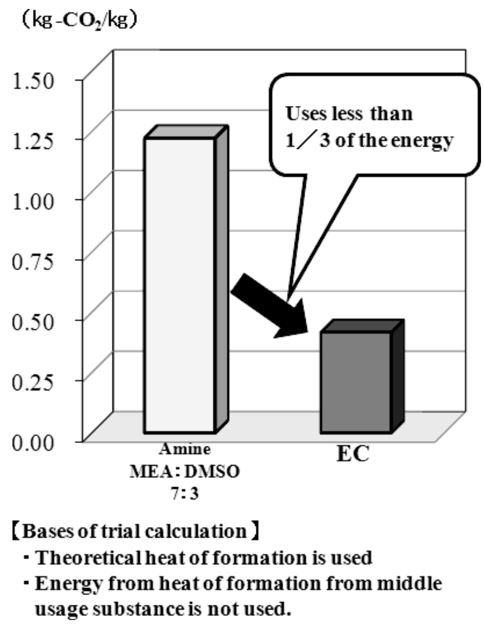

Fig. 2 Comparison of CO_2 emission between strippers.

Table 2 Photo resist stripping rate by EC temperature.

EC temperature (℃)	Stripping time (Sec)	Stripping rate (μm/min)
60	100	0.9
80	20	4.5
100	10	9.0
120	5	18.0

According to Muraoka, because EC is an aprotic polar solvent, dissolubility of ozone gas (will be abbreviated as O_3) is low. It is reported that EC does not easily decompose by O_3 [4].

Furthermore, according to Sato, the stripping rate of 1.5 μm photo resist with ion inputted at $^{11}B^{+}$ $1\times10^{14}/cm^2$ was 20 seconds at 80°C and 10 seconds at 100°C [5]. (See Table 2) It is reported that there is not much of a difference between the stripping rates of O_3 added photo resist dissolved EC and a brand new EC [5]. (See Table 3) The film thickness of photo resist used for photolithography in LCD process is about 1.0~2.5 μm. It is demanded to strip this in about 1 minute. It is possible to clear this demand by the stripping rate of EC. Furthermore, there are reports about As and P ion inputted photo resist other than B concerning photo resist stripping by EC [6], [7].

EC and Amine strips PR differently. Amine strips photo resist by chemically reacting with photo resist, decomposing the polymer chain. In this case, Amine molecules will come in contact with photo resist and will react

Table 3 Photo resist stripping rate of EC adding O_3.

Photo resist resolution (g/L)	Time O_3 added (min)	Efficiency of EC at 100℃ when photo resist (1.5μm) is ion-implanted by $B^{+}1\times10^{14}$	
		Stripping time (Sec)	Stripping rate (μm/min)
0 (New liquid)	0	10	9
1 (Recycling liquid)	60	9	10

from the surface. Therefore, Amine molecules will reduce by repeating the chemical reaction, and will be in need to change the solution because the photo resist stripping power will reduce.

Different to Amine, EC strips photo resist by resolution reaction. By using EC repetitiously, the photo resist concentration in the solution will increase and exchange of solution will be in need likewise to Amine. However, as mentioned previously, EC is durable to O_3. By adding O_3, it is able to decompose photo resist and the stripping power will reform making it possible to reuse EC.

Therefore, by utilizing the characteristic that EC is durable to O_3, the main 2 points were examined for a practical use of the reusing technology [8].

1. To confirm that EC is a stripper that does not decompose by O_3 when recycled [8].
2. To confirm the most efficient photo resist decomposing condition by O_3 and the by-products in that condition [8].

Furthermore, the adaptability of EC for the next generation Cu wiring was examined.

3. To confirm that EC is applicable without damaging the new Cu metal wiring.

2. Experiments and Results

2.1 Confirmation of Decomposing Condition of Photo Resist and Durability of O_3 for EC

2.1.1 Experiments

To recycle EC, the amount of O_3 needed to decompose photo resist will be an important factor. Therefore, the following experiment was performed to understand the decomposing of photo resist in EC by O_3. O_3 (concentration: 10 g/Nm^3) was added in the flow rate of 0.3 L/min to 50 g EC containing 0.2 wt% photo resist. The photo resist decomposition was confirmed using HPLC, examining the height of peak of Novolak Resin which is the main component of photo resist. Further experiment was conducted by EC alone to confirm the durability of EC to O_3.

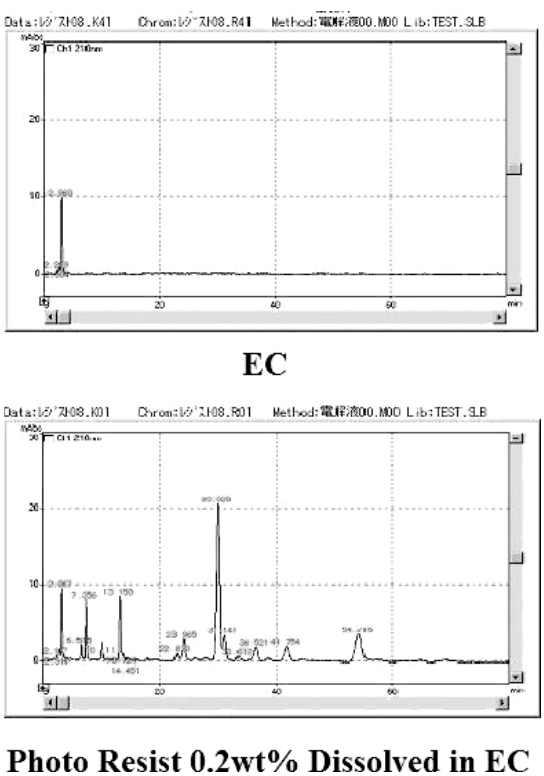

Fig. 3 HPLC analysis of EC before adding O_3.

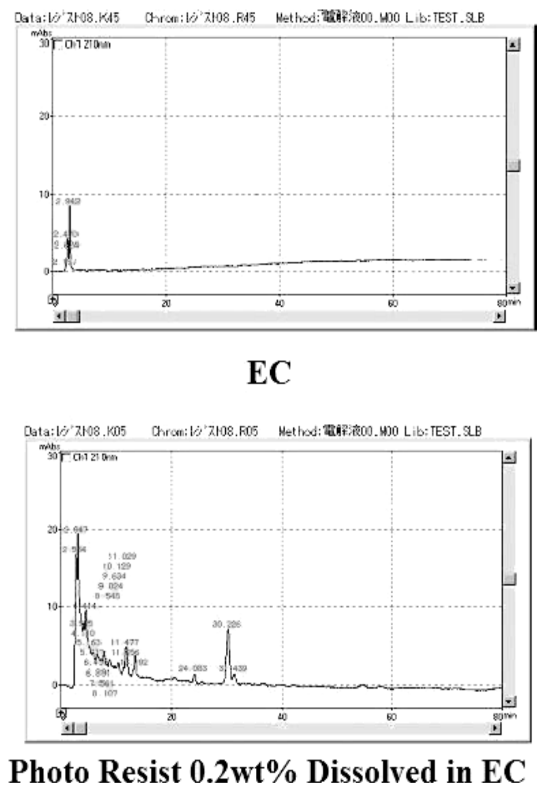

Fig. 4 HPLC analysis of EC after adding O_3.

2.1.2 Results

Figure 3 shows the result of chromatogram before adding O_3 by HPLC. With the HPLC analysis condition, there was no peak other than the peak at the retention time at 3 min for EC. Numerous peaks were detected for EC that contained 0.2 wt% photo resist. In these, the peaks at retention time around 30 min and 54 min were high and were specified as Novolak Resin. The decomposition condition was evaluated at these points.

From the HPLC measurement condition and Novolak Resin analysis result, it was interpreted that retention time over 20 min is the fundamental material of Novolak Resin and retention time under 20 min is photo conductor, remaining solvent, or photo resist decomposed by O_3.

Figure 4 shows the chromatogram after decomposing EC containing 0.2 wt% photo resist by O_3. "After decomposing" means the result of adding O_3 for 30 min. It was determined that chromatogram for EC alone did not differ from before adding O_3. From this, it was verified that EC has high durability to O_3. Moreover, it was verified that EC does not decompose easily by O_3 when recycled.

Next, it shows that the peak increased where retention time is less than 20 min, and it decreased where retention time is more than 20 min when EC contains photo resist 0.2 wt%. Moreover, the peak disappeared at retention time 54 min, and it decreased at retention time 30 min. From these two peaks, the quantity experiments of photo resist decomposition condition were determined.

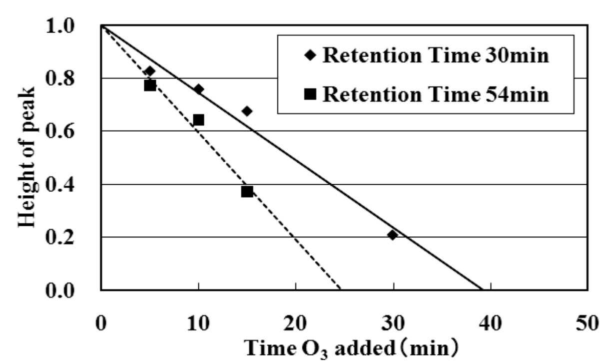

Fig. 5 Time O_3 added and peak height of novlak resin using HPLC.

Based on this, HPLC analysis was conducted using the same experimental process as before, adding O_3 at 5 min, 10 min, 15 min, and 30 min to EC containing photo resist 0.2 wt%.

Figure 5 shows the peak height of retention time 30 min and 54 min for each HPLC analysis result. From this, it was determine that adding time of O_3 and the height of the peak are proportional. Moreover, by stating the peak height of 0 min after adding O_3 as 1, it was able to find that when height of the peak is at 0, it is the time that the photo resist has fully decomposed. From this, it was able to find the most suitable condition of O_3 to decompose photo resist. It is able to decompose the photo resist in EC by adding the most sufficient amount of O_3 for the amount of photo resist in each process.

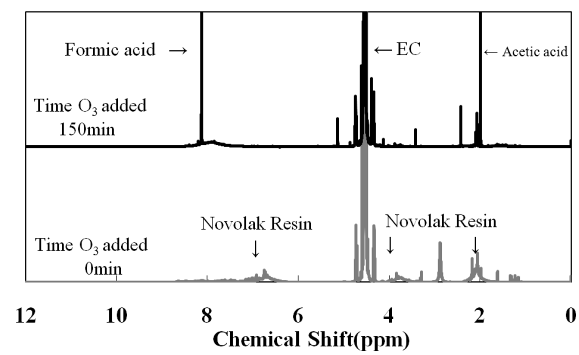

Fig. 6 Analysis of by-product by photo resist decomposition using 1H-NMR.

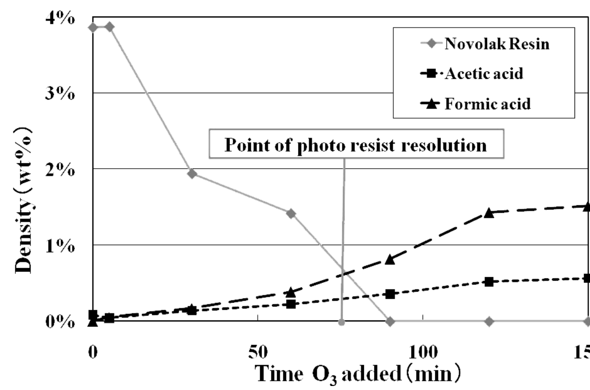

Fig. 7 Relationship between O_3 adding time and by-product using 1H-NMR.

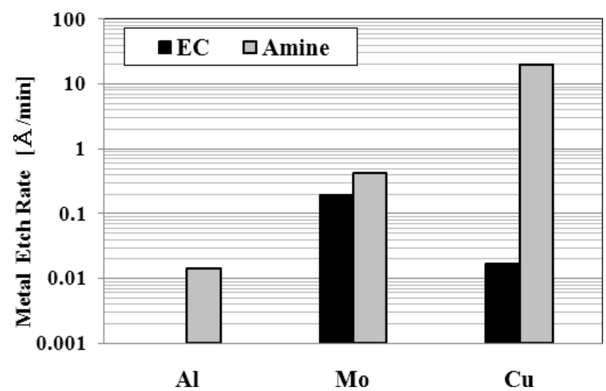

Fig. 8 Etching rate of metals by strippers.

2.2 Conformation of Decomposition of Photo Resist and By-Products

2.2.1 Experiments

From the experiments mentioned previously in Sect. 2.1.2, it is possible to hypothesize the amount of O_3 needed for the decomposition. However, it is not possible to specify the by-products from the decomposition. It is possible that these by-products may have a bad influence on LCD metals wiring during photo resist stripping. To determine the by-products, experiment was conducted with the same operation as stated above and analyzed using 1H-NMR method. This time, the experiment was performed with photo resist concentration 5 wt%, and O_3 concentration 70 g/Nm^3.

2.2.2 Results

Figure 6 shows the analysis of the hydrogen atom from the Novolak Resin, which is the main photo resist and by-products by 1H-NMR. The broadcloth peaks of Novolak Resin without adding O_3 were confirmed at 2 ppm (Ph-CH_3), 4 ppm (Ph-CH_2-Ph'), 7 ppm (Ph-H). However, those peaks disappeared when O_3 was added at 150 min. The peaks were confirmed for Formic acid (-H) at 8 ppm, and Acetic acid (-CH_3) at 1.9 ppm, although these were not confirmed at 0 min.

Figure 7 shows the analysis from the 1H-NMR data to see if the peaks of the Novolak Resin, Formic acid, and Acetic acid differ as the time after adding O_3. It shows the Novolak Resin, the main component of the photo resist, disappears and the by-products, formic acid and acetic acid, increased.

From this, we confirmed the decomposing point of the photo resist based on the analysis result by HPLC from Sect. 2.1.2. More than 80% of the photo resist was extinct and the concentration became about 0.5 wt%. Furthermore, it was recognized that the increase of the by-products were less than 1 wt%. Therefore, it was confirmed that by adding O_3 in the most suitable condition corresponding to the photo resist, it is able to restrain the by-products.

2.3 Experiments of Etching Using LCD Metal Wiring

2.3.1 Experiments

Glass base test sample sputtered with Al, Mo and Cu metals were dipped in 200 g EC at 80°C which is stirred for 100 min. The same test was performed with Amine (MEA:DMSO = 7:3) as well and the result was compared. However, the temperature of Amine was set at 60°C and because the etching rate was fast, the dipping time for Cu was changed to 80 min. The damage for each metal by the stripper was confirmed by calculating the etching rate using the metal quantity which eluted into the stripper which value was analyzed by ICP-MS.

2.3.2 Results

Figure 8 shows the etching rate by the strippers for 1 min of each metal. The etching rate for EC and Amine for Al was less than 0.02 Å/min, and for Mo it was less than 0.5 Å/min. Moreover, the Al and Mo etching rate of EC is slower than Amine. Especially, there were no elution for Al and was 0 Å/min. (Atomic diameter Al; 2.5 Å, Mo; 2.9 Å) Furthermore, the etching rate of Amine for Cu was very fast and was 20 Å/min, on the other hand, EC was less than

0.02 Å/min. (Atomic diameter Cu; 2.7 Å)

From these results, it can be said that EC does not damage as much as Amine for Al and Mo wiring and furthermore, there is no damage to the Cu wiring. Therefore, it is understood that not only it is suitable for the present stripper but is also suitable for the next generation stripper. As mentioned in Sect. 2.2.2, the by-products from photo resist decomposing are mainly carboxylic acid such as formic acid and acetic acid. There is a need to examine the effect on those metals wiring, however, it is able to control the by-products by recycling EC under the most suitable condition. Therefore, even when the recycling process using O_3 for EC is adopted, it is possible to present a process without any damage to the metal wiring in the LCD producing line.

3. Conclusions

The following was understood about EC.

1. EC is durable to O_3 compare to photo resist.
2. It is possible to decompose photo resist efficiently under the most suitable condition and is able to control the amount of by-products.
3. EC is efficient to not only the Al and Mo LCD metal wiring, but is also efficient to the next generation wiring using Cu.

The output of CO_2 in the process of producing EC is very low. Moreover, it can be recycled and reused by using O_3 and is eco and low cost compared to Amine. Also, it is able to control the amount of by-products in the process of decomposing photo resist in EC by using the efficient amount of O_3 for the amount of photo resist in each process. It can be said that using the recycling technology of EC using O_3, it is able to suggest a damage free process for not only for the present LCD metal wiring but also for the next generation LCD metal wiring. EC is a photo resist stripper which is safe and eco compared to Amine and it is low in cost for it can be recycled and be reused.

It is planned to develop this technology such as to improve the photo resist stripping efficiency.

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