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A Study on Reclaimed Photoresist Developer Using an Electrodialysis Method

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1. Introduction

A tetramethylammonium hydroxide (TMAH) is generally used as photoresist developer at lithography processes in large scale integration (LSI) and liquid crystal display (LCD) manufacturing. The developer waste (spent developer) consists of TMAH, water, photoresist, and other impurities, and is difficult to be treated. It is conventionally disposed off site as industrial waste or given into biological treatment to be decomposed [1,2]. These methods only treat TMAH as waste without reclamation, so that, it gives environmental load.

The purpose of this work is to present a newly developed photoresist developer reclamation system using an electrodialysis (ED) and an ion exchange (IE) technologies, moreover, a possibility that the reclaimed one can be reused as a photoresist developer. The system recovers stably more than 80% TMAH from waste, and reclaimed developer has the same purity as fresh one.

2. Developer Reclamation System

The schematic diagram of the reclamation system, which can also be installed to existing lines, is shown in Fig.1. It has a recovery unit concluding electrodialysis (ED) step, and a purification unit concluding ion exchange (IE) step followed by micro-filtration (MF) step. TMAH is selectively recovered from developer waste and concentrated by ED, whose principle illustrates in Fig.2 [3]. It has a stack in which anion exchange membranes and cation exchange membranes are alternately arranged with electrodes mounted on both sides. As TMAH is dissociated into TMA^+ cation and OH^- anion, TMA^+ passes through cation exchange membranes attracted by the cathode, but it does not pass through anion exchange membranes, and attracted by the anode, on the other hand, OH^- passes through anion exchange membranes but it does not pass through cation exchange membranes. Eventually TMAH is increasingly recovered in recovery solution. As photoresist is a large molecule with low charge, it hardly passes into recovery solution from developer waste through ion exchange membranes. The recovery solution is next led to the purification unit in order to make it high purity solution. Mixed-bed ion exchange resin column treatment, where the cation and the anion exchange resin is previously prepared to TMA^+ and OH^- form respectively, is required to remove ionic impurities such as residual photoresist, Na^+ and so on. MF treatment is finally put into for particle removal.

3. Experimental and Results

A Reclaimed developer sample was obtained from a waste containing a 1.0 wt% TMAH through the treatment of the reclamation system. In this experiment, 90% TMAH was recovered. An example of mass balance in this system is shown in Fig.3. The quality comparison among the waste, the reclaimed, and a fresh commercial developer standard is shown in Table 1. The reclaimed developer was found to feature the same purity as fresh one, whereas the waste had lower TMAH concentration than fresh one and contained photoresist and other impurities.

The property of the reclaimed developer was evaluated in the following procedure. A chemically amplified positive deep ultraviolet resist (Shipley UV6) films coated on silicon wafers was prebacked. The wafers were exposed by a KrF excimer laser stepper. Following the post exposure backing, wafers were cooled down. The resist films were developed at 23°C by the reclaimed and a fresh developer, both of which were accurately adjusted to the TMAH concentration of 2.38 wt%. Fig.4 shows the dissolution rates as a function of exposure dose. Fig.5 shows scanning electron microscope (SEM) images of line-and-space pattern formed by using 0.18μm line-and-space mask with two developers. No difference can be seen between the characteristics of two developers.

4. Conclusion

The photoresist deveroper reclamation system using ED and IE technologies has been studied. The reclaimed developer have high purity level and the same dissolution characteristics of the resist compared with a fresh one. It is utilized for reduction of developer volume and environmental load.

References

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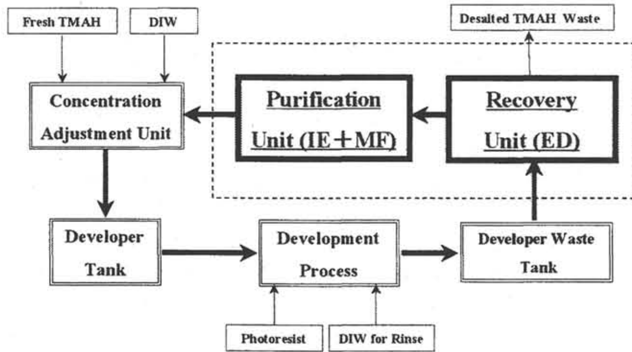


Fig.1 Schematic diagram of developer reclamation system.

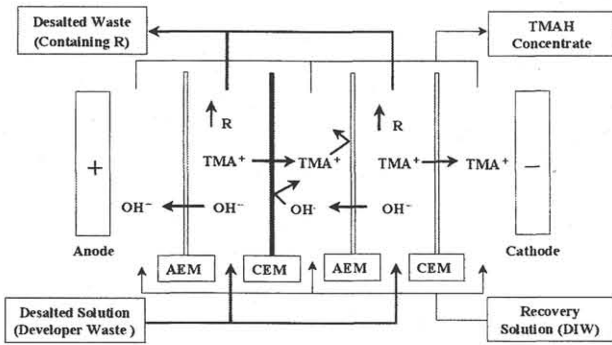


Fig.2 TMAH recovery method by electrodialysis.

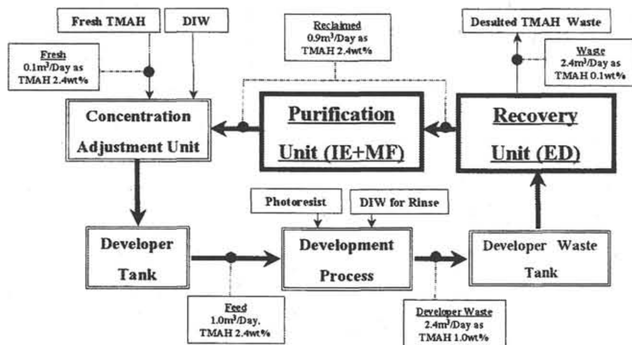


Fig. 3 Example of mass balance in reclamaition system

Table 1 Impurities level comparison *before and after* TMAH reclamation

Item	Standard	Weste	Reclaimed
TMA-OH (wt%)	2.38	1.02	2.34
TMA-CO3 (wt%)	<0.03	0.11	0.02
Resist (mg-C/L)	-	140	<0.1
Na (μg-Na/L)	<5	7	<1
K (μg-K/L)	<3	4	<1
Ca (μg-Ca/L)	<1	3	<1
Mg (μg-Mg/L)	<1	<1	<1
Fe (μg-Fe/L)	<5	8	3
Cu (μg-Cu/L)	<3	<1	<1
Mn (μg-Mn/L)	<3	<1	<1
Ag (μg-Ag/L)	<3	<1	<1
Cl (mg-Cl/L)	<0.2	-	<0.1

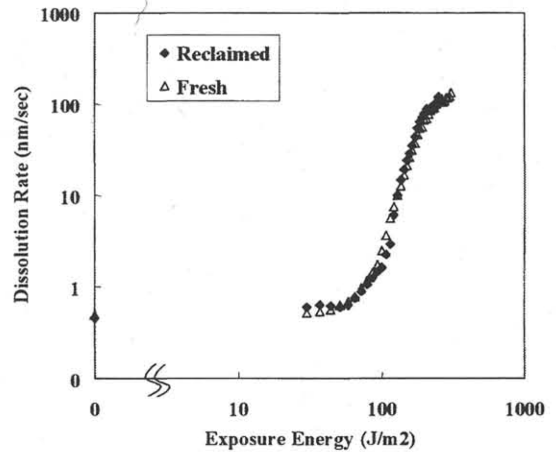
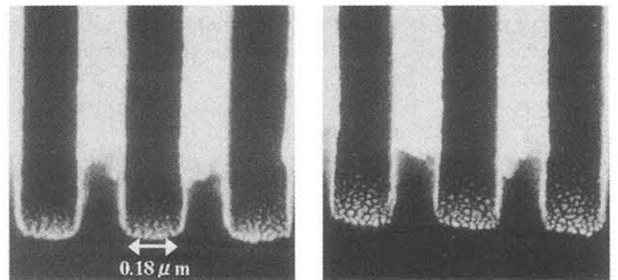


Fig.4 Dissolution characteristics of reclaimed and fresh developer.



(a) (b)

Fig.5 SEM images of 0.18μm line-and-space pattern formed with (a) reclaimed developer and (b) fresh developer.