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# Feasibility study of solvent recycle process in spin-on hard mask material manufacturing system

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**Abstract**−The spin-on hard mask material for photo resist in semiconductor industry is usually obtained from a small-scale batch process. To obtain high purity products requires multiple-step purification processes, during which a large amount of organic solvent waste is emitted. In this study, a process for regenerating high purity solvent was proposed and the economic efficiency of the proposed process was analyzed. Also, a sensitivity analysis was performed to analyze the changing economics regarding the main variables. From the analysis, the break-even point can be achieved within one year for different cases considered. On the basis of 4-year operation, the profit margins for each case were determined and compared. It is concluded that the waste solvent regeneration process for spin-on hard mask material production in semiconductor industry is feasible and recommended.

Keywords: Spin-on Hard Mask Material, Regeneration, Economic Analysis, Sensitivity Analysis

## INTRODUCTION

The hard mask in semiconductor manufacturing processes is a primary concern for producing highly integrated semiconductor, and it has become more prevalent in patterning of small features on semiconductors. If the photo resist (PR) materials, which have more than 300 nanometers in width, are used as hard mask materials, the aspect ratio will increase, and the patterns of PR materials will be collapsed. However, if the thickness of PR materials become overly thin, the deep patterns required in semiconductor processes cannot be carved because it is impossible for hard masks to play a role as substrates in etch processes. To solve these problems, the hard mask materials, which can transfer the patterns of PR, are usually used in semiconductor processes [1]. In current semiconductor manufacturing processes, hard masks materials are produced by chemical vapor deposition (CVD). The CVD hard mask has good physical properties in terms of etch selectivity and durability. Also, experiences and technologies for CVD hard mask in semiconductor industries have been accumulated consistently [2]. However, there are two major problems for the CVD hard mask. The first is low throughput caused by the requirement of independent facilities, expensive equipment, and the cost of maintenance [3]. The second problem is defects of hard mask caused by clusters of chemical vapor [4].

Recently, the hard mask material for spin coating has been studied vigorously as an alternative to CVD hard masks. There are many advantages to spin coating in which masks are coated as solution. It is possible to stack thin films with general coating equipment without independent facilities. In addition, spin-on hard mask materials have characteristics of flat surface of thin films, being process-friendly, and coping with changes of process stages flexibly [5]. With these reasons, the use of inexpensive spin coating equipment in semiconductor PR processes is getting more popular instead of stacking bottom anti-reflection coating (BARC) by using CVD equipment. Furthermore, a two-stage process using BARC and hard mask can be replaced by a one-stage process using spin-on hard mask materials, which tends to simplify the whole process [6].

The spin-on hard mask materials are manufactured through three stages, polymerization, purification, and filtration. Since the throughput of semiconductor materials is determined by the defects in wafer coating, the purification process is very important to achieve high-purity products after polymerization process. SAMSUNG SDI operates a ten-stage solvent purification and seven-stage solvent exchange process to produce high purity products [7]. The batch process with 0.5 tons of production capacity consumes about 11 tons of solvents, and solvent cost is about $35,000 per batch. That is about 60 percent of total manufacturing cost. More than twenty times of

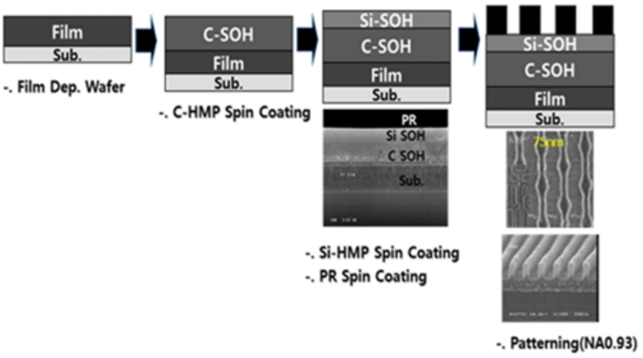

**Fig. 1. Use of spin-on hard mask materials in semiconductor's manufacturing system.**

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solvent in mass is required to produce a unit mass of spin-on hard mask resin. The disposal cost of organic waste solvent is about $400/ton, which brings about additional increase of spin-on hard mask manufacturing cost. In this plant, about 30 batches of spin-on hard mask materials are produced monthly with a disposal cost of $132,000 per month. Besides the environmental requirement of disposing wastes, the excessive use of solvents contributes to the increase of production cost. Therefore, an efficient solvent regeneration process has to be developed and its effectiveness has to be evaluated.

## PROCESS

### 1. Spin-on Hard Mask Manufacturing Process

A manufacturing process of spin-on hard mask materials is illustrated in Fig. 2. The product is manufactured through polymerization, purification, solvent exchange, and filtration. The first step of the process is the polymerization of monomer mixtures with solvent (PGMEA, propylene glycol monomethyl ether acetate) by a heating-cooling cycle in a single tank (1.5 m$^3$). After the polymerization, in purification step, the unreacted materials should be removed thoroughly with other solvent (water, cyclohexanone, n-hexane and methanol) and the purity of washing solvents inside the tank should be more than 99.0 percent. After washing, washing solvent should be replaced by the main solvent (cyclohexanone) for final product, which is a solvent exchange step. As described previously, the majority of solvents are used through ten stages of purification, and seven stages of solvent exchange process. After finishing these processes, the amount of waste solvent used is about 11 tons per a batch. Table 1 presents the amount of the required solvent and recoverable cost when one batch of spin-on hard mask materials is produced. Considering the amounts of consumption and prices of solvents, n-hexane, methanol and cyclohexanone are to be regenerated and recycled and the target purity of regenerated solvents is set to more than 99 percent in purity, which is the same or better than the raw solvents use in the spin-on hard mask material production process.

**Table 1. The amount of required solvent and recoverable cost per batch**

| Single batch | Feed (kg) | Waste (kg) | Unit price ($/kg) | Total amount ($) |
|---|---|---|---|---|
| PGMEA | 373 | 373 | 3.5 | 1,307 |
| n-Hexane | 3,502 | 3,502 | 5.0 | 17,512 |
| Methanol | 4,935 | 4,935 | 1.5 | 7,402 |
| $H_2O$ | 223 | 223 | 0.01 | 2 |
| Cyclohexanone | 2,209 | 1,769 | 5.3 | 9,376 |
| Total | 11,242 | 10,802 | | 35,599 |

### 2. Design of Regeneration Process for Waste Solvents

Fig. 3 is the process schematic diagram of waste solvent purification for base case (case 1), which is designed to separate n-hexane, methanol and cyclohexanone from a mixture of five solvents including water and PGMEA. With a series of distillation columns, the mixture can be separated depending on the boiling point. In the first column, n-hexane and methanol mixture is obtained as distillate product while the bottom product consists of PGMEA,

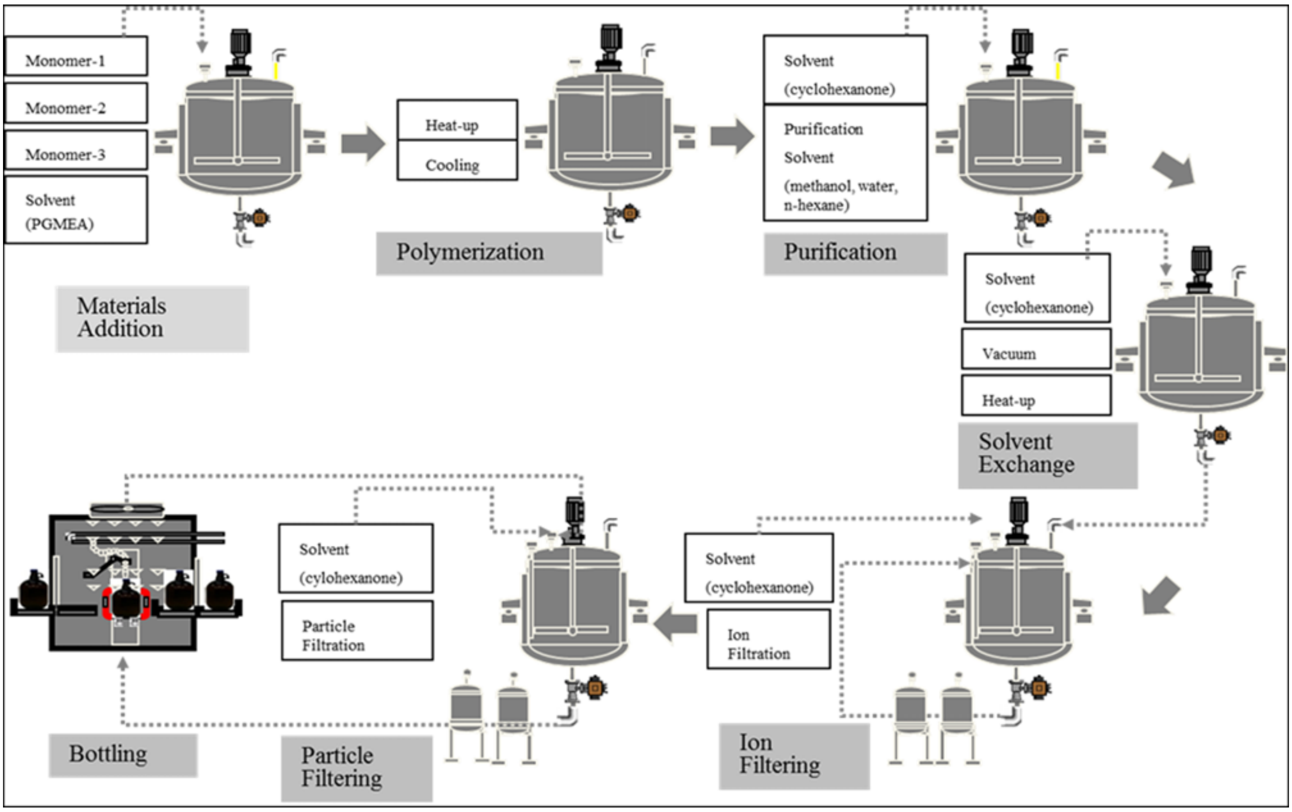

Fig. 2. Process diagram of spin-on hard mask material production.

$H_2O$ and cyclohexanone. It is reported that n-hexane and methanol form an azeotrope at 50.6 °C with composition of 72 wt% of n-hexane and 28 wt% of methanol [8]. This makes the separation between n-hexane and methanol difficult by distillation. However, if water is injected at the same amount as that of methanol to the mixture, the mixture can be separated into organic phase and aqueous phase and they can be separated easily by decanter. Thus, with the solvent waste given in Table 1, 3,246 kg of n-hexane is obtained through the decanter from the top phase and a mixture of 256 kg of n-hexane, 4,893 kg of methanol and 4,932 kg of water is obtained from the bottom phase of the decanter. Then the methanol can be separated through columns 2 and 3. The cyclohexanone from the bottom of column 1 is separated through the column 4 as a bottom product.

In case 1, all of the n-hexane and methanol are boiled to the distil-

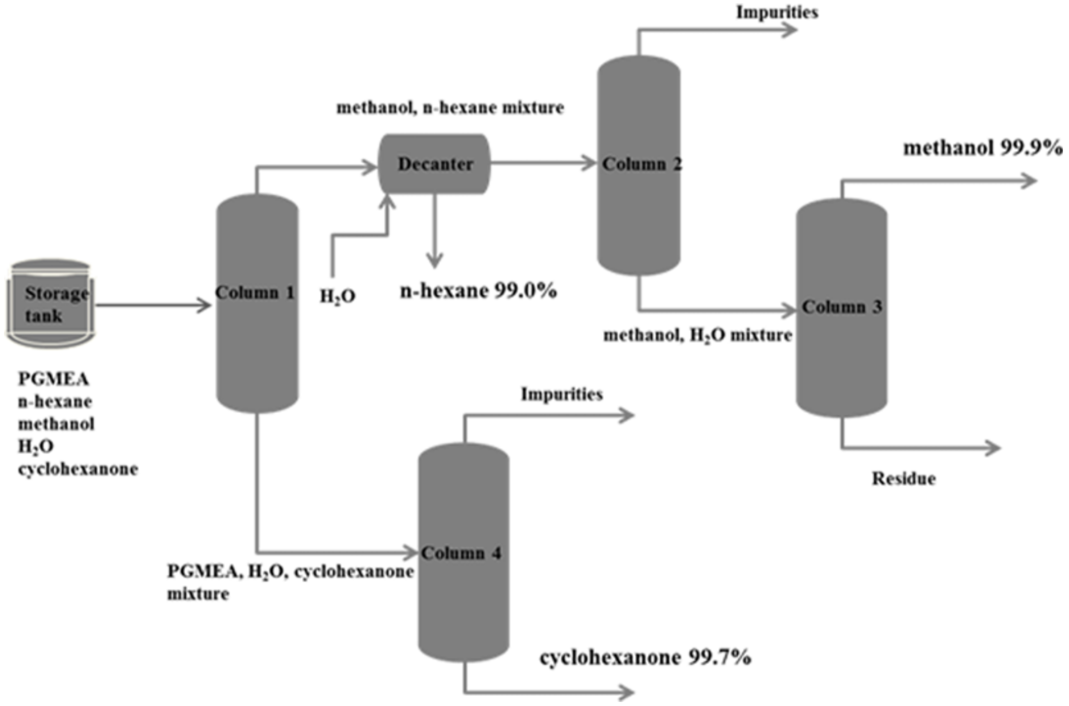

**Fig. 3. Process schematic diagram of purification of waste solution (case 1).**

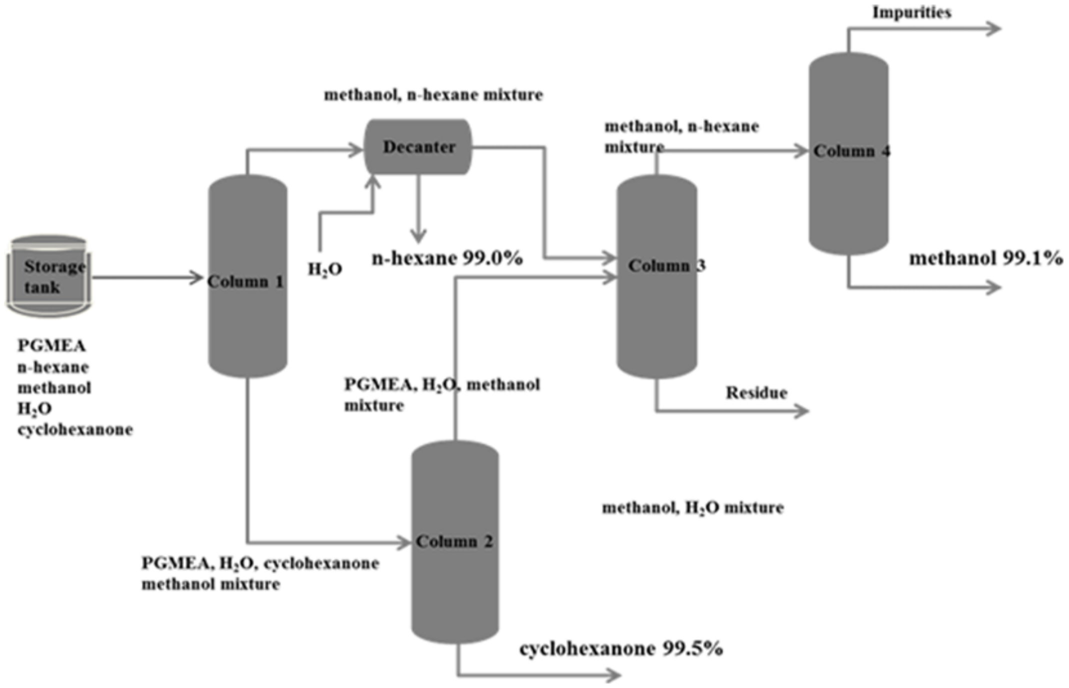

**Fig. 4. Process schematic diagram of purification of waste solution (case 2).**

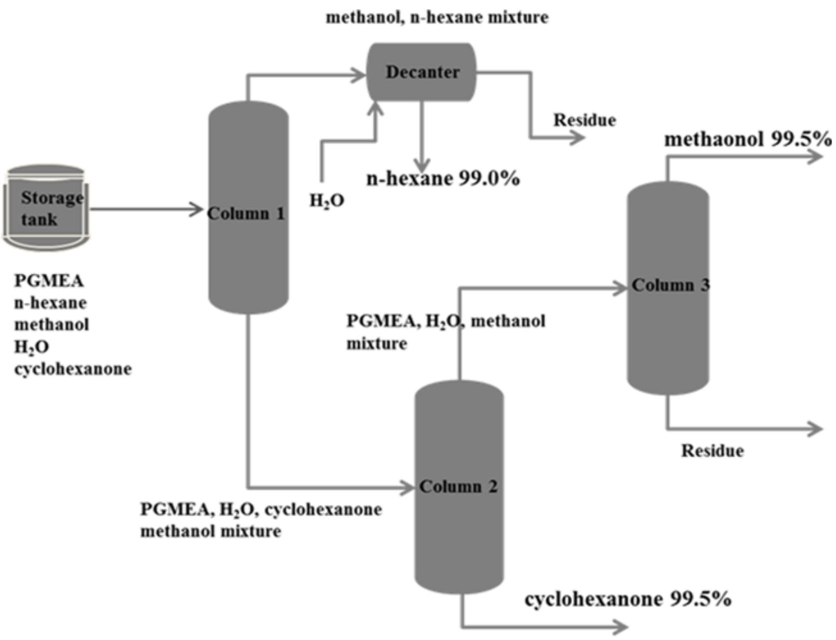

**Fig. 5. Process schematic diagram of purification of waste solution (case 3).**

late product and the heavier components are separated as bottom product. For this high purity separation, it requires many stages to satisfy the top product specification. As case 2, in the first column, instead of distilling the total amount of methanol and the n-hexane, only all n-hexane and azeotropic composition of methanol are recovered as distillate product. Thus, exactly 3,492 kg of n-hexane and 1,344 kg of methanol are sent to the top product of the column 1. Case 2, therefore, reduces significantly the number of stages required in the first column for case 2. Also, it reduces the amount of water used in the decanter to about one third of that used of the case 1 and the column loads thereafter are reduced.

The case 3 is an improvement of the case 2. In this case, since the cost of methanol is much cheaper than those of n-hexane and cyclohexanone, it is economically reasonable to discard the remaining methanol that is separated from the n-hexane in the decanter. Also, the amount of methanol discarded is not very significant. This, therefore, reduces the number of columns required for the whole process to one less than the other cases so that the capital cost can be saved.

## SIMULATION RESULT FOR PURIFICATION PROCESS

In this study, the simulation was performed using Aspen Plus in which NRTL (Non random two liquid mixture) models for liquid activity equation are used. Eq. (1) gives liquid activity coefficient for components in mixture.

$$\ln\gamma_i=\frac{\sum_j \tau_{ji}G_{ji}x_j}{\sum_k G_{ki}x_k}+\sum_j \frac{x_j G_{ij}}{\sum_k G_{kj}x_k}\left(\tau_{ij}-\frac{\sum_k x_k\tau_{kj}G_{kj}}{\sum_k G_{kj}x_k}\right) \tag{1}$$

$$\tau_{ij}=a_{ij}+\frac{b_{ij}}{T} \tag{2}$$

$$G_{ij}=\exp(-\alpha_{ij}\tau_{ij}) \tag{3}$$

where T is the absolute temperature (K), $\tau_{ij}$, and $G_{ij}$ are binary interaction parameters. The NRTL model can estimate phase equilibrium of multi-component using binary interaction parameters. This model is applied to highly non-ideal mixtures, and used for vapor-liquid and liquid-liquid phase equilibrium [9].

The reflux ratio and the number of stages were determined by the following procedure.

1) Separation possibility of the distillation columns was tested in the excess number of stages, which is more than 100 stages.

2) If the separation possibility was verified, the number of stages was determined by the concentration - stage curve. If there is no more concentration change after some stage number, the stages showing no concentration change could be verified as useless stages. So the minimum stage number could be determined.

3) Then, the reflux ratio was determined by solving optimization problem. The objective function is written in Eq. (4). The solution denotes minimum energy requirement of the distillation columns when the reflux ratio is applied.

The number of stages and reflux ratio were optimized for given specification with RadFrac distillation, and the results are shown in Table 2 [10]. For optimal values, the energy required in the reboiler is minimized while the product specifications are satisfied as follows:

$$\min_{r,\,N} J = Q_{reboiler}$$

$$\text{subject to}\left\{\begin{matrix} X_{n\text{-}hexane}\geq 0.99 \\ X_{cyclohexanone}\geq 0.99 \\ X_{methanol}\geq 0.99 \end{matrix}\right\} \tag{4}$$

where r is the reflux ratio, N denotes the number of stages, and $Q_{reboiler}$ is the heat duty of reboiler. Also, $X_{n\text{-}hexane}$, $X_{cyclohexanone}$ and $X_{methanol}$ are

**Table 2. The results of optimized design for number of stages and reflux ratio***

| Case 1 | Column 1 | Column 2 | Column 3 | Column 4 |
|---|---|---|---|---|
| Number of stages | 24 | 10 | 22 | 45 |
| Reflux ratio | 0.7 | 0.1 | 1.3 | 6.6 |
| Temperature (bottom stage, °C) | 99.65 | 76.38 | 99.52 | 154.88 |
| Temperature (top stage, °C) | 54.60 | 52.65 | 64.22 | 99.74 |
| **Case 2** | **Column 1** | **Column 2** | **Column 3** | **Column 4** |
| Number of stages | 10 | 42 | 13 | 6 |
| Reflux ratio | 0.7 | 2.6 | 2.5 | 0.7 |
| Temperature (bottom stage, °C) | 69.37 | 154.87 | 88.89 | 63.93 |
| Temperature (top stage, °C) | 53.48 | 65.92 | 63.64 | 60.71 |
| **Case 3** | **Column 1** | **Column 2** | **Column 3** | |
| Number of stages | 10 | 42 | 13 | |
| Reflux ratio | 0.7 | 2.6 | 1.2 | |
| Temperature (bottom stage, °C) | 69.37 | 154.87 | 97.63 | |
| Temperature (top stage, °C) | 53.48 | 65.92 | 64.14 | |

*The operating pressure in these columns is fixed as 1 bar

**Table 3. Purity and yield for each case**

| | | n-Hexane | Methanol | Cyclohexanone |
|---|---|---|---|---|
| Feed (kg) | | 3,502 | 4,935 | 1,769 |
| Case 1 | Purity (%) | 99.0 | 99.9 | 99.7 |
| | Yield (%) | 92.7 | 94.8 | 93.1 |
| Case 2 | Purity (%) | 99.0 | 99.1 | 99.5 |
| | Yield (%) | 97.8 | 86.4 | 99.0 |
| Case 3 | Purity (%) | 99.0 | 99.5 | 99.5 |
| | Yield (%) | 97.8 | 72.4 | 99.0 |

the purities of each solvent, which are given as constraints for the reuse of regenerated solvents in the process.

By discarding the methanol from the decanter, case 3 has three columns compared to cases 1 and 2 which have four columns each. Since the number of stages depends on the target separation of each column, the number of stages and reflux ratio were optimized with RadFrac distillation, and the results are shown in Table 2. Table 3 shows the purity and yield according to the optimization results for each case. The final product purity is over 99 percent and the obtained results are not significantly different from each other.

## ECONOMIC ANALYSIS

Feasibility on investment was analyzed by economic analysis with the simulation results. The annualized costs for economic analysis consist of fixed costs (CAPEX, capital expenditure) and variable costs (OPEX, operational expenditure). The fixed costs are the business expenses that are not dependent on the quality of products or services by the business [11]. The variable costs are the expenses that change in proportion by the activity of a business. Fixed costs include facility investment and labor costs, and variable costs include energy, quality control, repair, maintenance, and waste costs. Table 4 shows the basis of economic analysis from Samsung SDI Company in accordance with CAPEX and OPEX. The facility cost for the solvent regeneration plant was calculated by applying the six-

**Table 4. Basis of economic analysis for production rate of spin-on hard mask materials**

| CAPEX | | | OPEX | | |
|---|---|---|---|---|---|
| Item | | Cost | Item | | Cost |
| Labor cost | | $120,000/Year | Quality control | | $480/batch |
| | | | Consumables | | $1,000/batch |
| | | | Repair & maintenance | | $3,000/batch |
| Investment | Case 1 | $9,226,085 | Energy | Case 1 | $3,670/batch |
| | | | | Case 2 | $5,067/batch |
| | Case 2 | $8,641,665 | | Case 3 | $3.792/batch |
| | | | Waste solvent disposal | Case 1 | $2,423/batch |
| | | | | Case 2 | $1,028/batch |
| | Case 3 | $6,322,820 | | Case 3 | $1,312/batch |

tenths rule on the basis of current distillation column, and the capacity of recycle process was calculated based on the maximum capacity of that plant [12]. The six-tenths rule is given by

$$\frac{\mathrm{Dost}_{plant2}}{\mathrm{Dost}_{plant1}}=\left[\frac{\text{Plant Capacity}_{plant2}}{\text{Plant Capacity}_{plant1}}\right]^{m} \tag{5}$$

where m is the size exponent.

A convenient and plausible way for the comparison between investment decisions is to use the capital recovery factor (CRF). The capital recovery factor gives the amount of money that must be repaid each year if the initial amount is borrowed. Of course, the factor depends on the duration of the loan and the interest rate. A CRF is defined as a ratio of a constant annuity to the present value of receiving that annuity for a given length of time. Using an interest rate i, the capital recovery factor is defined as follow [13].

$$\mathrm{CRF}=\frac{(\mathrm{i}+1)^{n}-1}{\mathrm{i}(\mathrm{i}+1)^{n}}\quad \text{(i: interest, n: year)} \tag{6}$$

For each case considered for the investment decision, then profit per year (PPY) can be calculated using the equation below.

$$\begin{aligned}&\text{PPY}=\text{batch No.}\times[(\text{N}\times\text{unit price of N}+\text{M}\times\text{unit price of M}\\&+\text{C}\times\text{unit price of C})-(\text{POC}-\text{W})]-\text{LC}-\frac{\text{Investment cost}}{\text{CRF}}\end{aligned} \tag{7}$$

where N, M and C are the amount of solvent regeneration per batch for n-hexane, methanol and cyclohexanone, respectively. Eq. (7) is based on the process operating cost (POC) and labor cost (LC). Also, W is the outsourcing cost for waste disposal when the regeneration process is not applied. Generally, semiconductor materials are usually replaced every five years, and the lifetime of plants which handle semiconductor materials is very short compared to other chemical plants, since semiconductor processes change rapidly in accordance with industrial development. The lifetime of spin-on hard mask materials should also be set as five years, but it is reasonable to set up four years of the life time considering the construction period of regeneration plants.

## CASE STUDIES OF ECONOMIC ANALYSIS

The solvent prices of cases 1, 2, and 3 were set as \$5 for n-hexane, \$1.5 for methanol, and \$5.3 for cyclohexanone based on the current standard prices, and 5% for interest rate. Regenerated solvents are reused, and the lifetime of the regeneration process was set as four years. The PPY was calculated for four years in accordance with batch number. Though the initial investment cost of the case 1 came out as the highest, its profit rate also appeared to be the highest. Cases 2 and 3 are the cases of transferring the amount corresponding azeotropic composition to the distillate product while the case 3 discard methanol in the distillate product. The initial investment cost of the case 3 is the lowest since only three columns are used. Therefore, case 3 is the most effective case in terms of the initial investment cost. Fig. 6 shows the total profit in accordance with batch number during four years (360 batches a year) of operating a regeneration plant. Cases 1, 2, and 3 satisfy the breakeven point within a year when 30 batches are operated for a month. In other words, case 3 needs 0.6 year, and case 2 needs 0.8 year, case 1 needs 0.9 year to satisfy the breakeven point. It implies that these cases are all feasible for investment potential. In addition, the total profit of case 3 is the highest, \$28,500,000, and case 1 is the best in terms of a profit rate.

## ECONOMIC SENSITIVITY ANALYSIS

To check how the cash flow and net present values change in accordance with design conditions, an economic sensitivity analysis was performed. The major parameters were chosen to be the interest rate and raw material prices because the interest rate change affects the fixed cost significantly and the raw material costs affect

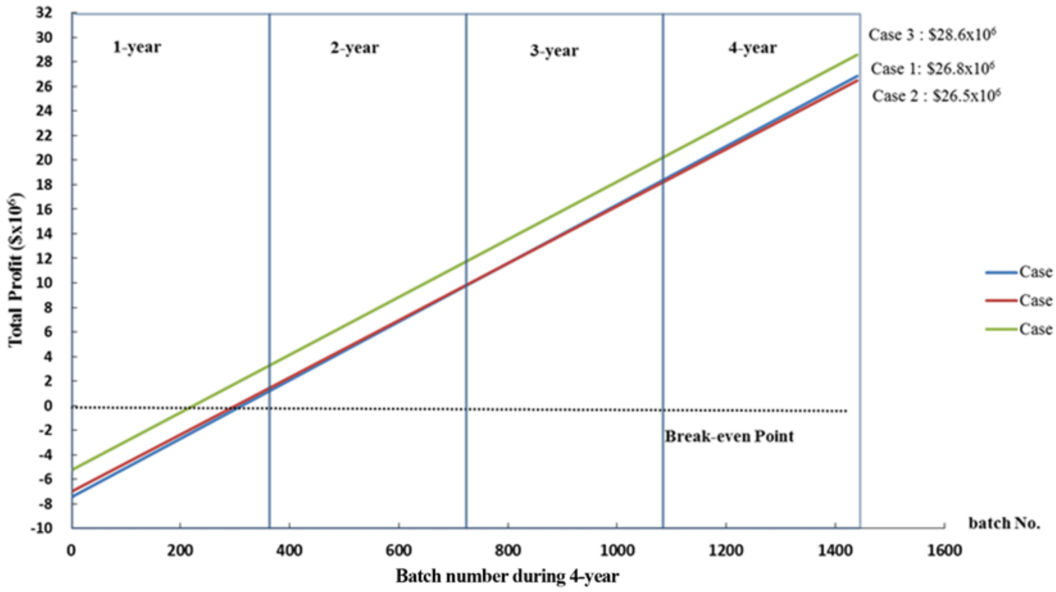

**Fig. 6. Comparison of accumulated profit with respect to batch number based on four-year operation.**

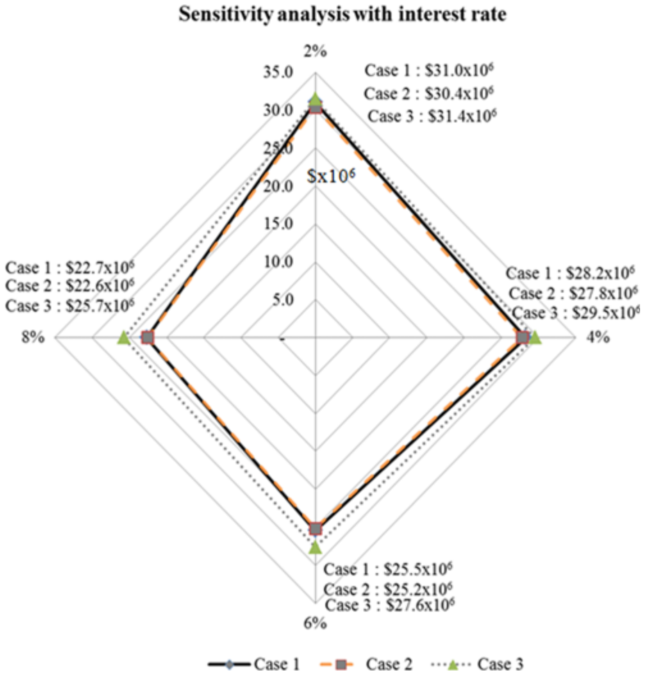

**Fig. 7. Total profit for 4-year operation when the interest rate is 2, 4, 6, and 8%.**

the variable cost and profit margin [14]. Fig. 7 shows that the lower the interest rate, the higher profit will increase as expected by reducing the facility investment cost.

As a result, case 3 has shown the best performance during four years of operations in term of the total profit regardless of the interest rate. For all range of interest rate, case 3 is the best and case 1 is a little bit better than case 2. The higher the interest rate is, the more the investment cost increases; thus case 3 is getting more lucrative.

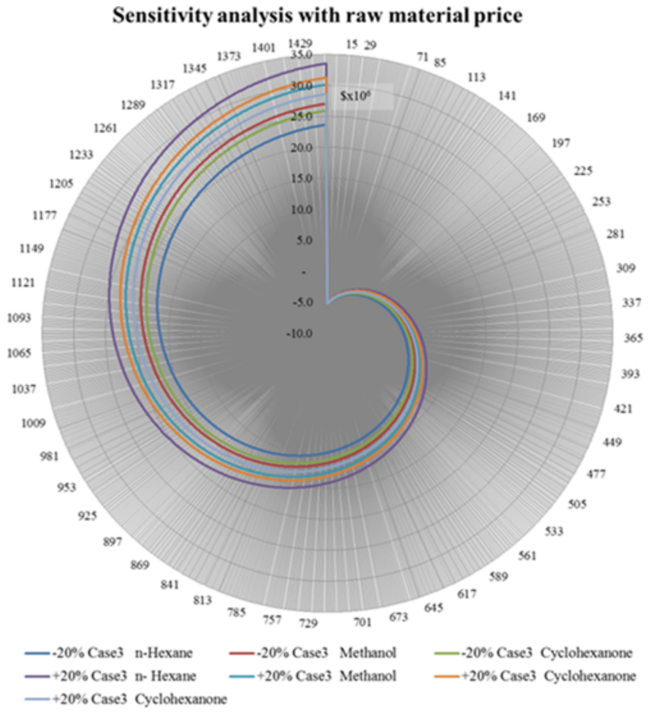

**Fig. 8. Profit changes of solvent price on total profit for 4-year operation (The clockwise direction indicates the increase in batch number).**

The difference in profits between cases is getting smaller when the interest rate is decreased. When the interest rate is 2%, the difference in profit between the best and worst cases is around $\$1.0\times10^6$, while the difference is increased about three times ($\$3.1\times10^6$) when the interest rate is increased to 8%. Then, the changes of the total profit with respect to the changes of the raw material cost (±20%) were

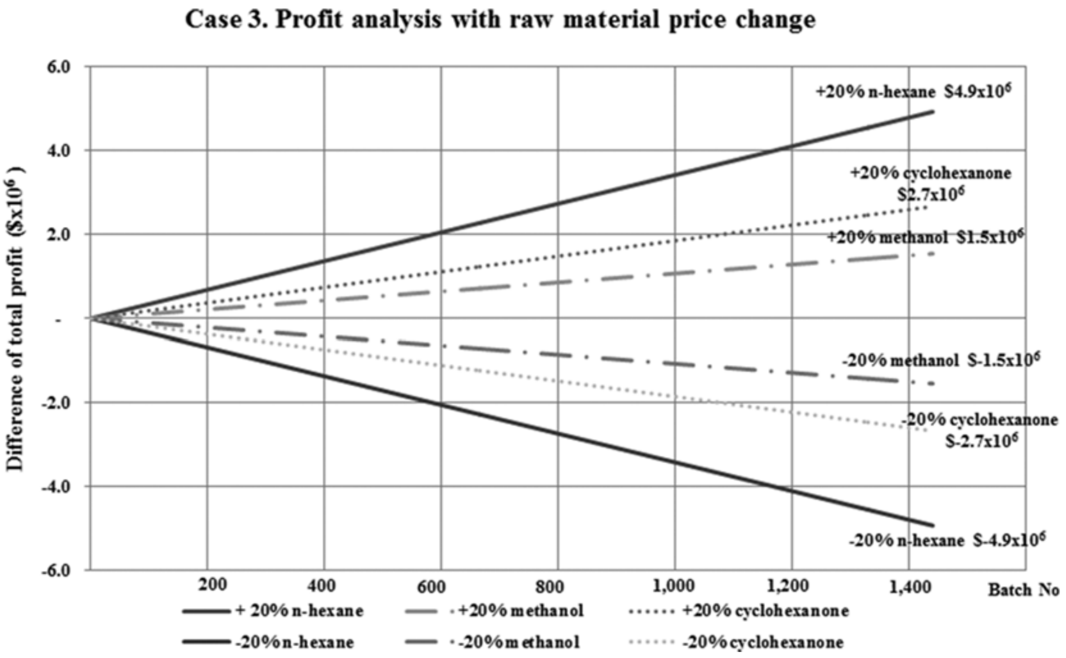

**Fig. 9. The change in total profit from base case when the raw material prices are changed by ±20% for case 3.**

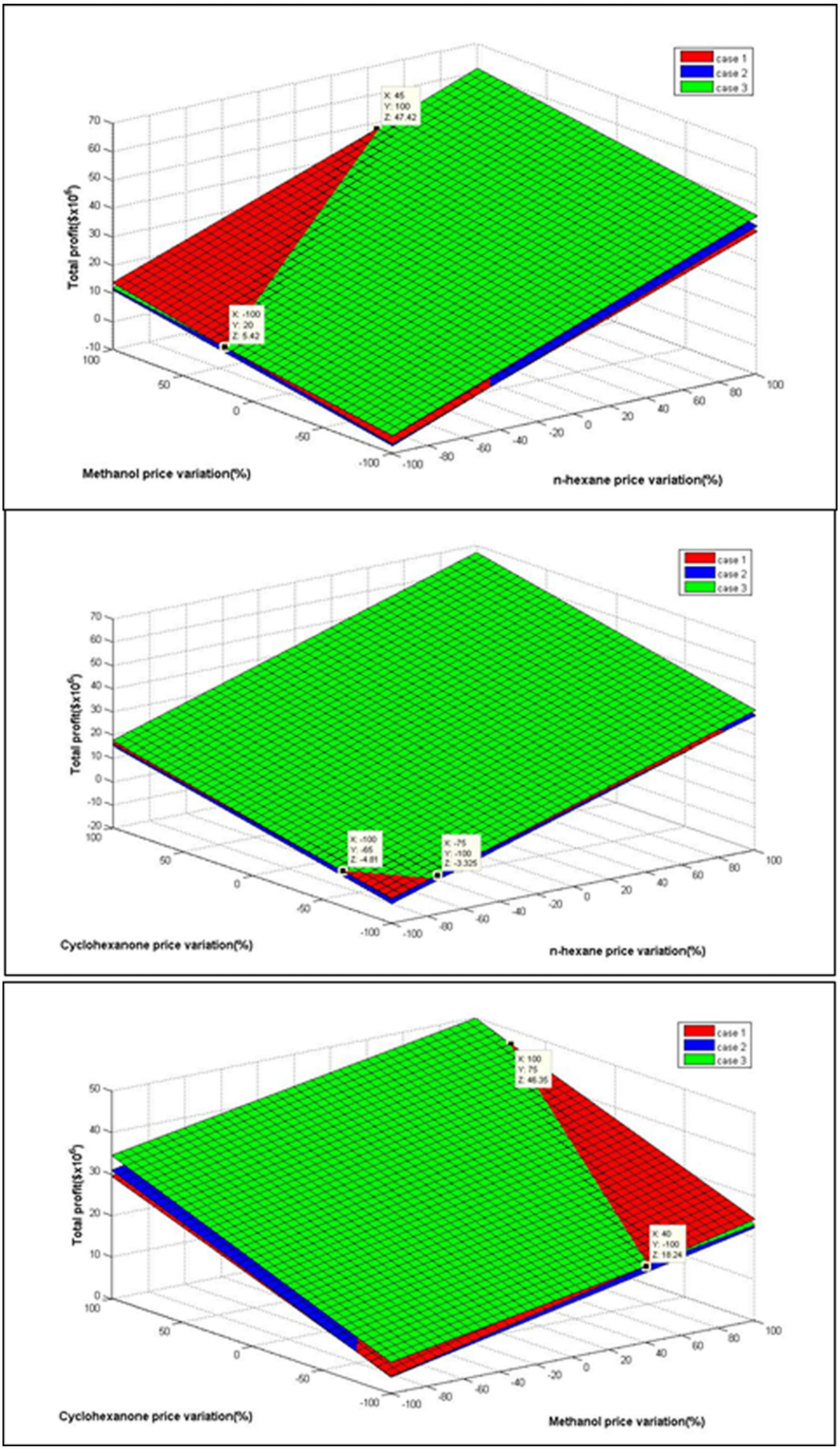

**Fig. 10. Change in total profit due to changes in raw material prices.**

analyzed. Based on the current prices of raw materials ($5 for n-hexane, $1.5 for methanol, and $5.3 for cyclohexanone), n-hexane, which has the largest amount regenerated among the three solvents, had the biggest sensitivity on total profit. Fig. 8 shows the change of the total profit for four years of operation. The profit of cyclohexanone is lower than that of n-hexane. Although cyclohexanone is the most expensive compared to the others, the amount of regeneration for cyclohexanone is smaller than that of n-hexane and the sensitivity of cyclohexanone price on total profit is smaller than that of n-hexane. Since the price of methanol, $1.5, is the lowest price, the economic sensitivity of methanol price is the lowest among all solvents.

We analyzed the changes in break-even point when the raw material prices changed, and found that all cases reached their break-even points faster when the price was increased as expected. Based on the base case 3 in which the break-even point was 0.6 year, the break-even point was calculated as 4.5% earlier for 20% increase in methanol price. Also, for cyclohexanone and n-hexane, the break-even point is shortened by 7.1% and 12.5% for 20% price increases in cyclohexanone and n-hexane, respectively. When the price is decreased by 20%, the break-even point is extended by 6.3%, 8.5% and 17.0% for price changes in methanol, cyclohexanone and n-hexane, respectively. Fig. 9 shows the comparison of the total profit changes for the case of ±20% variations in solvent prices.

Next, we analyzed whether the preferred case can be changed depending on the price changes in each raw material at the same time. The range of price change was set as ±100% from the base price for each solvent. Fig. 10 shows changes in total profit according to the variations in raw material prices. From the figure, the changes in darkness on the planes for total profit indicate the changes in the best case. For most ranges in price changes, case 3 has shown to be superior in terms of total profit. However, case 1 can be the best choice if the methanol price is increased relative to the prices of n-hexane and cyclohexanone. On the other hand, case 2 cannot surpass the other cases even for ±100% changes in solvent costs.

## CONCLUSIONS

A solvent regeneration process in the purification process of spin-on hard mask material has been proposed and investigated. By reusing solvents for spin-on hard mask manufacturing process, in which solvent cost takes account of 60% of manufacturing cost, a cost-efficient and environmentally beneficial alternative has been suggested. Three different cases were considered, and advantages and disadvantages of each case were compared based on the economic analysis. In case 1, a simulation was conducted where n-hexane and methanol was entirely separated as distillate product of column 1. Cases 2 and 3 separate methanol only up to the amount corresponding to the azeotropic composition with n-hexane to the top product of column 1. Additionally, case 3 does not recover the methanol from the decanter, so as to minimize the initial investment. With purity specification of 99% for each recovered solvent, the column designed and operating conditions are optimized. As a result, the yield of each solvent was calculated to be more than 90% in all the cases except 72% in case 3 due to unrecovered methanol from the decanter. Economic analysis concluded that all cases reach break-even point within a year despite their short lifetime. Regarding only efficiency against investment, case 3 exhibited the highest profit. Then, the effects in the aspect of interest rate and raw material cost variation were examined by the sensitivity analysis. As expected, the higher interest rate makes the case of large initial investment disadvantageous. The profit tended to vary with the solvent cost and the recovery, and the solvent cost of n-hexane was most sensitive in this research. As mentioned before, investment risk is not that big considering that all cases make profit more than $25,000,000 within four years of operation. The appropriate case could be selected for different situations at the point of investment. Finally, this study has demonstrated that the waste solvent regeneration in semiconductor spin-on hard mask material production process is feasible.

## ACKNOWLEDGEMENT

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