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Reduction of Waste in Semiconductor Manufacturing Plant (Sulfuric Acid Recycling Technology)

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Abstract

Technologies to collect and reuse sulfuric acid waste is attracting attention to reduce industrial waste in semiconductor manufacturing plants. Reusing sulfuric acid has a high economic value. By using sulfuric acid recycling equipment based on an atmospheric distillation method, we evaluated the recovery percentage of sulfuric acid, the concentration and quality of recycled sulfuric acid, and the influence of recycled sulfuric acid on semiconductor devices. The recovery percentage of sulfuric acid waste was 95% or more, and the quality of the recycled sulfuric acid was equivalent to or better than the sulfuric acid used for the electronic industry. Even when recycled sulfuric acid was used for resist stripping and wafer cleaning processes, the resist stripping capability and the dielectric breakdown voltage characteristics of gate oxide film were equivalent to or better than sulfuric acid used for the electronic industry. This indicated that the use of recycled sulfuric acid had no negative influence on semiconductor devices. By installing sulfuric acid recycling equipment based on an atmospheric distillation method, a semiconductor manufacturing plant can perform all collection, refinement and supply processes, and can contribute to decreasing industrial waste.

1. Introduction

The sulfuric acid used in semiconductor manufacturing plants is usually neutralized then finally disposed of (reclamation, etc.) by an outside industrial waste treatment company, or is used for such applications as cement material. Oki is also treating sulfuric acid waste in this manner. However, as the importance in the reduction of industrial waste is becoming recognized, a technology to recover and purity the waste fluid of sulfuric acid is receiving attention because the reuse of sulfuric acid is highly valuable in the semiconductor manufacturing process.

There are two types of technology to recover and purity the waste fluid of sulfuric acid: an atmospheric distillation method and a low pressure distillation method. The atmospheric distillation method is more commonly used throughout the world, but in Japan only a few recovery and purification equipment based on this method are in operation[1] because Japan has just begun to evaluate the practicality of sulfuric acid recycling. This time Oki evaluated the recovery ratio, the recovery concentration, the quality of sulfuric acid and the influence on semiconductor devices using recovery and purification equipment based on the atmospheric distillation method, and examined the possibility of recycling sulfuric acid in semiconductor manufacturing plants. The targets that we set in this examination were a 95% or more recovery ratio, a recovery concentration of 96% or more, and a quality and electrical reliability of recycled sulfuric acid equivalent to those of sulfuric acid used for the electronic industry. This paper first describes the necessity and problems of recovery and reuse technology for sulfuric acid, and then describes a sulfuric acid recovery and purification methods. The performance and quality of these methods are also described. The recycled sulfuric acid was used for resist stripping and other processes. Finally the influence of recycled sulfuric acid on semiconductor devices is described.

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2. Necessity and problems of sulfuric acid recovery and reuse technology

A semiconductor plant uses huge amounts of sulfuric acid for resist stripping and wafer cleaning. Figure 1 shows the flow of sulfuric acid supply and waste fluid at a semiconductor manufacturing plant. Sulfuric acid is delivered from a sulfuric acid manufacturer to a semiconductor

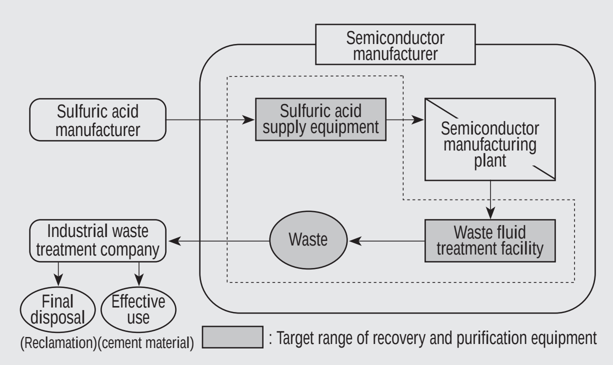

Figure 1: Sulfuric acid supply system flow and recovery target scope on semiconductor manufacturing

manufacturer via truck or other means of transportation, and is then supplied to the plant via chemical supply equipment. At the manufacturing plant, sulfuric acid is used for wafer cleaning in each manufacturing process, and is then drained. This waste fluid becomes a non soluble harmless salt waste in the waste fluid treatment facility by neutralization and removal of harmful materials. To dispose of sulfuric acid, neutralization chemicals and other additives are mixed, and the quantity of waste therefore exceeds the quantity of the used sulfuric acid. Sulfuric acid makes up about 17% of the entire quantity of waste acid in the semiconductor industrial waste at Oki, so the reuse of sulfuric acid is highly demanded.

If sulfuric acid recovery and purification equipment is installed in the range indicated by the dotted line in Figure 1, sulfuric acid waste can be recovered, purified and supplied, which considerably decreases industrial waste, and reduces the cost in purchasing new sulfuric acid, in constructing and operating waste fluid treatment systems, and in ordering waste treatment services from industrial waste treatment companies.

On the other hand, the cleaning capability required for wafer cleaning is becoming higher as the integration of semiconductor devices increases. Sulfuric acid used for semiconductor manufacturing plants is now demanded to remove from μg/kg (ppb) to the ng/kg (ppt) level of impurities. The same quality is also required for recycled sulfuric acid reused in semiconductor manufacturing plants. Therefore, sulfuric acid recovery and purification equipment must implement a high recovery ratio and high purity. In terms of a stable supply, the equipment must also be able to process recovery, purification and supply continuously.

3. Sulfuric acid recovery and purification method

3.1 Performance comparison of recovery and purification methods

Typical sulfuric acid recovery and purification methods are an atmospheric distillation method and a low pressure distillation method. An outline of sulfuric acid recovery and purification equipment and its performance by each method is as follows.

1. Atmospheric distillation method

   In the atmospheric distillation method, sulfuric acid is distilled and impurities are removed under atmospheric pressure. Sulfuric acid recovery and purification equipment based on the atmospheric distillation method consists of a moisture removal still, to remove moisture, and an impurities removal still, to remove metallic impurities. Figure 2 shows the treatment processing flow. With this distillation method, the recovery rate of sulfuric acid waste is high, 95%, and the purity of sulfuric acid is high (concentration of recycled sulfuric acid is 97% (manufacturer guaranteed value)) with a low residual impurities concentration in the purified sulfuric acid. However, the power consumption is high to maintain a distillation temperature during the purification process to about 340˚C (boiling point of sulfuric acid). This means that the problems of this method lie in operation costs and in energy savings. Maintenance and safety of equipment have been well considered.

2. Low pressure distillation method

   In the low pressure distillation method, sulfuric acid is distilled and impurities are removed under low pressure

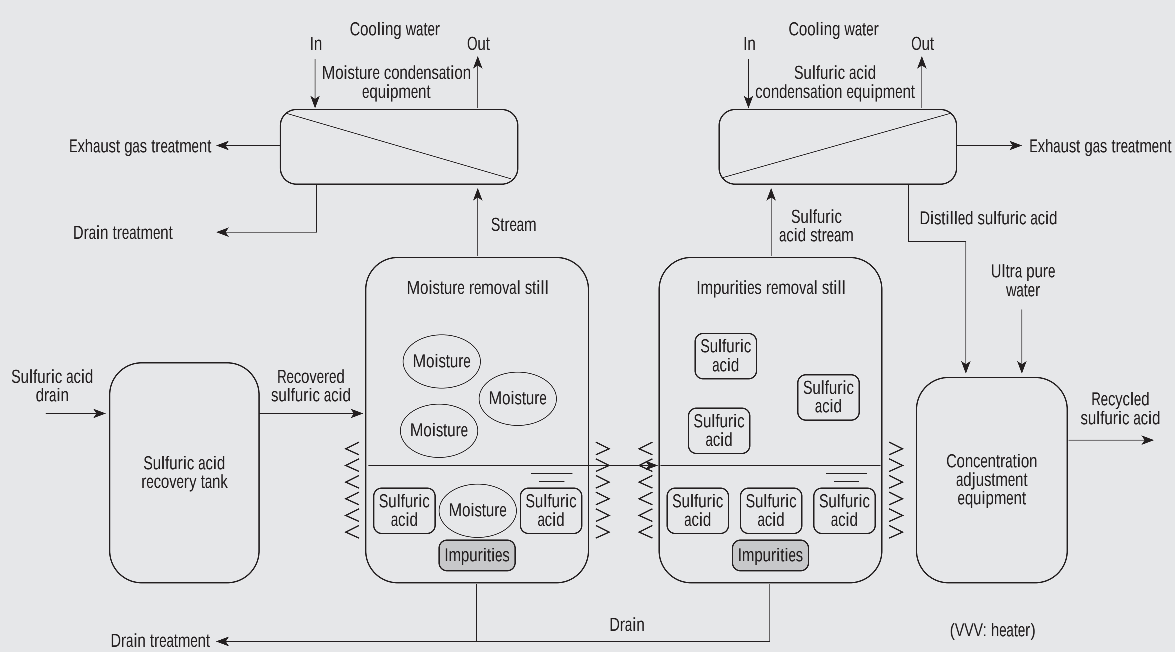

Figure 2: Treatment flow of sulfuric acid recovery and purification equipment based on atmospheric distillation method

to improve the distilling efficiency of sulfuric acid, which has a high boiling point. The basic configuration of sulfuric acid recovery and purification equipment based on the low pressure distillation method is the same as the atmospheric distillation method. The recovery rate of sulfuric acid waste is also the same as the atmospheric distillation method, but the residual impurities concentration in purified sulfuric acid is higher than the atmospheric distillation method, and the residual impurities concentration and purity of sulfuric acid fluctuates (concentration of recycled sulfuric acid (manufacturer guaranteed value) is 93%) because it is structurally (using seal material) difficult to maintain a high temperature and constant low pressure status. Power consumption is low since distillation temperature during the purification process is maintained to about 200˚C under low pressure, but the equipment is large and complicated to maintain low pressure status, so the problems involve maintenance and safety.

Considering the characteristics of both methods, we determined that the atmospheric distillation method is better to recover a higher purity sulfuric acid more stable with a higher recovery rate than the low pressure distillation method.

3.2 Evaluation of recycled sulfuric acid based on atmospheric distillation method

To evaluate the quality of recycled sulfuric acid using the atmospheric pressure distillation method, we compared the quality of sulfuric acid recovered and purified by the atmospheric pressure distillation method and the quality of sulfuric acid for the electronic industry purchased from a chemical manufacturer after using both types sulfuric acids in the semiconductor manufacturing process. Chemically analyzed values were used for this comparison. Table 1 shows the guaranteed values and analyzed values of the residual impurities concentration of the recycled sulfuric acid and the sulfuric acid for the electronic industry. The guaranteed values of recycled sulfuric acid are from the specifications of the recovery and purification equipment manufacturer, and the guaranteed values of the sulfuric acid for the electronic industry are from the specifications provided when chemicals for semiconductor manufacturing plants are purchased. The analyzed values of recycled sulfuric acid are much lower than the guaranteed values, which are almost the same as the analyzed values of sulfuric acid for the electronic industry. The Si (silicon) concentration, however, is higher in the recycled sulfuric acid than the sulfuric acid for the electronic industry. Quartz, a major component material of a still, is the source of generation of Si.

3.3 Problems of chemical analysis

To commercialize sulfuric acid recovery and purification equipment, it is important to establish a chemical analysis and evaluation method for the results. When a chemical has a high boiling point, strong acid and high viscosity at the same time, like sulfuric acid, a method to supply the chemical to an analyzer and the handling of components and parts are the problems. Also, when microanalysis is performed for residual impurities in sulfuric acid, the physical properties of the equipment in the pretreatment conditions of the sample to be supplied to the analyzer (container, concentration percentage, etc.) cause major problems in analysis sensitivity and accuracy.

Unit: μg/kg

Target substance	Residual impurities concentration			
	Sulfuric acid for electronic industry		Recycled sulfuric acid	
	Guaranteed values (specifications)	Analyzed values	Guaranteed values (specifications)	Analyzed values
Na	20	1	3	1
Al	10	0.2	3	0.2
K	10	0.1	1	0.3
Ca	10	0.5	1	0.4
Cr	2	0.04	1	<0.01
Fe	20	0.2	1	0.2
Ni	2	<0.02	1	<0.02
Cu	2	<0.01	1	<0.01
Si	—	20	100	40

Table 1: Comparison of residual impurities concentration in sulfuric acid

For microanalysis, the mixing of impurities from the outside must be prevented so that the reliability of results become high. In the quality evaluation that we had this time, we used a condensed sample for analysis and evaluation, so that measurement is possible even if the detection sensitivity is low. For an analysis which requires continuous quality control, it is effective to supply a sample directly to the analyzer. The development of a frameless atomic absorption equipment-based analyzer, which allows high sensitive measurement without such pretreatments as concentration, is expected.

4. Influence on semiconductor devices

We evaluated the influence of recycled sulfuric acid and sulfuric acid used for the electronic industry on semiconductor devices when they are used for semiconductor manufacturing processes. For this evaluation, we tested the resist stripping capability and electric characteristics in wafer cleaning. The evaluation result is as follows.

4.1 Evaluation of residual particle in resist stripping process

Using a sample on which resist was physically damaged by adding impurities by an ion implantation method, we stripped resist by a mixed chemical of sulfuric acid and hydrogen peroxide water, and measured the quantity of residual particles on the wafer surface. When recycled sulfuric acid was used, the quantity of residual particles was about 10% less compared to the case when sulfuric acid for the electronic industry was used. However, this difference is small and the resist stripping capability of both sulfuric acids is about the same for the quantity of residual particles.

4.2 Evaluation of dielectric breakdown voltage by using cleaning process before gate oxidation

Using recycled sulfuric acid and sulfuric acid for the electronic industry in the wafer cleaning process before creating gate oxidation, we measured the dielectric breakdown withstand voltage characteristics of gate oxide film and evaluated the breakdown failure ratio. For both the low voltage side and the high voltage side of the dielectric breakdown voltage characteristics, the breakdown failure ratio was about 1% better when using recycled sulfuric acid than using sulfuric acid for the electronic industry. This shows that the use of recycled sulfuric acid does not affect the breakdown failure ratio of gate oxide film.

4.3 Evaluation of dielectric breakdown voltage by using cleaning process before creating polysilicon electrode film deposition

Using recycled sulfuric acid and sulfuric acid for the electronic industry in the wafer cleaning process before creating polysilicon electrode film deposition, we measured the dielectric breakdown voltage characteristics of gate oxide film, and evaluated the breakdown failure ratio. In both cases, the breakdown failure ratio is almost the same at the low voltage side of dielectric breakdown characteristics. At the high voltage side, the breakdown failure ratio is about 3% better when using recycled sulfuric acid than using sulfuric acid for the electronic industry. This shows that the use of recycled sulfuric acid does not affect the breakdown failure ratio of gate oxide film.

As the evaluation results in Sections 4.1 ~ 4.3 show, recycled sulfuric acid does not affect semiconductor devices when used as a chemical for resist stripping and the wafer cleaning process of the semiconductor manufacturing process, just like sulfuric acid for the electronic industry.

5. Conclusion

To decrease industrial waste at semiconductor plants, we evaluated the recovery ratio, recovered concentration and quality, and the influence on semiconductor device for recycled sulfuric acid after it is used at semiconductor manufacturing plants, and examined whether recycling sulfuric acid is possible. As a result, we judged that the recovery and reuse of sulfuric acid is possible by using the atmospheric distillation method. When the atmospheric distillation method is used, the recovery ratio of sulfuric acid waste is 95% or more, and the recovered concentration is 97% or more. The quantity of residual impurities in recycled sulfuric acid is equivalent to that of sulfuric acid for the electronic industry. For the influence on semiconductor devices, the dielectric breakdown withstand voltage failure ratio is better when recycled sulfuric acid is used. As a consequence, by using sulfuric acid recovery and purification equipment based on the atmospheric distillation method, sulfuric acid can be recovered, purified and supplied consistently in a semiconductor manufacturing plant. This can decrease industrial waste considerably.

In the future, we will work on improving the quality of the atmospheric distillation method-based recovery and purification equipment, as well as saving energy and resources, so that sulfuric acid recycling technology, that can further contribute to environmental protection, will be established.

6. References

1. Yoshihiro Koyama. “Sulfuric acid recovery and purification technology,” *Ultra Clean Technology*, 9, 3, (1997): 159~162.