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Recovering low-turbidity cutting liquid from silicon slurry waste

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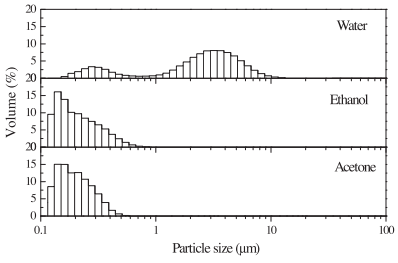
HIGHLIGHTS

- Recovering clean cutting liquids was achieved by sedimentation with a diluent.
- Water as a diluent was better than ethanol and acetone.
- The recovered liquids (<100 NTU) could be reused in the cutting process.

GRAPHICAL ABSTRACT

The particles in the solution of glycol (PAG) and water were larger than those in PAG–ethanol or PAG–acetone solutions, showing that water interfered with the adsorption of PAG molecules and weakened the steric stabilization. Using water as a diluent for sedimentation facilitated the separation of solids from cutting liquids.



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ABSTRACT

In order to recover a low-turbidity polyalkylene glycol (PAG) liquid from silicon slurry waste by sedimentation, temperatures were adjusted, and acetone, ethanol or water was used as a diluent. The experimental results show that the particles in the waste would aggregate and settle readily by using water as a diluent. This is because particle surfaces had lower surface potential value and weaker steric stabilization in PAG–water than in PAG–ethanol or PAG–acetone solutions. Therefore, water is the suggested diluent for recovering a low-turbidity PAG (<100 NTU) by sedimentation. After 50 wt.% water-assisted sedimentation for 21 days, the solid content of the upper liquid reduced to 0.122 g/L, and the turbidity decreased to 44 NTU. The obtained upper liquid was then vacuum-distillated to remove water. The final recovered PAG with 0.37 NTU had similar viscosity and density to the unused PAG and could be reused in the cutting process.

1. Introduction

The rapid development of photovoltaic industries has increased the need for silicon wafers. However, substantial silicon slurry waste is formed during the cutting process from silicon ingot to wafers [1,2]. More than 50% of this waste comes from the cutting liquid. For a factory with a polysilicon throughput of 2000 tons annually, the required cutting liquid is about 1600 tons annually. Meanwhile, at least 3200 tons of silicon slurry waste is generated [3]. The cutting liquid generally consists of water-soluble glycol molecules, which can be classified as small molecules or polymers. The former includes ethylene glycol (EG), propylene glycol (PG) or diethylene glycol (DEG); the latter includes polyethylene glycol or copolymer of ethylene oxide and propylene oxide, also known as polyalkylene glycol (PAG). The long chain molecules in polymer-type cutting liquid provide good dispersion of abrasives, high lubricity and heat tolerance, resulting in an excellent cutting yield [4]. However, the polymer-type cutting liquid forms

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wastewater with high COD, which is difficult to treat and becomes a major environmental issue. Recycling this glycol liquid from sawing waste would greatly reduce the amount of waste, and thereby the total slicing cost can be efficiently reduced [5].

Manufacturers and recyclers currently recover small-molecule cutting liquids by distillation, which heats the waste beyond the boiling point of glycol so that the obtained vapor can be separated from the solid waste. High-purity glycol can then be collected by condensation [6]. The collected liquid can be reused in the cutting process after adding additives. However, PAG cutting liquid dissociates or oxidizes at high temperature and is not recoverable through the collected vapor during distillation. Therefore, some manufacturers and recyclers use low-temperature methods to separate cutting liquids from silicon slurry waste, such as centrifugal separation [7,8] and filtration [5,8]. Furthermore, SiC, Si particles and metal fragments suspended in PAG liquid are so stable that recyclers have difficulty obtaining a low-turbidity PAG liquid from silicon slurry waste. In recent years, many patents proposed the techniques or skills to recovery and renew polymer cutting liquids, including predilution [5,7,8] for enhancing separation of solid and liquid, coagulation [9], membrane filtering [10] or ultrafiltration [11] for separation of particles, ion exchange treatment [12], reverse osmosis treatment [10] or vacuum evaporation [13] for removing water, and decolorizing for adsorbing impurities [13]. However, the suggested methods were only patented, i.e. no practical data could be available for their use in recovering PAG liquid from silicon slurry waste.

This study, therefore, used sedimentation process to recover PAG cutting liquid from silicon slurry waste. Sedimentation is the simplest way to separate solids from liquids and is easily performed in factories, such as the cases for recycling lubricant [14] and heavy oil [15]. To obtain a low-turbidity PAG liquid (<100 NTU) from silicon slurry waste, this study adjusted temperatures and employed acetone, ethanol or deionized water as a diluent during sedimentation. Observation of the settling behaviors revealed the separation mechanism of particles during recovery of PAG liquids from silicon slurry waste. Finally, the recovering process to obtain a clean PAG liquid was built up.

2. Experimental

2.1. Analysis of silicon slurry waste

Silicon slurry waste was obtained from Sino-American Silicon Products, Inc. (Chu-Nan, Taiwan). After preliminary recycling of large SiC particles with a centrifugal decanter, the slurry waste with low solid content was transferred to our laboratory for the sequential analysis and recovery of cutting liquids.

The obtained silicon slurry waste contained kerf Si, SiC abrasives, metal fragments from cutting wire and polyalkylene glycol (PAG) cutting liquid. The average molecular weight of PAG was 750. To analyze its composition, each waste sample was first heated to 500 °C to remove liquids. The solid content percentage (S_1) was then calculated as the mass of the residual solid powder dividing by the mass of the original obtained waste. The particle size distribution (PSD) in the obtained silicon slurry waste was measured using static light scattering (model: LA300, HORIBA). Viscosity was measured using a Viscometer (model: LVDV-I Prime, BROOKFIELD), and turbidity was measured with a turbidity meter (model: 2100Q, HACH).

2.2. Separation process

Silicon slurry waste (100 ml) was transferred to a graduated cylinder for the sedimentation experiment. In order to control the sample temperature during sedimentation, the graduated cylinder was put in an oven set to temperatures of 25, 40 and 80 °C. Moreover, three liquids, acetone, ethanol and deionized water, were used as diluents and mixed with the obtained silicon slurry waste by 5-min stirring. After thoroughly mixing the waste and diluents, 100-ml diluted waste was poured into a graduated cylinder to allow the particles to settle freely.

2.3. Analysis of the recovered liquid

After sedimentation for different days, the upper liquid or the recovered liquid, in the cylinder was analyzed. Particle size distribution (PSD) was measured by static light scattering (model: LA300, HORIBA). Viscosity was measured with a viscometer (model: LVDV-I Prime, BROOKFIELD). Turbidity was measured with a turbidity meter (model: 2100Q, HACH). In addition, the recovery liquid was heated to 500 °C to remove glycol or diluents, and the solid content percentage (S_2) was obtained by the mass of the residual solid dividing by the mass of the original recovered liquid.

Due to the hygroscopicity of PAG molecules, the obtained waste or recovered liquid would contain water. The water content was measured with a Karl Fischer titrator (model: 870 plus, HACH). When the diluent was deionized water, the measured water content percentage in the obtained waste (W_1) and in the recovered liquid (W_2) could determine the recovery percentage of glycol by the following equation

$$\text{Recovery percentage of glycol (\%)} = \frac{(\text{Mass of the recovered liquid}) \times (1 - S_2 - W_2)}{(\text{Mass of the obtained waste}) \times (1 - S_1 - W_1)} \times 100\% \quad (1)$$

3. Results and discussion

Fig. 1(a) shows that the obtained slurry waste had a black and opaque appearance. The measured density, viscosity at 25 °C, and solid content of the waste were 1.009 g/cm^3, 72 cp and 15.6 wt.%, respectively. The particle size distribution of the waste (Fig. 1(b)) indicated that the particle size of the obtained waste was below 7 μm, and the main peaks of the particle sizes were 0.3 and 1.2 μm, which showed that most of the large SiC (around 15 μm as used originally) was recycled before delivery to our laboratory. These micron particles in spent slurry waste included kerf Si, metal fragments and broken SiC abrasives. Because of their small size, the particles were suspended stably in PAG cutting liquid, which produced an opaque appearance and high nephelometric turbidity units (NTU). The turbidity of the obtained waste exceeded 1000 NTU, which was the detection limit of the turbidity meter (model: 2100Q, HACH) used in this study.

To recovery a clean PAG liquid, lowering the solid content and turbidity is essential. Generally, low turbidity indicates a low solid content, but suspension liquids with the same solid content might have different nephelometric turbidity units due to different particle sizes. Therefore, before recovery of a low-turbidity cutting liquid, a standard value corresponding to a clean PAG liquid was examined by adding approximately 1 μm silicon particles into PGA. The prepared PAG-Si suspension was used in analyzing the relations among solid content, turbidity and appearance of PAG-Si suspension. Table 1 shows how the solid content and nephelometric turbidity units affected the appearance of the prepared PAG-Si suspension. Notably, the suspension was not transparent, and the turbidity exceeded 1000 NTU when the solid content reached 0.5 g/L. The appearance was clean and resembled an unused cutting liquid through visual inspection when the solid content decreased to 0.0075 g/L and the turbidity reduced to 109 NTU. The smaller particles at the same solid content had a higher turbidity. Since the