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Performance of integrated membrane filtration and electrodialysis processes for copper recovery from wafer polishing wastewater

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ABSTRACT

This study assesses the efficiency of a combining ultrafiltration (UF) and electrodialysis (ED) processes to treat and reclaim wastewater, a discharge of the copper chemical mechanical planarization (Cu-CMP) process typical among semiconductor manufacturing procedures. The Cu-CMP wastewater generally contains nano-scale slurry particles and metal residues from polishing a wafer. The permeate water turbidity and UF flux for the removal of slurry particles using dilute solutions containing two commercial silica slurries were investigated. For both dilute silica slurries, permeate flux declined markedly as the particle concentration increased (500–2000 mg/l). Particle rejection rate exceeded 99.7%, and was independent of particle concentration. The ED process for removal of Cu^{2+} exceeded 99.3% with applied field strength of 1.5 V/cm and reaction time of 3 h. The Cu^{2+} was removed primarily from the solutions through adsorption onto cationic exchange membranes (CEMs) in the ED reactor. The continuous-flow ED study for low Cu^{2+} concentrations typical of Cu-CMP waste streams also had an excellent removal >98%. Additionally, the Cu^{2+} adsorbed on the CEMs was effectively recovered by 3% (w/w) HCl extraction but not by a reverse electrical field. Applications of the UF/ED system for treating actual Cu-CMP wastewater demonstrates sequential particle removal by UF and Cu^{2+} removal by ED, confirming the feasibility of the combined process to reclaim Cu-CMP wastewater. Cost estimate based on the laboratory data also suggests that the integrated process is economically competitive as compared to the convention coagulation process for treating Cu-CMP wastewater.

1. Introduction

The sheer volume of water demanded by microelectronics (semiconductors) and opto-electronics fabrication processes is the main obstacle to balancing environmental burden and industrial growth [1,2], and has thus rendered water reclamation a necessity. The wastewater from wafer polishing via chemical mechanical planarization (CMP) processes, which are used by upstream substrate suppliers and in back-end device fabrication, has been targeted as a source for water reclamation [3]. The CMP slurry provides both chemical action due to the slurry chemistry and mechanical effects due to slurry abrasives. Consequently, CMP waste streams typically contain nano-scale particles such as silica (SiO_2) or alumina (Al_3O_4), as well as chemicals for slurry dispersion and surface etching control. Further, since copper metallization technology, which has replaced aluminum and tungsten, is utilized by most semiconductor manufacturers, and CMP waste streams containing copper (Cu-CMP) have become a treatment challenge since the copper concentration range usually exceeds discharge limits, yet is often too low for cost-effective recovery [4].

The efficacy of various treatment technologies has been assessed to remove nano-scale particles from CMP wastewater: chemical coagulation [5–7], electro-coagulation [8–11], and membrane filtration [12–14]. Recently, magnetic separation techniques have also been used to remove charged particles from industrial wastewater. These techniques, based on the high gradient of the magnetic field, use magnetic seeding [15,16] or ferromagnetic filters [17]. To date, membrane filtration techniques have been used by industrial due to their technical maturity, and they may be applied either as a wastewater purification step in conjunction with the aforementioned particle separation techniques [18,19], or as a single treatment process for particle-containing wastewater [20,21]. As

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with many other water purification applications, controlling membrane fouling due to various resistance-forming mechanisms is essential to process efficiency and membrane stability. Additionally, ultrafiltration (UF) has been applied as a particle recovery and re-concentration method for slurry reprocessing; both Kim et al. [12] and Testa et al. [22] achieved successful applications of polymeric UF membranes to separate nano-sized silica particles from effluent streams collected from point-of-use CMP tools. Particularly, a pilot-study reported by Testa et al. demonstrated that the UF membrane system can achieve a particle concentration factor of 10 using a polysulfone hollow-fiber membrane while maintaining a steady flux at 55 l/m^2/h (1.32 m^3/m^2/d). Because this membrane is part of a tool's post-processing steps, frequent backwashing controlled by a turbidity sensor and diverter valve is necessary to prevent irreversible membrane fouling.

Relative few studies have examined copper removal from Cu-CMP wastewater. Biosorption [23,24] and selective chelation [25] are the most common techniques tested in a laboratory using synthetic Cu-CMP wastewater. These techniques effectively remove copper from waste effluents, but the addition of chemicals prevents copper recovery. Conversely, electrodialysis (ED), a membrane separation process based on selective migration of aqueous ions through ion-exchange membranes (IEMs), uses an electrical driving force. The transport direction and transport rate for each ion depends on its charge and mobility, solution conductivity, relative concentrations and applied voltage. Notably, ED has been widely used for desalinating sea/brine water, producing ultrapure water (UPW), and concentrating dilute solutions. It has also been applied to remove heavy metal ions from industrial wastewaters [26,27].

This study evaluates the feasibility of combining UF membrane filtration and an ED process for sequential separation of abrasive particles and Cu^{2+} from Cu-CMP waste streams. As neither the membrane filtration (for particle separation) nor ED process (for copper ion retention) adds chemical to the water, particle re-concentration and copper recovery can be achieved. Given that successful application of membrane separation for silica particles has been demonstrated, this report focuses on the characteristics of ion exchange membrane adsorption of Cu^{2+} and the range of suitable ED operating conditions. Technical feasibility of the combined UF-ED process is also tested using actual Cu-CMP waste streams from a semiconductor manufacturing plant.

2. Materials and methods

2.1. Apparatus and equipment

To treat and recover Cu from Cu-CMP waste streams, this study employed a UF membrane filtration process coupled with an ED membrane. For the ED process, a batch-type and a continuous-flow-type system were used. The batch studies were designed to evaluate the effects of particle concentration, Cu^{2+} concentration, and electric field strength on Cu^{2+} removal, whereas the continuous-flow experiments were designed for confirmatory purpose to study the Cu^{2+} removal efficiency for both artificial and real wastewater using the appropriate applied field strength determined from the batch test, similar to the approach applied in other studies [28,29]. The batch-type reactor had glass shell with external dimensions of 50 cm (length) × 20 cm (width) × 40 cm (height). The reactor was separated into five compartments (two for diluted and three for concentrated solutions) by three 1 cm-thick graphite electrodes (20 cm × 40 cm) 5 cm wide. The IEMs were in the middle of each compartment. The reactor's effective volume was 28 l. The continuous-flow reactor was constructed in acrylic shell with overall dimensions of 8 cm (L) × 5 cm (W) × 5 cm (H). The reactor was flanked with a pair of graphite electrodes. Three pairs of cationic and anionic membranes divided the ED reactor into five intermembrane compartments through which the waste stream flowed. The Cu concentration, pH, and conductivity in effluent discharged from the three diluents channels were measured. The diluent channels were designated as D1 (farthest from the anode), D2 (middle), and D3 (nearest the anode). The reactor's effective volume was 2.4 l.

2.2. UF membrane filtration system

To remove SiO_2 particles from waste streams, this laboratory-scale membrane filtration study used flat-sheet cross-flow equipment (SEPA CF II, GE Osmonics, USA). The test membrane was a GE Osmonics polyvinylidene fluoride (PVDF) flat-sheet membrane with a molecular-weight cut-off (MWCO) of 30 kDa (roughly 4 nm in pore diameter) and had a wide pH tolerance range (1–11). This type of UF membrane was selected according to the nominal pore size appropriate for separating nanosized particles and the high mechanical strength to withstand particle abrasion. UF filtration tests used synthetic waste streams containing a SiO_2 concentration of 500, 1000, 1500, and 2000 mg/l, a cross-flow velocity (CFV) of 1.0 m/s, and a transmembrane pressure (TMP) of 2.75 kgf/cm^2 (275 kPa). The feed suspension volume remained fixed by recirculating the permeate back into the feed tank.

The synthetic wastewater containing SiO_2 particles was prepared using two commercially available CMP oxide (SiO_2) slurries: Klebosol 1501-50 (Rohm and Haas, USA) with a mean particle size 75 ± 5 nm; and Cabot SS-25 (Cabot, USA) with a mean size of 150 ± 7 nm. The particles in these two SiO_2 slurries have similar surface ζ-potential, but have notably different size distributions as measured by a particle size analyzer (DelsaNano, Beckman Coulter, USA). Particle concentrations were determined by correlating turbidity (WTW Turb 550, Nova Analytics Company, Germany) with dry solid weight suspended in the particle solutions. The typical particle concentration range in CMP wastewater is 400–1000 mg/l. The particle rejection efficiency, determined by turbidity measurements in feed and permeate streams, is derived as follows:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (1)$$

The degree of membrane fouling was calculated using a resistance-in-series model based on Darcy's law, i.e., $J = \Delta P/\mu R$, where J is permeate flux, μ is solution viscosity, and ΔP is applied TMP. Total resistance includes intrinsic membrane resistance (R_m), cake resistance (R_c), and pore-blocking resistance (R_p). Notably, R_m can be calculated directly from permeate flux (J_1) for clean membrane experiments, whereas R_p is calculated based on flux data after the cake layer is physically removed (J_2) from the membrane surface. Then R_c, remaining resistance, is calculated using the steady-state flux of the suspension (J_s). Those resistances are calculated using the following equations:

$$R_m = \frac{\Delta P}{J_1 \mu} \quad (2)$$

$$R_p = \frac{\Delta P}{J_2 \mu} - R_m \quad (3)$$

$$R_c = \frac{\Delta P}{J_s \mu} - R_m - R_p \quad (4)$$

To identify the blocking mechanism, analysis of membrane pore blocking in the UF membrane was performed using Hermia models:

$$\frac{d^2 t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (5)$$

where k is a constant, V is total filtered volume, t is filtration time; and n is the blocking index, which equals 2, 1.5, 1, or 0, representing complete blocking, standard blocking, intermediate blocking, and