Synthesis of Fibrous Metal Adsorbent with a Piperazinyl-Dithiocarbamate Group by Radiation-Induced Grafting and Its Performance

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ABSTRACT: A fibrous grafted metal adsorbent with a piperazinyl-dithiocarbamate (PZ-DTC) group was synthesized by radiation-induced emulsion grafting of glycidyl methacrylate onto a polyethylene-coated polypropylene nonwoven fabric (PE/PP-NF) and subsequent three-step chemical modifications consisting of amination with N-[(tert-butoxycarbonyl)piperazine (N-Boc-piperazine, NBPZ), deprotection of the Boc group with HCl, and dithiocarbamation with carbon disulfide (CS₂). By using the NBPZ reagent in the amination step, the self-cross-linking of piperazine (PZ) could be completely suppressed, unlike using the PZ reagent. Consequently, the PZ-DTC group density of the fibrous grafted metal adsorbent synthesized through NBPZ attained 2.122 mmol-PZ-DTC/g-adsorbent, which was approximately 6 times higher than that of the metal adsorbent synthesized through PZ. The fibrous grafted metal adsorbent with the PZ-DTC group selectively adsorbed heavy metal ions over light metal ions. Furthermore, it exhibited high adsorption capacity, particularly for Cu²⁺. The Cu²⁺ adsorption capacity was determined to be 1.903 mmol-Cu²⁺/g-adsorbent by a batchwise adsorption test using a single-metal-ion aqueous solution at pH 6. The order of metal ion selectivity of the fibrous grafted metal adsorbent with the PZ-DTC group was Na⁺ < Mg²⁺, Ca²⁺, Cd²⁺ < Pb²⁺ ≪ Cu²⁺, and Co²⁺ ≈ Ni²⁺ < Zn²⁺ ≪ Cu²⁺. In addition, the fibrous grafted metal adsorbent with the PZ-DTC group did not lose its metal adsorption function even under highly alkaline conditions (pH 15). It could recover Cu²⁺ efficiently and selectively from a high-concentration Na⁺ aqueous solution at this pH. The Cu²⁺ adsorption capacity of the fibrous grafted metal adsorbent with the PZ-DTC group was 0.754 mmol-Cu²⁺/g-adsorbent under a highly alkaline condition, a 10 M NaOH aqueous solution at pH 15. This value was approximately 2.4 times higher than that of the other grafted adsorbent with an amine-type functional group.

INTRODUCTION

The high integration of semiconductor devices, which constitute a key factor that has impelled the development of modern society, has been achieved by innovations in microfabrication technology. The number of transistors in densely integrated circuits continues to increase adhering to the empirical rule called Moore’s law, which states that the density doubles roughly every 2 years. While the linewidth of the earliest integrated circuits (in the early 1970s) was 10 μm, it has recently been announced by Taiwan Semiconductor Manufacturing Co., Ltd. that a test chip with a circuit line width of 5 nm will be prototyped on the production line. Si wafers for the 5 nm process technology are required to exhibit exceptionally high surface smoothness on the order of nanometers. If the chemical solution for the surface etching of Si wafers is contaminated with a concentration of a few μg/g (ppm), the Cu²⁺ diffuses into the Si wafer and develops pits on the surface of the wafer after the polishing treatment. Therefore, the development of a novel adsorbent for removing Cu²⁺ and other ionic species from etchants is highly desired.

Radiation-induced grafting, a convenient technique for surface modification of polymers, can impart the desired functional groups into commercially available trunk polymers without deteriorating their physical or chemical properties. This technique is suitable for synthesizing new high-performance materials. Examples include metal adsorbents for collecting useful metals or removing harmful metals, ion exchange fiber for antibody purification, dyes adsorbent for wastewater treatment, proton-conductive membrane for fuel cell devices, solid catalysts for biodiesel fuel production, flame-retardant fabric, superhydrophobic fabrics, drug-
eluting material, wiper blade rubber, and so forth have been researched and developed. Especially, the fibrous adsorbents synthesized by the radiation-induced grafting have a large specific surface area and high contact efficiency, so they can capture target substances even under high flow rate conditions. In the column treatment, the adsorption rate of the fibrous grafted adsorbent was 10–100 times higher than those of commercially available granular resin. The high adsorption rate of the grafted adsorbent was explained by the negligible diffusional mass-transfer resistance of target substances to functional groups. The mass transfer of the grafted adsorbent was aided by the convective flow through the fabric, whereas the mass transfer of the granular resin was suppressed by the slow diffusion rate into the resin. Recently, we have succeeded in developing water purifier for radioactive cesium removal from contaminated natural water by making full use of the high-speed adsorption characteristics of the fibrous grafted adsorbent. In our previous study, we developed a metal adsorbent for an alkaline etching aqueous solution for Si wafers by radiation-induced emulsion grafting of glycidyl methacrylate (GMA) onto the polyethylene nonwoven fabric and subsequent amination with 2,2'-glycidyl methacrylate (GMA) solution for Si wafers by radiation-induced emulsion grafting of glycidyl methacrylate (GMA) onto the polyethylene nonwoven fabric and subsequent amination with 2,2'-glycidyl methacrylate (GMA) onto the polyethylene nonwoven fabric. The fibrous grafted metal adsorbent with the IDE group could selectively remove trace amounts of Ni2+ and Cu2+ that were dissolved in highly alkaline solutions (such as 48 wt % NaOH and 48 wt % KOH aqueous solutions) used in the surface etching process of Si wafers. The liquid-passage rate and the lifetime of the fibrous grafted metal adsorbent with the IDE group were 20 times higher and 30 times longer, respectively, than those of the commercial resin with a tertiary amine group (DUOLITE A378D, Sumika Chemtex Co., Ltd., Osaka, Japan). These performances satisfy the requirement for adsorbents in removing metal ions from Si wafer etchants. Therefore, and because its adsorption capacity is significantly higher than that of the commercial resin used in Si wafer processing, the fibrous grafted metal adsorbent with the IDE group was commercialized as METOLATE.

With the remarkable evolution and innovation of semiconductor technology in recent years, the development of higher performance adsorbents for removing contaminating trace metal ions in Si wafer etchants is highly desirable. Although conventional chelating functional groups such as IDE, iminodiacetic acid (IDA), and ethylenediamine (EDA) groups (which have been used as metal-adsorptive functional groups) have a certain degree of metal ion selectivity, their use does not result in further improvement in the adsorbent performance. This is because the conventional chelating functional groups adsorb heavy metal ions as well as Na+(which is the main component of Si wafer etchants) simultaneously. In order to further improve the adsorption performance from those of available metal adsorbents, it is necessary to design a new functional group that can selectively recognize and efficiently adsorb trace amounts of heavy metal ions from a highly concentrated matrix solution. An index indicating the affinity between metal ions and functional groups is the hard and soft acids and bases (HSAB) theory. The concept underlying the HSAB theory can be summarized as a simple rule: hard species favor interacting with hard species, and soft species tend to favor interacting with soft species. Based on this theory, the oxygen-based and nitrogen-based functional groups such as IDE, IDA, and EDA are classified into the “hard base” and “medium base.” Moreover, these functional groups exhibit relatively high affinities for light metal ions. Therefore, the oxygen-based and nitrogen-based functional groups are not necessarily optimal for the capturing of heavy metal ions. Meanwhile, it is well established that sulfur is a relatively soft atom, and a sulfur-based functional group is classified as a “soft” base. A sulfur-based functional group is likely to exhibit a relatively high affinity for heavy metal ions than the oxygen-based and nitrogen-based functional groups. Therefore, it is considered that a metal adsorbent having a sulfur-based functional group can selectively and efficiently remove heavy metal ions from high-concentration alkali aqueous solutions such as Si wafer etchants.

The objective of this study was to synthesize a metal adsorbent having a sulfur-based functional group, with high affinity for heavy metals, by radiation-induced grafting and subsequent chemical modifications. In order to evaluate the metal adsorption capacity and selectivity of the synthesized metal adsorbent, we conducted batchwise metal adsorption tests. Furthermore, the metal adsorption performance under a highly alkaline condition (a 10 M NaOH aqueous solution at pH 15) was also evaluated.

### RESULTS AND DISCUSSION

#### Synthesis of Fibrous Grafted Metal Adsorbent with Piperazinyl-Dithiocarbamate Group. Radiation-Induced Emulsion Grafting

Fibrous grafted metal adsorbent with the piperazinyl-dithiocarbamate (PZ-DTC) group was synthesized by a radiation-induced emulsion grafting technique and subsequent chemical modifications. The synthesis scheme of the fibrous grafted metal adsorbent with the PZ-DTC group is shown in Figure 1. In this study, the fibrous grafted metal...
adsorbent with PZ-DTC was synthesized through two chemical modification pathways.

GMA and chloromethylstyrene (CMS) have been used as grafting monomers because these monomers can easily introduce functional groups onto the graft chains by chemical modification after grafting onto the trunk polymer. It is well known that CMS is more carcinogenic than GMA. For this reason, CMS is very difficult to use in adsorbent manufacturing plants and is not a very suitable monomer from an industrial point of view. In this study, the GMA was used as a grafting monomer and a polyethylene-coated polypropylene nonwoven fabric (PE/PP-NF) was used as a trunk material.

Regarding the grafting technique, it has been reported that emulsion grafting proceeded the graft polymerization effectively, and in the case of the vinyl acetate monomer, the value of degree of grafting (Dg [%]) of emulsion grafting enhanced 100 times higher compared with using an organic solvent such as methanol. It has been found that polyoxyethylene (20) sorbitan monolaurate (Tween 20) is a suitable surfactant for the stabilization of GMA micelle in water. For these reasons, we adopted GMA emulsion grafting in this study. As for the degree of grafting value, when Dg is 200%, the molar density of epoxy group is 4.7 mmol/g-grafted PE/PP-NF. If the conversion of the epoxy group is assumed to be greater than 50% in the amination step, the PZ-DTC group density of the synthesized adsorbent would be at least 1.6 mmol-PZ-DTC/g-adsorbent. This value is comparable to those of commercially available resins and is sufficient for practical use as a metal adsorbent.

Therefore, the GMA-grafted PE/PP-NF (PE/PP-NF-GMA) was used as a graft chain because it does not have a reaction site with the epoxy group. Therefore, to introduce the PZ-DTC groups onto the GMA-graft chain, a highly concentrated PZ solution was used. In the amination of PZ, only one amine group density of each adsorbent. The dithiocarbamate (DTC) group was introduced into the GMA-grafted polymer by the ring-opening reaction of the epoxy group of the GMA-graft chain. Dipotassium piperazine-1,4-bis(carbodiithioate) has PZ-DTC groups. Although this reagent functions as a chelating reagent for heavy metals, it cannot be introduced directly onto the GMA-graft chain because it does not have a reaction site with the epoxy group. Therefore, to introduce the PZ-DTC groups onto the GMA-graft chains in this study, a two-step chemical modification consisting of the amination with piperazine (PZ) (step 1) and the subsequent dithiocarbamation with carbon disulfide (CS₂) (step 2) was attempted.

It is well established that in general, the type of solvent substantially influences the degree of amination (Da [%]) in the amination process. Therefore, the effect of the solvent on Da was investigated, and these results are summarized in Table 1. The PZ group density (PZ density [mmol-PZ/g-adsorbent]), self-cross-linked PZ ratio (C-PZ ratio [%]), and PZ-DTC group density (PZ-DTC density [mmol-PZ-DTC/g-adsorbent]) are also listed in this table. In the case where water was used as the solvent, the Da, PZ density, and PZ-DTC group density were 5.2%, 0.244 mmol-PZ/g-adsorbent and 0.005 mmol-PZ-DTC/g-adsorbent, respectively. These values were too low for metal adsorbents.

Meanwhile, in the case where organic solvents were used, the amination of PZ could be performed efficiently as compared with the water solvent, and Da exceeded 50% regardless of the organic solvent types. However, even after a 24 h amination, Da remained at approximately 50 and did not attain 100%. Additionally, the PZ-DTC group densities of the final products (PE/PP-NF-g-GMA-PZ-DTC) were considerably lower than the values predicted based on the PZ densities of each adsorbent. The dithiocarbamate (DTC) group was introduced onto only 12% or less of the existing PZ group in the adsorbent. The reason for these lower PZ-DTC densities was considered to be that most of the PZ was self-cross-linked in the GMA-graft chain. That is, two nitrogen atoms of PZ both reacted quickly with two epoxy groups on the GMA-graft chains, and the self-cross-linking structures of GMA-graft chains were formed through PZ, as shown in Figure 2. The C-

| amination condition (PZ conc. solvent) | Da [%] | PZ density [mmol-PZ/g] | C-PZ ratio [%] | PZ-DTC density [mmol-PZ-DTC/g] |
|---------------------------------------|-------|------------------------|----------------|-------------------------------|
| 0.5 M PZ/H₂O                          | 5.2   | 0.244                  | 0.005          |                               |
| 0.5 M PZ/ethanol                      | 51.6  | 1.982                  | 94.6           | 0.106                         |
| 0.5 M PZ/n-propanol                   | 51.1  | 1.983                  | 95.0           | 0.098                         |
| 0.5 M PZ/n-butanol                    | 51.1  | 1.964                  | 93.3           | 0.131                         |
| 0.5 M PZ/DMSO                         | 57.5  | 2.185                  | 88.9           | 0.242                         |
| 0.5 M PZ/DMF                          | 58.4  | 2.236                  | 88.0           | 0.268                         |
| 0.5 M PZ/5% DMSO                      | 59.0  | 2.267                  | 89.0           | 0.249                         |
| 0.5 M PZ/ethanol                      | 51.6  | 1.982                  | 94.6           | 0.106                         |
| 1.0 M PZ/ethanol                      | 54.9  | 2.125                  | 92.1           | 0.167                         |
| 2.0 M PZ/ethanol                      | 60.8  | 2.282                  | 92.1           | 0.179                         |
| 5.0 M PZ/ethanol                      | 72.5  | 2.632                  | 86.4           | 0.358                         |
| 0.25 M NBpz/H₂O                       | 96.2  | 2.496                  | 0.0             | 2.122                         |

*Including the Boc group, NBpz density [mmol-NBpz/g].

Figure 2. Self-cross-linking structure of PZ in GMA-graft chains.

Table 1. Effect of Amination Condition on Da, PZ Density, C-PZ Ratio, and PZ-DTC Density

PZ ratio exceeded 85% regardless of the organic solvent types because of the rapid amination of epoxy groups with PZ. Furthermore, observing the FT-IR spectra of PE/PP-NF-g-GMA-PZ-PZ samples with a high C-PZ ratio, it was proved that the self-cross-linking had occurred because several peaks derived from the epoxy group disappeared completely. In the case where ethanol was used, the PZ-DTC density was 0.106 mmol-PZ-DTC/g-adsorbent, which was 1/20 of the value predicted based on the introduction amount of PZ. This low PZ-DTC density was also insufficient for practical use.

To suppress the self-cross-linking of the PZ, that is, to increase the proportion of noncross-linked PZ groups in the GMA-graft chains, a highly concentrated PZ solution was used. With regard to the noncross-linked PZ group, only one amine group of the PZ group is bound to the epoxy group of the GMA-graft chain (resembling a pendant) so that the DTC...
group could be efficiently introduced in the next dithiocarbam- 
mation process with CS₂. As presented in Table 1, the self-
cross-linking of the PZ could be suppressed slightly by using 
the highly concentrated PZ solution. The PZ-DTC density of 
the 5 M PZ-ethanol became 0.358 mmol-PZ-DTC/g-
adsorbent, which was approximately 3.5 times higher than 
that of the 0.5 M PZ-ethanol solution. As mentioned above, 
although this attempt to use highly concentrated PZ solution 
could improve the metal adsorption performance marginally, 
most of the PZ introduced onto the GMA-graft chains were 
consumed for self-cross-linking. The C-PZ ratio of the fibrous 
grafted adsorbent treated with 5 M PZ-ethanol became 86.4%, 
which was also inadequate for practical use.

Introduction of PZ-DTC Group through NBPZ. In the case 
of the introduction of the PZ-DTC group through PZ, the self-
cross-linking of PZ could not be completely suppressed. This is 
because the PZ had two NH groups that functioned as reactive 
sites with the epoxy group. Therefore, in the experiment 
described in this section, N-(tert-butoxycarbonyl)piperazine 
(N-Boc-piperazine, NBPZ) was used as an amination reagent 
in order to prevent self-cross-linking of PZ completely. The 
NBPZ was a PZ derivative exhibiting a structure in which a 
NH group of PZ was protected by the tert-butoxycarbonyl 
(Boc) group, and the other NH group remained intact. The 
Boc group is one of the most widely used amine-protecting 
groups. The amine group protected with a Boc group loses its 
reactivity. The Boc group is stable under a basic hydrolysis 
condition. In addition, it is well established that the Boc group 
can be conveniently deprotected under acidic conditions to 
obtain the free amine, which can be used for further chemical 
modifications. In the case where NBPZ was used as an 
amination reagent, the self-cross-linking of PZ could be 
completely prevented. This was because the NBPZ had only 
one NH group that could contribute to the amination. As a 
result, Da, (NBPZ density [mmol-NBPZ/g-adsorbent]), and the C-PZ ratio of the PE/PP-NF-GMA-NBPZ sample were 
96.2%, 2.496 mmol-NBPZ/g-adsorbent, and 0%, respectively 
(Table 1). Furthermore, the effect of the amination time on Da was investigated. It was observed that the amination using NBPZ proceeded smoothly and rapidly, 
and it was completed within 1 h. The Boc groups of NBPZ did 
not cleave even after 24 h because this amination process was 
carried out under a basic condition (pH 10.5). Consequently, 
the self-cross-linking reaction through PZ did not occur.

To introduce the DTC group onto the NBPZ group, the 
Boc group of NBPZ must be deprotected. Therefore, the effect 
of the deprotection temperature and time on the degree of 
deprotection of the Boc group (Dd [%]) when the PE/PP-NF-
g-GMA-NBPZ sample was treated with a 1 M HCl aqueous 
solution was investigated. As expected, higher deprotection 
temperatures resulted in faster deprotection of the Boc group. 
In particular, the deprotection was remarkably accelerated at 
extremely high temperatures. As is evident from Figure 3, at 50 
°C, complete deprotection of the Boc group required 
approximately 3 h. In contrast, at 80 °C, complete 
deprotection required 1 h, which is less than one-third of the 
time required at 50 °C. The above results reveal that the 
optimum temperature and time for complete deprotection of 
the Boc group in the PE/PP-NF-g-GMA-NBPZ sample were 
80 °C and 1 h or higher, respectively. In addition, in this Boc-
deprotection process, the self-cross-linking reaction of PZ did 
not occur after deprotection. This was because there was no

Figure 3. Effect of deprotection temperature on Dd of the Boc group of NBPZ.

epoxy group capable of reacting with the terminal NH groups 
of Boc-deprotected NBPZ.

We succeeded in completely preventing self-cross-linking of 
PZ by first introducing NBPZ onto the GMA-graft chain and 
then deprotecting its Boc groups. Next, the effect of the 
dithiocarbamation condition with CS₂ on the PZ-DTC density 
was investigated. The results are provided in Figure 4. In cases 
of the 2 wt % CS₂ solution, 32 wt % 1 M NaOH aqueous 
solution, and 66 wt % methanol, although the PZ-DTC density 
of the final product was improved with an increase in the 
reaction temperature, the introduction rate of the DTC group 
to the PZ group of the final products did not attain 100% even 
after 24 h. If it is assumed that the introduction rate of the 
DTC group to the PZ group of the final products is 100%, the 
PZ-DTC density of the final product is likely to be 2.516 
mmol-PZ-DTC/g-adsorbent. After 24 h of the 2 wt % CS₂ 
treatment, the PZ-DTC densities at 20, 30, and 40 °C were 
0.283, 1.004, and 1.669 mmol-PZ-DTC/g-adsorbent, respec-
tively. The introduction rate of the DTC group to the PZ 
group at 20, 30, and 40 °C were 11, 39, and 66%, respectively.

To improve the PZ-DTC density, it is generally preferable to 
perform the CS₂ treatment at a high reaction temperature. 
However, because the boiling point of CS₂ is 46.3 °C, 
increasing the reaction temperature above 45 °C is hazardous. 
Therefore, next, we attempted treatment with a highly 
concentrated CS₂ solution. As shown in Figure 4, in cases of 
20 wt % CS₂ solution, 35 wt % 10 M NaOH aqueous solution, 
and 45 wt % methanol, the dithiocarbamation with CS₂ was 
accelerated remarkably. The PZ-DTC density leveled off after 
a 12 h dithiocarbamation, and the highest obtained PZ-DTC 
density was 2.122 mmol-PZ-DTC/g-adsorbent. At this time, 
the introduction rate of the DTC group onto the PZ group 
was approximately 85%. The fact that the experimentally 
obtained values of the PZ-DTC density and the introduction rate of the
DTC group onto the PZ group were lower than the theoretical values appears to be owing to the steric hindrance of CS₂. Although this PZ-DTC density of the metal adsorbent synthesized through NBPZ was marginally lower than the theoretical value, the PZ-DTC density of the metal adsorbent synthesized through NBPZ became approximately 6 times higher than that of the metal adsorbent synthesized through PZ. Specifically, the PZ-DTC density of the fibrous grafted adsorbent treated with 5 M phosphoric acid solution was 0.338 mmol-PZ-DTC/g-adsorbent. Meanwhile, the PZ-DTC density of the fibrous grafted adsorbent synthesized through NBPZ attained 2.122 mmol-PZ-DTC/g-adsorbent. Moreover, its PZ-DTC density was sufficient for its practical use as a metal adsorbent. The above results reveal that the self-cross-linking of PZ in the synthesis of a metal adsorbent with a PZ-DTC group can be prevented by interposing NBPZ. Thereby, a remarkable metal adsorbent exhibiting a high functional group density can be synthesized.

**FTIR-ATR Analysis.** The pristine PE/PP-NF, the grafting of GMA onto PE/PP-NF, the introduction of NBPZ group to GMA-graft chain, the deprotection of Boc group from NBPZ group, and the introduction of DTC group to PZ group can be verified using an attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometer (model Spectrum One equipped with ATR accessory, Perkin-Elmer Inc., MA, USA). The samples were scanned in the range of 250–2300 cm⁻¹ with a resolution of 1 cm⁻¹. Figure 5 shows the results of the FTIR analysis. The FTIR spectrum of pristine PE/PP-NF, Figure 5A, had peaks characteristic of its olefinic nature: 1472 cm⁻¹ (CH₂, ben.), 1462 cm⁻¹ (CH₂, ben.), 1375 cm⁻¹ (CH₃ wag. and/or sym. CH₃ movements), 731 cm⁻¹ (CH₂ rock.), and 718 cm⁻¹ (CH₃ rock.). After grafting with GMA, as shown in Figure 5B, several new peaks attributed to the GMA-graft chain appeared in the spectrum of the PE/PP-NF-GMA: 1724 cm⁻¹ (C=O str.), 1254 cm⁻¹ (−C=O− str.), 1146 cm⁻¹ (−C−O− str.), 905 cm⁻¹ (antisym. epoxy group def.), 842 cm⁻¹ (sym. epoxy group def.), and 757 cm⁻¹ (epoxy group def.). Postgrafting with NBPZ resulted in the ring-opening reaction of the epoxy groups and introduction of the NBPZ group. As shown in Figure 5C, the epoxy ring-opening reaction led to the disappearance of the epoxy group peaks, and the introduction of the NBPZ group appeared in the appearance of new peaks: 1693 cm⁻¹ (C=O str. in Boc group), 1364 cm⁻¹ (CH₂ ben. tert-butyl group in Boc group), and 1165 cm⁻¹ (−C−N str.). After deprotection, as shown in Figure 5D, several peaks attributed to the Boc group disappeared, and a new broad peak appeared at around 1595 cm⁻¹, which is attributed to the NH stretching mode. After dithiocarbamation, as shown in Figure 5E, several new peaks attributed to the DTC group appeared in the spectrum of the PE/PP-NF-GMA-PZ-DTC: 1406 cm⁻¹ (C=S str.), 1211 cm⁻¹ (C=S str.), 988 cm⁻¹ (asym. CS₂ str.), and 919 cm⁻¹ (sym. CS₂ str.). These features indicate that the PZ-DTC groups were successfully imparted to the PE/PP-NF-GMA sample through the three-step chemical modifications consisting of amination with NBPZ, deprotection of Boc group with HCl, and dithiocarbamation with CS₂. Table 2 presents the summary of the properties of the fibrous grafted metal adsorbent with the PZ-DTC group synthesized through NBPZ.

| Table 2. Summary of the Properties of the Fibrous Grafted Metal Adsorbent with the PZ-DTC Group |
|-----------------------------------------------|
| parameter                                      | value                        |
| functional group                               | piprazinyl-dithiocarbamate (PZ-DTC) group |
| functional group density                       | 2.112 mmol-PZ-DTC/g-adsorbent |
| self-cross-linked PZ ratio                     | 0%                           |
| fiber diameter                                 | 25 μm                        |
| mass per unit area                             | 330 g/m²                     |

**Metal Adsorption Tests.** Saturated Metal Adsorption Capacity for Each Metal Ion with Single-Metal Mode. Table 3 is the summarized results of batchwise metal adsorption tests using single-metal-ion aqueous solutions.

**Table 3. Metal Adsorption Capacity of Fibrous Grafted Metal Adsorbent with the PZ-DTC Group by Batchwise Adsorption Tests Using Single-Metal-Ion Aqueous Solution**

| metal ion | metal adsorption capacity [mmol/g-adsorbent] | metal ion | metal adsorption capacity [mmol/g-adsorbent] |
|-----------|---------------------------------------------|-----------|---------------------------------------------|
| B(OH)₄⁻   | 0.000                                       | Cu²⁺      | 1.903                                       |
| Mg²⁺      | 0.669                                       | Zn²⁺      | 0.867                                       |
| Ca²⁺      | 0.872                                       | Sr²⁺      | 0.705                                       |
| Mn²⁺      | 0.878                                       | Cd²⁺      | 0.988                                       |
| Cu²⁺      | 0.851                                       | Ba²⁺      | 0.711                                       |
| Ni²⁺      | 0.829                                       | Pb²⁺      | 1.061                                       |

with the synthesized adsorbent with the PZ-DTC group. In this adsorption tests, the metal ion aqueous solution containing a single element was used. As expected, the synthesized adsorbent having the PZ-DTC group could adsorb cationic species. In particular, the fibrous grafted metal adsorbent having the PZ-DTC group exhibits a high adsorption capacity for Cu²⁺ (1.903 mmol-Cu²⁺/g-adsorbent). Meanwhile, the metal adsorption capacities for the light metals such as Mg²⁺, Sr²⁺, and Ba²⁺ became marginally smaller than those for the heavy metals. The above results reveal that the synthesized adsorbent with the PZ-DTC group functioned as a metal adsorbent, and its metal adsorption capacity was sufficient for practical use.

**Metal Ion Selectivity with Binary Mixed Metal Mode.** Secondly, the metal ion selectivity of the fibrous grafted metal adsorbent with the PZ-DTC group was examined through batchwise adsorption tests using metal ion aqueous solutions containing two elements, such as Pb²⁺ and another metal ion. This adsorption test (Test 1), six types of binary mixed metal ion aqueous solutions (containing Na⁺/Pb²⁺, Mg²⁺/Pb²⁺, Ca²⁺/Pb²⁺, Cd²⁺/Pb²⁺, Co³⁺/Pb²⁺, and Cu²⁺/Pb²⁺) were used. The results are summarized in Table 4 (A). As shown in the table, in the case of the Na⁺/Pb²⁺ mixed aqueous...
solution, only Pb\textsuperscript{2+} (a heavy metal ion) was selectively adsorbed, and Na\textsuperscript{+} was not adsorbed. In the cases of Mg\textsuperscript{2+}/Pb\textsuperscript{2+}, Ca\textsuperscript{2+}/Pb\textsuperscript{2+}, Co\textsuperscript{2+}/Pb\textsuperscript{2+}, and Cd\textsuperscript{2+}/Pb\textsuperscript{2+} mixed aqueous solutions, Pb\textsuperscript{2+} (the heavier metal ion) was selectively adsorbed. The adsorption capacity of Pb\textsuperscript{2+} was over 3 times that of the adsorption capacities of Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Co\textsuperscript{2+}, and Cd\textsuperscript{2+}. The metal adsorption capacities of each metal ion per gram of the adsorbent were 0.279 mmol-Mg\textsuperscript{2+}/0.958 mmol-Pb\textsuperscript{2+}, 0.240 mmol-Ca\textsuperscript{2+}/0.818 mmol-Pb\textsuperscript{2+}, 0.208 mmol-Co\textsuperscript{2+}/1.021 mmol-Pb\textsuperscript{2+}, and 0.127 mmol-Cd\textsuperscript{2+}/0.828 mmol-Pb\textsuperscript{2+}, respectively. In this Cu\textsuperscript{2+} adsorption test, a 100 ppm Cu\textsuperscript{2+} aqueous solution adjusted to pH 15 with 10 M NaOH was used, and the result is summarized in Table 5. For comparison, the results of fibrous grafted metal absorbents with other functional groups such as diol (Diol), sulfonic acid (SA), iminodiacetic acid (IDA), ethylenediamine (EDA), and iminodethanol groups (IDE) are listed in Table 5. The Diol-, SA-, IDA-, EDA-, and IDE-type absorbents were synthesized according to previously reported methods by Kim et al., Ogawa et al., Dafader et al., Sekine et al., and Ozawa et al., respectively.\cite{42–46}

In this batchwise adsorption test, a marginal amount of Cu\textsuperscript{2+} was dissolved in a high-concentration NaOH aqueous solution in order to adjust the pH to 15. The molar concentrations of Na\textsuperscript{+} and Cu\textsuperscript{2+} in the 100 ppm Cu\textsuperscript{2+} aqueous solution at pH 15 corresponded to 10 M and 1.573 mM, respectively. Therefore, the Na\textsuperscript{+} concentration was approximately 6400 times higher than the Cu\textsuperscript{2+} concentration, and the fibrous grafted metal absorbents were compelled to selectively adsorb a marginal amount of Cu\textsuperscript{2+} from the solution with the high concentration of Na\textsuperscript{+}. As illustrated in Table 5, the Diol-type absorbent could hardly adsorb Cu\textsuperscript{2+}. This was expected because the diol group is a hydrophilic group and has no metal ion adsorption capability. Similarly, the SA-type absorbent could hardly adsorb Cu\textsuperscript{2+}.
selectively from a high-concentration Na\(^+\) aqueous solution at pH 15. The Cu\(^{2+}\) adsorption capacity per gram of the SA-type adsorbent under a highly alkaline condition (pH 15) was 0.005 mmol-Cu\(^{2+}\)/g-adsorbent. This exceptionally low Cu\(^{2+}\) adsorption capacity of the SA-type adsorbent was considered to be because the SA group, whose metal ion selectivity was generally low, adsorbed metal ions by electrostatic interaction.

Meanwhile, in the case of the metal adsorbent with chelating functional groups such as PZ-DTC, IDA, EDA, and IDE groups, although each chelate-type adsorbent could selectively adsorb Cu\(^{2+}\) even from a high-concentration Na\(^+\) aqueous solution at pH 15, the Cu\(^{2+}\) adsorption capacities varied substantially depending on the type of chelate groups. The IDA- and EDA-type adsorbents could selectively remove a trace amount of Cu\(^{2+}\), which was dissolved in a high-concentration Na\(^+\) aqueous solution at pH 15. The Cu\(^{2+}\) adsorption capacities per gram of the IDA- and EDA-type adsorbents under a highly alkaline condition (pH 15) were 0.082 and 0.128 mmol-Cu\(^{2+}\)/g-adsorbent, respectively. In addition, the Cu\(^{2+}\) adsorption capacity of the IDE-type adsorbent, which was used to clean the highly alkaline etching aqueous solution of Si wafer and exhibited the highest performance in a previous study, at pH 15, was approximately 0.314 mmol-Cu\(^{2+}\)/g-adsorbent. The reason for these lower Cu\(^{2+}\) adsorption capacities was considered to be that the constituent atoms of IDA, EDA, and IDE groups contained oxygen and nitrogen atoms, which exhibit a high affinity for Na\(^+\). Therefore, it is considered that various chelate groups such as IDA, EDA, and IDE groups could adsorb Cu\(^{2+}\) and Na\(^+\) simultaneously.

Meanwhile, in the case of the PZ-DTC-type adsorbent, the Cu\(^{2+}\) adsorption capacity at pH 15 improved dramatically, attaining 0.754 mmol-Cu\(^{2+}\)/g-adsorbent. This was approximately 2.4 times higher than that of the IDE-type adsorbent, which had been the highest level until then. The reason for this higher Cu\(^{2+}\) adsorption capacity was considered to be that the constituent atom of the PZ-DTC group did not contain an oxygen atom (which exhibits a high affinity for Na\(^+\)) and contained a sulfur atom (which exhibits a low affinity for Na\(^+\)). Therefore, it is considered that the PZ-DTC groups could preferentially adsorb Cu\(^{2+}\) while excluding Na\(^+\). Additionally, regarding the stability of the adsorbent at pH 15, the PZ-DTC-type adsorbent was not physically destroyed and the introduced PZ-DTC groups were not released from the adsorbent, even after being immersed in the highly alkaline solution at pH 15 for 1 week.

The above results revealed that the fibrous grafted metal adsorbent with the PZ-DTC type adsorbent did not lose its metal adsorption function even under a highly alkaline condition (pH 15). In addition, it was observed that the PZ-DTC-type adsorbent could recover Cu\(^{2+}\) efficiently and selectively from a high-concentration Na\(^+\) aqueous solution at pH 15.

CONCLUSIONS

A novel metal adsorbent with the PZ-DTC group for heavy metal ions was developed by radiation-induced emulsion grafting of GMA onto PE/PP-NF and subsequent chemical modifications involving amination with NBPZ, deprotection with HCl, and dithiocarbamation with CS\(_2\). In the amination step, when the metal adsorbent was synthesized through NBPZ, self-cross-linking of PZ could be completely suppressed. Thereby, the metal adsorbent exhibiting a practically sufficient PZ-DTC density was obtained. The PZ-DTC density of the metal adsorbent synthesized through NBPZ attained 2.122 mmol-PZ-DTC/g-adsorbent, which was approximately 6 times higher than that of the metal adsorbent synthesized through PZ.

The metal adsorbent with the PZ-DTC group exhibited higher adsorption performance for heavy metal ions than for light metal ions and specific selectivity for Pb\(^{2+}\) and Cu\(^{2+}\). In particular, the Cu\(^{2+}\) adsorbing function of this adsorbent could function even under a highly alkaline condition (pH 15). Moreover, it could recover Cu\(^{2+}\) efficiently and selectively from a high-concentration Na\(^+\) aqueous solution at pH 15. The Cu\(^{2+}\) adsorption capacity of the adsorbent was approximately 2.4 times higher than that of the metal adsorbent with the IDE group. Therefore, it is apparent that the metal adsorbent with the PZ-DTC group synthesized by the graft polymerization technique and subsequent chemical modifications is a potential and long-life material for removing metal ions from highly alkaline aqueous solution such as etching solutions for Si wafer.

EXPERIMENTAL SECTION

Materials. PE/PP-NF was supplied by Kurashiki Textile Manufacturing Co., Ltd. (Osaka, Japan) and used as a trunk material for the metal adsorbent. The average fiber diameter and the mass per unit area of the PE/PP-NF were 13 μm and 62 g/m\(^2\), respectively. GMA was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Tween 20, which was used as a nonionic surfactant for preparing the monomer emulsion, was obtained from Kanto Chemical Co., Inc. (Tokyo). Dipotassium piperazine-1,4-bis(carboxidotiate) was obtained from Oriental Giken Co., Ltd. (Saitama, Japan). All the other chemicals such as PZ, NBPZ, CS\(_3\), NaOH, HCl, methanol, ethanol, n-propanol, n-butanol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), 1,4-dioxane (DOX), inorganic metal salts, and so forth were also obtained from Kanto Chemical. GMA and other reagents were of highest commercially available purity and used as received without further purification. The water used for monomer emulsions was purified with a Milli-Q deionization system (Nihon Millipore K.K., Tokyo).

Synthesis of Fibrous Grafted Metal Adsorbent with PZ-DTC Group. Radiation-Induced Emulsion Grafting. The radiation-induced emulsion grafting procedure was almost the same as in the previous studies. The PE/PP-NF was cut into 3 × 3 cm square pieces. These were placed in polyethylene bags. The air inside the polyethylene bags was replaced with nitrogen gas. The PE/PP-NF samples were irradiated to produce starting sites of the grafting with an electron beam at a dose of 20 kGy. This electron beam irradiation was applied using a low-energy electron accelerator (type: EC250/30/180LS, Iwasaki Electric Co., Ltd., Tokyo) under the following conditions: an acceleration voltage of 250 kV and an irradiation current of 2.7 mA. Then, the irradiated PE/PP-NF samples were placed in a glass ampoule from which air was evacuated immediately using a vacuum line. Subsequently, a previously deaerated GMA emulsion (5 wt % GMA, 0.5 wt % Tween20/94.5 wt % H\(_2\)O) was drawn into the glass ampoule. The grafting was carried out by keeping the glass ampoule in a thermostated water bath at 40 °C for 1 h. After grafting, the GMA-grafted PE/PP-NF (PE/PP-NF-g-GMA) samples were washed repeatedly with methanol to remove the remaining nonreacted GMA and dried in vacuo. The amount of GMA grafted onto PE/PP-NF was expressed in terms of the Dg and was calculated by the following equation.
where \( W_0 \) and \( W_i \) are the weights of the PE/PP-NF before and after grafting, respectively. Five parallel samples were grafted, and the Dg value is reported as an average.

**Chemical Modification through PZ.** The introduction of the PZ-DTC group through PZ was carried out by a two-step chemical modification. First, the PE/PP-NF-g-GMA sample was aminated with a 0.5 M \( \text{PZ} \) solution at 80 °C for 24 h to introduce \( \text{PZ} \) groups into the GMA-graft chains of PE/PP-NF-g-GMA. After amination, the sample of PE/PP-NF-g-GMA (PE/PP-NF-g-GMA-PZ) to which the PZ groups were introduced was washed repeatedly with deionized water to remove the remaining nonreacted PZ. Second, the PE/PP-NF-g-GMA-PZ sample was treated further with a CS\(_2\) solution (20 wt % \( \text{CS}_2 \) at 40 °C for 24 h) to introduce the DTC group at the terminal nitrogen on the PZ group. After dithiocarboxylation, the dithiocarbamated PE/PP-NF-g-GMA-PZ (PE/PP-NF-g-GMA-PZ-DTC) sample was washed repeatedly with methanol and deionized water to eliminate the remaining nonreacted reagents. Then, it was dried in vacuo to obtain the fibrous grafted metal adsorbent having the PZ-DTC group, which is the objective of this study. The \( \text{Da} \), PZ density, C-PZ ratio, and PZ-DTC density are defined as follows

\[
\text{Da} \; [\%] = 100 \times \left[ 142 \times \frac{(W_i - W_0)}{W_i - W_0} - 142 \right] \times \frac{1}{86}
\]

PZ density [mmol - PZ/g - adsorbent]  
\[
= 100 \times \frac{(W_i - W_0)}{86} \times \frac{1}{W_i}
\]

C - PZ ratio [\%] = 100 \left[ 1 - \frac{(W_i - W_0)}{99} \right] \times \frac{86}{(W_i - W_0)}

PZ - DTC density [mmol - PZ - DTC/g - adsorbent]  
\[
= 100 \times \frac{(W_i - W_0)}{99} \times \frac{1}{W_i}
\]

where \( W_0 \), \( W_i \), and \( W_2 \) are the weights of PE/PP-NF-g-GMA-PZ and PE/PP-NF-g-GMA-PZ-DTC, respectively. The numbers 142, 86, and 99 are the molecular weights of GMA, PZ, and \( \text{CS}_2\)-Na, respectively.

**Metal Absorption Tests.** The metal adsorption capacity and selectivity of the synthesized fibrous grafted metal adsorbent with the PZ-DTC group was evaluated through batchwise adsorption tests. In this study, 12 types of metal ions (\( \text{B(OH)}_4^- \), \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{Mn}^{2+} \), \( \text{Co}^{2+} \), \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Ba}^{2+} \), and \( \text{Pb}^{2+} \)) were used as the target elements. To evaluate the saturated metal adsorption capacity of each metal ion, a metal ion aqueous solution containing a single element was used. To evaluate the metal ion selectivity of the fibrous grafted metal adsorbent with the PZ-DTC group, a metal ion aqueous solution containing two elements (e.g., \( \text{Na}^+ / \text{Pb}^{2+} \) and \( \text{Co}^{2+} / \text{Ni}^{2+} \)) was used. The adsorption tests of the single metal ions and the binary mixed metal ions were conducted at pH 6. To evaluate the metal adsorption capacity under a highly alkaline condition, a Cu\(^{2+}\) aqueous solution adjusted to pH 15 was used.

Approximately 25 mg of fibrous grafted metal adsorbent was immersed in 100 mL of various metal ion aqueous solutions of 100 ppm for 24 h at room temperature with the stirring rate maintained at 300 rpm. After 24 h, the fibrous grafted metal adsorbent was removed from the metal ion aqueous solution, and the concentration of the remaining metal ion in each solution was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) (model Optima 8300, Perkin-Elmer Inc.). Before and after adsorption tests, the metal ion aqueous solutions were filtered through a membrane.
filter with a 0.2 micrometer pore size in order to remove the precipitates. The metal adsorption capacity (mmol/g-adsorbent) of the synthesized fibrous grafted metal adsorbent was calculated by the following equation

\[
\text{metal adsorption capacity [mmol/g - adsorbent]} = \left( \frac{C_0 - C}{A_{\text{metal}}} \right) \times \frac{V}{W_{\text{adsorbent}}}
\]

where \(C_0\) and \(C\) are the initial and final concentrations (ppm), respectively, of the metal ion in the aqueous phase; \(V\) is the volume of the metal ion aqueous solution (mL); \(A_{\text{metal}}\) is the atomic weight of each metal ion (mol/g); and \(W_{\text{adsorbent}}\) is the mass of the fibrous grafted metal adsorbent (mg).

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**Notes**

The authors declare no competing financial interest.

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