Molecular environment of Ni after its use for removal of CMP nanoparticle

Y.-L. Wei a,*, K.-W. Chen a, Y.-S. Peng a, H. Paul Wang b,c

a Department of Environmental Science and Engineering, Tunghai University, Taichung City 40704, Taiwan
b Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan
c Sustainable Environmental Research Center, National Cheng Kung University, Tainan 70101, Taiwan

A R T I C L E   I N F O

Keywords:
Ni K-edge XANES
Ni K-edge EXAFS
Nanoparticle
CMP waste water

A B S T R A C T

X-ray absorption spectroscopy (XAS) is employed to investigate the molecular environment around nickel that, in the form of nickel sulfate solution, has been added to precipitate nanoparticles in chemical mechanical polishing (CMP) waste water. After phase separation, for the liquid-phase sample, both the white line intensity in the normalized Ni K-edge X-ray absorption near edge structure (XANES) spectrum and the amplitude of the extended X-ray absorption fine structure (EXAFS) spectrum are enhanced due to the presence of solvation of water molecules, as compared to the solid-phase sample. Meanwhile, with the presence of water molecules, the coordination number increases; yet the Debye-Waller factor slightly decreases. The lack of chemical reduction of Ni²⁺ in the CMP solution is suggested as the main reason why the charge neutralization precipitation method through the use of Ni²⁺ is less effective than the system using Cu²⁺ to precipitate nanoparticles as previously reported.

1. Introduction

Nanoparticles can disperse in the living environment and may do great harm to the human body. It was pointed out in a previous report [1] that particle size affects the extent of damage inflicted on a rat. During wafer manufacture, chemical mechanical polishing (CMP) is an important process [2,3]. However, this process discharges great amount of wastewater containing nanoparticles. Frequently used nanoparticles in CMP process are silica, magnesia, alumina, and ceria [4]. Nanoparticles in the CMP wastewater have been a problem for most conventional particle control technology due to their nanoscale size [5–7]. In 1997, the Semiconductor International Association of USA set three main goals: to reduce the water usage by half, to keep the environment safe, and to maintain human health. To remove the nanoparticles, various techniques including floatation technology [8], electrocoagulation [4] along with precipitation around an electrode, and charge neutralization precipitation [9] have been developed. Among these methods, charge neutralization precipitation with copper sulfate has been demonstrated to significantly remove nanoparticles from wastewater [9], and Cu²⁺ ions were partially reduced to Cu[0]. However, with the addition of nickel ions, the precipitation rate of nanosilica particles was not as efficient as the case utilizing Cu²⁺ ions. Thus the nickel molecular environment that is related to the interaction between nanoparticles and nickel ions needs to be examined. XAS methods are employed in the present study to investigate the nickel molecular environment caused by this interaction.

2. Experimental

The CMP wastewater was sampled from a wafer manufacturing plant located in Central Science-based Industrial Park in central Taiwan. The pH value of the CMP wastewater is 7.3. The volume-average particle size of the total solid is around 90 nm with a particle size range 40–200 nm. Without any further pre-treatment, aliquots of 50 mL were mixed by the use of magnetic stirring at 250 rpm with 5 mL of nickel sulfate solution (containing 50.0 mg Ni²⁺) for 10 min. Upon finishing the mixing, the nanoparticles were allowed to precipitate at the bottom of containers for 5 min. The liquid phase was removed with a dropper and the solid phase was allowed to dry. The molecular environment of nickel in both the liquid phase and dry solid phase was then studied with X-ray absorption spectroscopy (XAS).

All Ni K-edge (8333 eV) XAS spectra were recorded in transmission mode at room temperature on the wiggler C (BL-17C) beamline at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. During the XAS experiments, the facility had a ring storage energy of 1.5 GeV, and a beam current of 120–200 mA. The span of the monochromator in the wiggler C beamline is 4–15 keV, with an energy resolution of 1.9 × 10⁻⁴. Ni references used for comparison in the present study were NiO, Ni(NO₃)₂·6H₂O, and Ni(OH)₂; all of them are of reagent

* Corresponding author at: #381, Sector 3, Taichung-Harbour Road, Taichung 40704, Taiwan. Tel.: +886 4 2359 1368; fax: +886 4 2359 6858.
E-mail address: yulin@thu.edu.tw (Y.-L. Wei).
0168-9002/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
grade and high purity. WinXAS 3.0 software was used for data reduction [10].

3. Results and discussion

Fig. 1 depicts the difference between the normalized Ni K-edge XANES spectra from the solid-phase and liquid-phase samples. It shows that the liquid-phase sample has a greater intensity in white band than the solid-phase sample. The liquid-phase sample also has slightly greater photon energy with an approximately +1.0 eV energy shift. This observation is suggested to be due to the formation of hydrogen bonding between nickel compounds and their hydration shell; the formed hydrogen bonding might cause the oxygen in the first coordinated shell to pull the electron away from nickel, and this would shift the edge jump to greater photon energy.

To obtain a better insight into the difference in the XANES from the solid-phase and liquid-phase samples, these spectra were simulated with linear combination of various nickel references, and the results are shown in Fig. 2. The liquid-phase sample can be satisfactorily simulated with pure nickel sulfate; this fact indicates that although nickel sulfate is water soluble, the nickel cations and sulfate anions still stay close to each other due to electrostatic attraction force in water. Thus the Ni XANES spectra of the liquid-phase sample and the nickel sulfate reference quite resemble each other. In contrast, to well simulate the solid-phase sample, other than nickel sulfate, nickel hydroxide and nickel oxide references are needed. The simulation results show that nickel in the solid-phase sample is approximately 54% nickel sulfate + 34% nickel hydroxide + 12% nickel oxide. To explain the mechanism of the coagulation of the nanoparticles with addition of nickel sulfate, the present study suggests that the form of the nickel hydroxide can be considered as Ni$^{2+}$ - [(OH)$_2$]-Si - [(OH)$_2$]-Ni$^{2+}$, which results from the electrostatic attraction between Ni$^{2+}$ and the negatively charged nanosilica that has a zero potential charge at approximately pH 2–3. In the present study, the pH value of the CMP waste water is 7.3; thus the nanosilica particles carry negative charge and they tend to attract Ni$^{2+}$ through electrostatic force. A blank test was performed and the result confirmed that Ni$^{2+}$ does not precipitate in aqueous solution at pH 7.3.

![Fig. 1](image1.png)  
**Fig. 1.** Difference between the normalized Ni K-edge XANES spectra from the solid-phase and liquid-phase samples.

![Fig. 2](image2.png)  
**Fig. 2.** Results from XANES simulation of the liquid-phase and solid-phase samples with various nickel references.

![Fig. 3](image3.png)  
**Fig. 3.** Fourier transforms of the EXAFS spectra from the liquid-phase and solid-phase samples in R space.
Fig. 3 shows the Fourier transforms of the EXAFS spectra from the "liquid" and "solid" samples in radial space (R space). The solid curves represent the experimental spectra, and the open-circle curves are the first-shell fitting spectra in the range 1.028–2.085 Å. The spectrum of the "liquid" sample is characterized with higher amplitude in the first-shell peak, as compared with the "solid" sample. The amplitude of the first coordination shell is affected by the magnitude of coordination number and the degree of the Debye–Waller factor; greater amplitude implies higher coordination number and/or greater disorder of the shell. As indicated in Table 1, the coordination numbers of the first shell for the liquid and solid samples are 6.12 and 3.87, respectively, and the respective Debye–Waller factors are 0.00496 and 0.00598. The reason for the great difference in the first-shell coordination number is given as follows. For the liquid sample, we suggest that water molecules have moved to a position that was close enough to affect the molecular structure of the first coordination shell and contribute to the coordination number of the first Ni–O shell. This fact is similar to the observation previously reported for CrO$_4^{2-}$ in aqueous solution [11]. However, the results in the present study indicate that the Debye–Waller factor ($\sigma^2$) is not enhanced by the incorporation of oxygen of water in the first coordination shell. In fact, the Debye–Waller factor is slightly reduced in the liquid sample, compared to the solid sample, and this observation is contrary to the previous study [11]. This implies that the water molecules are positioned with very good order in the first coordination shell around nickel.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>Coordination number at R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>0.00496</td>
<td>6.12 at 2.04</td>
</tr>
<tr>
<td>Solid</td>
<td>0.00598</td>
<td>3.87 at 2.04</td>
</tr>
</tbody>
</table>

**4. Conclusion**

Both the white line intensity in the normalized XANES spectrum and the amplitude of the EXAFS spectrum were enhanced due to the presence of water molecules in the nickel sulfate-containing liquid sample. The coordination number and Debye–Waller factor of the first coordination shell were affected with the water molecules which were suggested to move into the first coordination shell around the nickel target element in the liquid-phase sample. The coordination number increases with the presence of water molecules; meanwhile, the Debye–Waller factor slightly decreases.

The lack of chemical reduction of Ni$^{2+}$ is the main reason why the charge neutralization precipitation method is less effective by the use of Ni$^{2+}$ than the system that used Cu$^{2+}$ to precipitate nanoparticles.

**Acknowledgements**

This research was supported by the Taiwan National Science Council. We thank Dr. J.F. Lee and other staff of the Taiwan National Synchrotron Radiation Research Center (NSRRC) for their XAS experimental assistances.

**References**