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Mechanism of Ni Removal from Si Materials Using Hydrogen Cyanide Aqueous Solutions

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The mechanism of Ni removal from SiO_2-covered Si specimens by HCN aqueous solutions has been investigated by means of total reflection X-ray fluorescence spectroscopy and X-ray photoelectron spectroscopy measurements. Ni contaminants on the SiO_2 surface are present in the form of SiO-NiOH. The removal mechanism consists of two steps, i.e., an initial fast process followed by a slow process. The rate-determining steps of both the processes are of the first order with respect to the concentration of cyanide ions (CN^-). The fast and slow processes are tentatively attributed to the removal of SiO-NiOH on terraces and in sub-nanometer pores, respectively. The cleaning ability of the HCN aqueous solutions is much better than ammonia aqueous solutions, because of high reactivity to form nickel-cyanide complex ions and avoidance of readsorption of $Ni(CN)_4^{2-}$ complex ions in the solutions.
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Complete removal of metal contaminants is required for the fabrication of Si devices because heavy metals such as Cu, Fe, Ni, and Co form trap states in the Si bandgap.[1] In the fabrication process of Si devices, surface contaminants are usually removed by the RCA method, i.e., alkaline and acid solutions containing hydrogen peroxide.[2] The conventional RCA method requires high concentration (e.g., ~5%) cleaning solutions and heating at 50 ~ 80°C. Moreover, the RCA method causes surface etching, which makes the device fabrication processes complicated and possibly forms rough surfaces and defect states. To avoid etching, RCA cleaning solutions using dilute varieties are recently employed in LSI fabrication processes.

Solutions containing chelating agents such as EDTA are found to have an effect to prevent readsorption of metal species in cleaning solutions.[3,4]

We have recently developed semiconductor cleaning solutions which contain cyanide ions (CN^-).[5-8] Due to the strong reactivity of CN^- ions with metal species, semiconductor cleaning can be performed at room temperature using low concentration (e.g., 0.2%) solutions. Due to the large complex stability constant of CN^- ions compared with other chelating agents,[9] metal-cyanide complex ions in the cleaning solutions are not readsorbed on the surface, which makes it possible to remove metal contaminants completely and to use the cleaning solutions repeatedly. We have already found that CN^- ions selectively react with semiconductor defect states such as Si dangling bonds, resulting in the defect passivation.[10-14] The defect passivation by CN^- ions greatly improves various-type Si solar cells[10-13] and decreases the density of a leakage current flowing through an ultrathin SiO_2 layer of metal-oxide-semiconductor (MOS) diodes.[14] Therefore, cyanide solutions can be applied to not only semiconductor cleaning but also defect passivation.

In the present study, HCN aqueous solutions were found to possess a great effect of removing Ni contaminants and the removal mechanism is investigated by means of total reflection X-ray fluorescence spectroscopy (TXRF) and X-ray photoelectron spectroscopy (XPS). It was found that the removal proceeds with an initial fast process followed by a slow process, and their activation energies and preexponential factors are obtained.

Experimental

Boron-doped p-type CZ Si(100) wafers with 10–15 Ω cm resistivity were thermally oxidized to form ~5 nm thick silicon dioxide (SiO_2) layers. The wafers were cut into 2 × 3 cm pieces and preliminary cleaned by the RCA cleaning method.[2] A rinse in ultrapure water (UPW) was carried out after each cleaning step.

For intentional Ni contamination, SiO_2/Si specimens were immersed in 20 ppm nickel(II) nitrate [$Ni(NO_3)_2$, 99.95%, Kanto Chemical Co., Inc.] aqueous solutions at room temperature for 10 min. The pH of the $Ni(NO_3)_2$ aqueous solutions was set at 9 by addition of ammonia aqueous solutions, and then the specimens were rinsed with UPW.

HCN gas was generated by addition of concentrated sulfuric acid (H_2SO_4, EL grade, Kanto Chemical Co., Inc.) to solid sodium cyanide (NaCN, 97%, Wako Co., Inc.). The generated HCN gas was introduced to a reservoir cooled below −20°C by liquefied nitrogen, to solidify HCN with the freezing point of −13.3°C.[15] Then, the solidified HCN was dissolved in UPW.

The concentration of the HCN aqueous solutions was determined by the Liebig titration method using silver nitrate ($AgNO_3$, 99.8%, Wako Co. Inc.) aqueous solutions.[15] Before titration, a 6 M NH_4OH solution was added to the HCN aqueous solution to adjust pH, to prevent vaporization of HCN from the solution. Then, a 10% potassium iodide (KI, Wako Co. Inc.) aqueous solution was added as an indicator. When all CN^- ions in the solutions were consumed for the formation of silver-cyanide complex ions, $Ag(CN)_2^-$, milky-white precipitates of silver iodide (AgI) were formed, indicating completion of the titration.

Results and Discussion

Figure 1 shows the XPS spectrum in the Ni $2p_{3/2}$ region for Ni-contaminated SiO_2/Si specimens. Two intense peaks were observed at 857.0 and 862.5 eV, attributable to $Ni(OH)_2$.[16] This result shows that Ni contaminants on the SiO_2 surface are present in the chemical state similar to $Ni(OH)_2$.

Figure 2 compares the cleaning ability of HCN aqueous solutions with ammonia aqueous solutions. pH of the ammonia aqueous solutions was set at 10.7, i.e., the same as that for the HCN aqueous solutions, for direct comparison. The Si cleaning was performed at room temperature for 3 min for both the solutions. It is clearly seen that HCN aqueous solutions are more effective for Ni removal than ammonia aqueous solutions. Although Ni^{2+} ions form complex ions with both CN^- and NH_3, and $Ni(CN)_2$ and $Ni(OH)_2$ are dissolved in both HCN solutions and ammonia aqueous solutions,[17,18] the stability constants of nickel-cyanide complex ions are much larger than those of other complex ions,[9] as displayed in Table I. The great cleaning ability of HCN solutions results from high reactivity of CN^- ions to form nickel-cyanide complex ions and avoidance of readsorption.

It is likely that Ni contaminants are adsorbed on SiO_2 surfaces by reacting with surface Si-OH groups.[19] This mechanism is based on the behavior of silica gel where Si-OH groups act as weakly acidic

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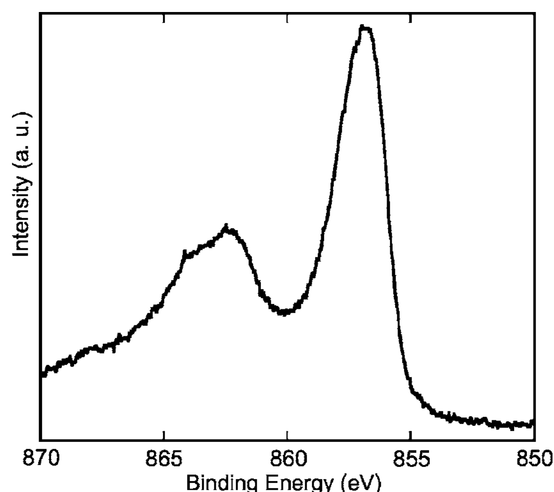
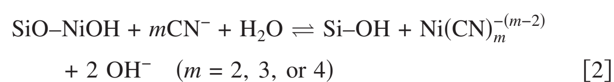


Figure 1. XPS spectrum in the Ni $2p_{3/2}$ region for the Ni-contaminated SiO_2/Si specimens.

ion exchangers.[20-22] Hoshino et al.[23] have reported that metal hydroxide reacts with Si-OH, resulting in the formation of Si-O-metal species

$$Ni(OH)_2 + Si\text{–}OH \rightarrow SiO\text{–}NiOH + H_2O \quad [1]$$

Therefore, the removal of Ni contaminants by the HCN aqueous solutions is likely to proceed with the following reaction formula



$$SiO\text{–}NiOH + mCN^- + H_2O \rightleftharpoons Si\text{–}OH + Ni(CN)_m^{-(m-2)} + 2\ OH^- \quad (m = 2,\ 3,\ \text{or}\ 4) \quad [2]$$

We have already shown that in the case of Si/SiO_2 cleaning with HCN aqueous solutions, readsorption of metal species in HCN solutions does not occur.[6,8] This result shows that the reverse reaction in Eq. 2 can be ignored. Thus, the reaction rate is written as

$$\frac{d[Ni^{2+}]}{dt} \approx -k[Ni^{2+}][CN^-]^m \quad [3]$$

where k is the reaction rate constant and Ni^{2+} denotes SiO-NiOH. Since $[CN^-]$ is much higher than $[Ni^{2+}]$, $[CN^-]$ is almost constant with time. Therefore, Eq. 3 is simplified to

$$\frac{d[Ni^{2+}]}{dt} \cong -k'[Ni^{2+}] \quad [4]$$

where

$$k' = k[CN^-]^m \quad [5]$$

Integration of Eq. 4 leads to

$$[Ni^{2+}] = [Ni^{2+}]_0 e^{-k't} \quad [6]$$

where $[Ni^{2+}]_0$ is the initial surface Ni concentration. Therefore, we have

Table I. Stability constants of Ni^{2+} complex ions with various ligands.[9] β_n denotes the stability constants of complex ions with n ligands.

Ligand	Stability constants (logarithmic values)			
CN^-				30.3 (β_4)
NH_3	2.21(β_1)	4.50(β_2)	6.86(β_3)	8.89(β_4)
Ethylenediamine (en)	7.35(β_1)	13.54(β_2)	17.71(β_3)	

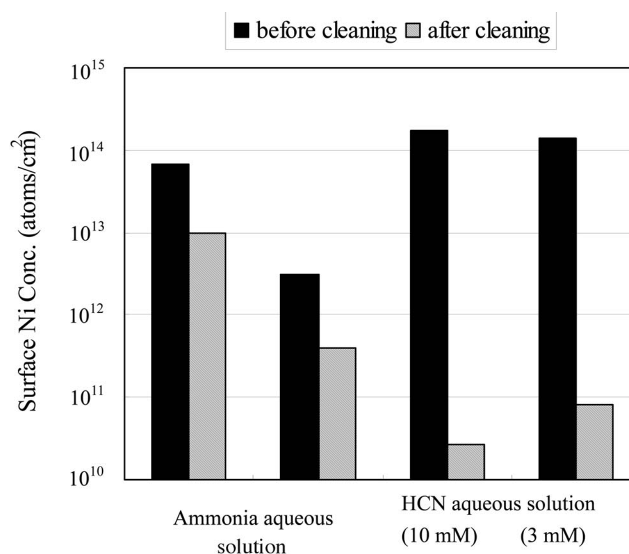


Figure 2. Surface Ni concentrations measured before and after cleaning in ammonia aqueous solutions and HCN aqueous solutions with pH set at 10.7 for 3 min.

$$\ln \frac{[Ni^{2+}]}{[Ni^{2+}]_0} = -k't \quad [7]$$

The surface Ni concentrations after cleaning the specimens with an initial Ni concentration of $\sim 10^{14}$ atoms/cm^2 were measured as a function of the cleaning time, t. The semi-logarithmic plots of $[Ni^{2+}]/[Ni^{2+}]_0$ vs t at 19°C for various HCN concentrations are shown in Fig. 3. The experimental results can be well fitted by two straight lines. From the slops of the straight lines, k' can be estimated.

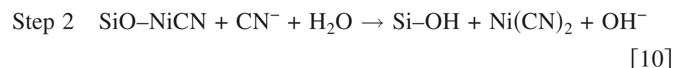
From Eq. 5, we have

$$\ln k' = m \ln[CN^-] + \ln k \quad [8]$$

Therefore, from the slope of the plot of $\ln k'$ vs $\ln[CN^-]$ shown in Fig. 4, m can be determined to be unity for both the fast and slow reactions. This result indicates that the rate-determining steps for both the reactions are of the first order with respect to $[CN^-]$.

The reaction formula for the removal of Ni contaminants by HCN aqueous solutions is written as

Step 1 $\quad SiO\text{–}NiOH + CN^- \rightarrow SiO\text{–}NiCN + OH^- \quad [9]$



Step 2 $\quad SiO\text{–}NiCN + CN^- + H_2O \rightarrow Si\text{–}OH + Ni(CN)_2 + OH^- \quad [10]$

$Ni(CN)_2$ is soluble, and thus it desorbs from the surface.[17,18] In the solutions, the following reaction proceeds

Step 3 $\quad Ni(CN)_2 + CN^- \rightarrow Ni(CN)_3^- \quad [11]$

The fourth CN^- ion reacts with $Ni(CN)_3^-$ in HCN solutions to form $Ni(CN)_4^{2-}$, which is the most stable Ni-cyanide complex ion with a high stability constant of 2.0×10^{30} [9]

Step 4 $\quad Ni(CN)_3^- + CN^- \rightarrow Ni(CN)_4^{2-} \quad [12]$

Readsorption of Ni contaminants to the surface does not occur because of the high stability of $Ni(CN)_4^{2-}$ in HCN aqueous solutions.

Similar experiments were carried out at various temperatures to obtain the temperature dependence of the rate constant, k_s. k_s is generally given by the Arrhenius equation

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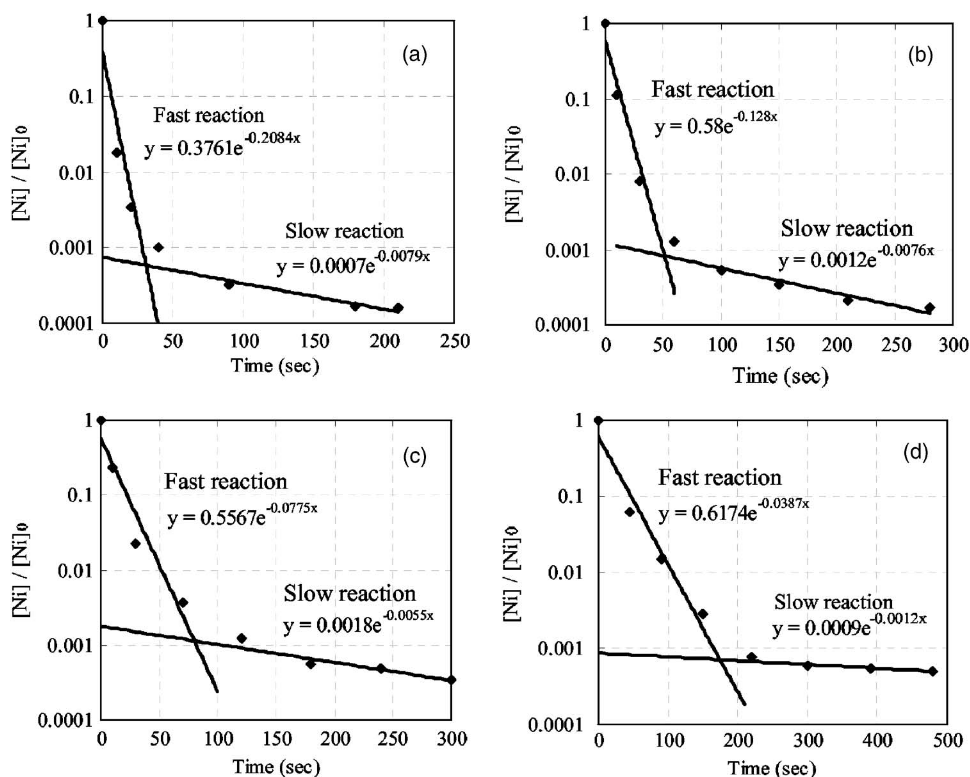

Figure 3. Surface Ni concentration divided by the initial surface Ni concentration on the SiO_2 surfaces vs the time of immersion in the HCN aqueous solutions at 19°C with pH of 10.7. The concentrations of the HCN solutions were (a) 10.7, (b) 6.6, (c) 3.0, and (d) 1.4 mM.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad [13]$$

or

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \quad [14]$$

where A is the preexponential factor and E_a is the activation energy. From the slope and the intercept of the semilog plot of the rate constant vs the reciprocal temperature (Fig. 5), E_a and A are determined to be 43 kJ/mol and 1.4×10^{10} for the fast reaction, and 24 kJ/mol and 2.3×10^4 for the slow reaction, respectively.

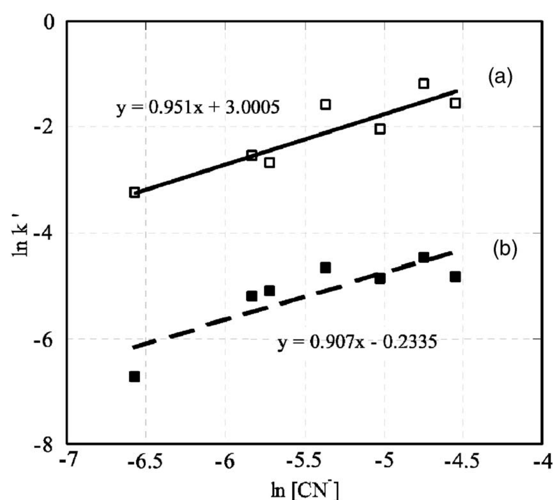

Figure 4. Log-log plots of k' (cf. Eq. 8) vs the concentration of CN^- ions in the HCN aqueous solutions (a) for the fast reaction and (b) for the slow reaction.

For the fast reaction, the value of A is very large, indicating that CN^- ions easily react with Ni contaminants. If SiO-NiOH is present on terraces, CN^- ions easily attack the species, leading to the large A value.

The slow reaction becomes dominant when the surface Ni concentration is less than $\sim 10^{12}$ atoms/cm^2. For the slow reaction, on

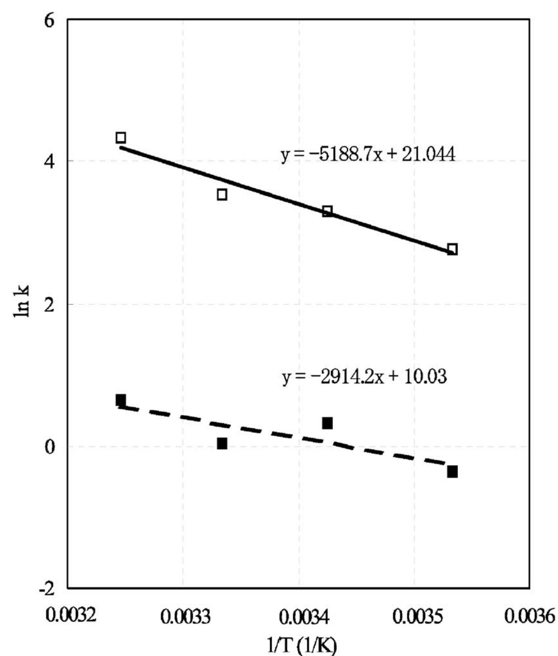

Figure 5. Semilog plots of the rate constant vs the reciprocal of temperature, where the open squares and the solid line are for the fast reaction, and the full squares and the broken line are for the slow reaction.

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the other hand, A has a low value, indicating that the reaction probability of CN^- ions is low. If the slow reaction species is due to Ni species in sub-nanometer size pores, CN^- ions have difficulty in approaching, resulting in the small A value. The fast and slow removal species are tentatively attributed to SiO-NiOH on terraces and in sub-nanometer pores, respectively, although no direct evidence has been obtained in the present study. Ni-O bonds in the slow reaction species are likely to be weakened by the adsorption in the pores, resulting in the relatively low activation energy of 24 kJ/mol.

In the present study, Ni contamination with the 10^{14} atoms/cm^2 order concentration has been investigated to elucidate the removal mechanism, and dilute HCN aqueous solutions between 10.7 and 1.4 mM concentrations have been employed in order to decrease the removal rate (cf. Fig. 3). Even in the case of the 10.7 mM (0.029 wt %) HCN solutions, the Ni concentration of 10^{11} atoms/cm^2 is decreased by one order of magnitude by immersion for $\sim$3 min. When 30 mM HCN aqueous solutions are used for the cleaning, the Ni contaminants can be removed to less than $\sim 3 \times 10^9$ atoms/cm^2 (i.e., below the lower detection limit of TXRF). Therefore, we think that HCN solutions can be used for semiconductor cleaning in LSI fabrication processes. For practical use, the pH of the HCN aqueous solutions should be adjusted to above 10 to avoid vaporization of poisonous HCN gas. In fact, the saturated vapor pressure of HCN aqueous solutions with pH above 10 is less than 10 ppm, and in addition, the cleaning ability increases with pH due to an increase in the electrolytic dissociation probability of HCN.[8] Etching of SiO_2 does not occur at all even in such a high pH HCN aqueous solution.[7] Moreover, it is found that HCN aqueous solutions have the capability of removing various metals such as Cu, Fe, Cr, Co, Mn, and Ca from SiO_2 surfaces. It is also evident that the HCN aqueous solutions can dissolve metal Ni from the following experimental result. After metal Ni was immersed in 50 mM HCN aqueous solutions, the absorption spectra of the HCN aqueous solutions showed a peak at $\sim$270 nm, attributable to Ni-cyanide complex ions.[24] However, the detailed behavior of HCN aqueous solutions for Ni removal from HF-etched bare Si surfaces and changes in Si surface roughness caused by HCN solutions are not known.

Conclusion

Ni contaminants on Si/SiO_2 are present in the form of SiO-NiOH and this species can be removed by immersion in the HCN aqueous solutions. The Ni removal proceeds with the initial fast reaction, followed by the slow reaction. The rate-determining steps for both the fast and slow reactions are of the first order with respect to the concentration of CN^- ions. The activation energy and the preexponential factor of the rate constant for the fast reaction (or slow reaction) are determined to be 43 kJ/mol and 1.4×10^{10}, respectively (or 24 kJ/mol and 2.3×10^4, respectively). Ni contaminants for the fast and slow reactions are attributed to SiO-NiOH on terraces and sub-nanometer pores, respectively.

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