



Characterization and modeling of the metal diffusion from deep ultraviolet photoresist and silicon-based substrate

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Abstract

The radioactive tracer technique was applied to investigate the out-diffusion of the transition metals (Cu, Fe and Co) from deep ultraviolet (DUV) photoresist into underlying substrate. Two important process parameters, viz., baking temperatures and substrate types (i.e., bare silicon, polysilicon, silicon oxide and silicon nitride), were evaluated. Results indicate that the out-diffusion of Co is insignificant, irrespective of the substrate type and baking temperature. The out-diffusion of Cu is significant for substrates of bare silicon and polysilicon but not for silicon oxide and nitride; for Fe, the story is reversed. The substrate type appears to strongly affect the diffusion, while the baking temperature does not. Also, the effect of solvent evaporation was found to play an important role in impurity diffusion. Using the method of numerical analysis, a diffusion profile was depicted in this work to describe the out-diffusion of metallic impurities from photoresist layer under various baking conditions. In addition, the effectiveness of various wet-cleaning recipes in removing metallic impurities such as Cu, Fe and Co was also studied using the radioactive tracer technique. Among the six cleaning solutions studied, SC2 and SPM are the most effective in impurity removal. An out-diffusion cleaning model was first proposed to describe the cleaning process. A new cleaning coefficient, $h(T)$, was suggested to explain the cleaning effect. The cleaning model could explain the tracer results. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: DUV photoresist; Impurity diffusion; Radioactive tracer technique; Out-diffusion cleaning model; Cleaning coefficient

1. Introduction

With an increasing degree of circuit integration on silicon wafer, metal contamination on the silicon wafer process is becoming a subject of more and more concern. According to the prediction of the International Technology Roadmap for Semiconductors (SIA, 1997), metallic contaminant is the most important factor influencing the manufacturing yield. Some disadvantageous electrical effects, including leakage current and

minority carrier lifetime, can originate from metal contamination. Especially for thin gate oxide, the oxide quality is seriously degraded by even little metal. Therefore, high-purity material and reliable cleaning technique are required to avoid metal contamination (Anttila et al., 1992; Chang and Sze, 1996; Ward, 1982; Miyazaki et al., 1991; Rotondaro et al., 1996).

In order to suppress the metal contamination to a level below the threshold value, both the purity of incoming materials (e.g., cleaning solution and photoresist) and the cleaning of manufacturing equipment have to be considered carefully (Joly, 1998). Chemically amplified photoresists have been widely used in deep ultraviolet (DUV) photolithography to manufacture integrated circuit devices with feature size smaller than 0.35 μm (Shi, 1999). Proper control of metal impurity in

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the “high-purity” DUV photoresist would be very crucial for the fast proliferation of DUV photoresist in the IC industry in the coming years (Semiconductor Industry Association, 1997). Therefore, knowledge on the behavior of metallic contaminants in DUV photoresist and their diffusion into the underlying substrate is of great importance. Our previous study found that the diffusion of Mn and Zn from DUV photoresist was lower than 6%. In this work, the behavior of other transition metals, including Cu, Fe and Co, is studied. While numerous studies have contributed to contamination analysis in semiconductor fabrication, the use of radioactive tracer technique (Borg and Dienes, 1998; Glekas, 1995; Choppin and Rydberg, 1980) is rare. However, the tracer technique possesses the capability of high throughput, easy operation, freedom from stable isotope interference and reliability. This technique is used in this work; the ratios of metallic impurities diffusing from DUV photoresist into its underlying substrate during baking process and the effect of various baking temperatures are evaluated using radioactive tracer. In addition, a numerical analysis method is applied in this work to describe the diffusion behavior of metal impurity both in the photoresist layer and in the underlying substrate.

The contamination after silicon processes is cleaned with various recipes. Wet cleaning process plays a very important role in the removal of contaminants. For metallic contaminants, the degree of contamination depends on the thermodynamics of surface state and the cleaning chemical. Therefore, the substrate type and the cleaning solution temperature are the critical factors affecting the cleaning efficiency. The effectiveness of various cleaning methods on metal impurity is also evaluated in this work using radioactive tracer. Possible mechanisms relevant to the amount of impurity diffusion under various substrates are discussed. It is known that the fast diffusion of specific substrate metal into the cleaning solution can enhance the cleaning efficiency, while a proper model to describe the diffusion behavior needs to be investigated. A new out-diffusion cleaning model, together with a cleaning coefficient, $h(T)$, is developed in this work to explain the cleaning effect.

2. Out-diffusion of impurities from DUV photoresist into underlying substrate

2.1. Experimental

Carrier-free radioactive tracers ^{60}Co and ^{59}Fe were purchased from DAMRI (France). Their compositions were $13\ \mu\text{g/g}$ of CoCl_2 and $10\ \mu\text{g/g}$ of FeCl_3 in 0.1 N hydrogen chloride solution. The carrier-free radioactive tracer ^{64}Cu was produced by THOR (Tsing Hua Open-

Pool Reactor). Its composition was 5 mg of Cu in 20 ml nitric acid.

The photoresist used in this work was SEPR-401H positive-type photoresist from Shin-Etsu Chemical (Japan). It is a popular photoresist for gate and metal layer applications in the state-of-the art ULSI (ultra-large-scale integration) manufacturing. It can be used in KrF excimer-laser exposure at a wavelength of 248 nm. The photoresist stripper was 1-methyl-2-pyrrolidone (NMP) from E. Merck (Germany). Radioactive photoresist solution was prepared using one volume of diluted radioactive tracer mixed with five volumes of photoresist.

P-type $\langle 100 \rangle$ wafers with 15 cm diam were first passivated with various films (i.e., polysilicon, silicon dioxide, silicon nitride, and non-passivated or bare silicon control) and cut into $2\ \text{cm} \times 2\ \text{cm}$ pieces to serve as test samples. Radioactive photoresist layer was then coated on each sample. The coating process was performed by spinning at 1500 rpm for 30 s. Samples were then split and subjected to various baking temperatures at 80, 100 and 120°C for 2 min by a hot plate. The photoresist film thickness was measured to be $\sim 7500\ \text{\AA}$ using a Nanospec optical film thickness monitor.

After solvent evaporation, the test samples were counted by a high-resolution gamma-ray spectrometer. The countings were made against the 511, 1099.2 and 1173 keV/1332 keV gamma rays from ^{64}Cu , ^{59}Fe and ^{60}Co , respectively. The counting system consists of an HPGe detector coupled with a multi-channel analyzer and the usual electronics. The energy resolution of the system is 2.4 keV at 1332 keV. After counting, the photoresist layer was removed by dipping in a 100 ml NMP solution at 60°C for 5 min, and dried using a hot plate. The radioactivity of the impurities left on the wafer was then checked by the same HPGe detection system. The diffusion ratio of Cu, Fe and Co impurities from photoresist into the underlying substrate was determined by the ratio of the time-average counts after and before the photoresist stripping.

2.2. Results and discussion

Table 1 summarizes the diffusion ratio of Cu, Fe and Co impurities from DUV photoresist into various underlying substrates for three different baking temperatures. It can be seen that the Co (percentage) diffusion ratios are all below 5%, irrespective of the underlying substrates and baking temperatures. The diffusion ratios of Cu are below 5% for the underlying substrates of silicon dioxide and silicon nitride. Conversely, for bare silicon and poly silicon, the diffusion ratios of Cu are in excess of 19%. Cu has higher residual in bare silicon and poly silicon than in silicon dioxide and silicon nitride. The diffusion ratios of Fe are above

Table 1
The diffusion ratio for impurity transported from DUV photoresist into underlying substrates at various baking temperatures

Bare-Si	80°C	100°C	120°C
Cu	30.4 ± 0.40	28.6 ± 0.42	20.1 ± 0.34
Fe	10.3 ± 0.40	11.3 ± 0.42	10.8 ± 0.36
Co	4.0 ± 0.26	4.1 ± 0.26	1.7 ± 0.22
Poly-Si			
Cu	20.7 ± 0.37	19.8 ± 0.39	23.0 ± 0.43
Fe	11.1 ± 0.37	12.9 ± 0.41	12.0 ± 0.40
Co	2.6 ± 0.27	1.1 ± 0.13	1.4 ± 0.15
SiO ₂			
Cu	1.0 ± 0.08	0.9 ± 0.08	2.2 ± 0.12
Fe	18.4 ± 0.46	14.5 ± 0.40	13.4 ± 0.39
Co	0.0	0.8 ± 0.12	0.0
Si ₃ N ₄			
Cu	1.9 ± 0.11	2.7 ± 0.13	4.2 ± 0.17
Fe	31.3 ± 0.56	26.2 ± 0.51	27.3 ± 0.50
Co	0.0	1.1 ± 0.13	1.0 ± 0.17

10%, irrespective of the underlying substrates and baking temperatures. This shows that Cu and Fe have higher residual than Co in the DUV photoresist at the normal baking temperatures used in this study. The higher diffusion amounts of Cu and Fe from DUV photoresist reveal the contamination problem in micro-lithography.

Literature (Weber, 1983; Zoth and Bergholz, 1990; Weber and Riotte, 1980) reports that Fe, Co and Cu can diffuse interstitially in the underlying substrate and stay in the interstitial site in thermal equilibrium at the diffusion temperature. Since the photoresist layer after baking is an amorphous polymer, it is supposed that the impurities can diffuse interstitially through the photoresist layer. The mechanism of diffusion seems to be very simple when atoms jump over a single lower potential barrier between different sites. The motion of metals should depend on the diffusion ambient temperature and impurity segregation coefficient at the photoresist–substrate interface. It is therefore anticipated that the metal diffusion may be promoted by elevating the baking temperature. However, as can be seen from Table 1, the diffusion ratio does not follow this prediction. This behavior can be explained by the migration mechanism proposed previously by the present authors (Wang et al., 1999), as described below.

Metallic ion (i.e., Fe, Co and Cu) can be solvated with the residual photoresist solvent and/or H₂O to form $M(\text{solvent})_x^{n+}$ and/or $M(\text{H}_2\text{O})_x^{n+}$ in the photoresist layer. As the film is heated, two pathways are competing with one other. The baking temperature accelerates the metallic species to move toward the substrate, while the solvated solvent and/or H₂O on the metallic species

evaporate in the opposite direction. The net driving force of metallic species, changing with the imposing temperature and the metal types, determines the final diffusion ratios and can be classified into four types. Type I describes the condition when the diffusion ratio increases with temperature. Type II is the condition when the diffusion ratio decreases with temperature. Type III has a turnover temperature T_i . In the $T < T_i$ region, diffusion behaves like type I; whereas, when $T > T_i$, it behaves like type II. Type IV shows the opposite tendency as compared with type III.

Based on the above model, the experimental results appearing in Table 1 can be realized. The tendency of Cu diffusion for bare silicon substrate can be attributed to type II, whereas for substrate of silicon nitride, it shows the opposite tendency. Cu impurity belongs to type IV in the substrates of poly silicon and silicon oxide. It is found that Fe has type III diffusion for substrates of bare silicon and poly silicon. The diffusion ratio for Fe in silicon oxide reveals the type II tendency, and the type IV tendency is seen in silicon nitride. It is also found that Co has type IV diffusion in the substrate of poly silicon. The diffusion ratios of Co for other substrates belong to type III. Overall, if we disregard the small differences in diffusion ratios, the diffusion of metal impurities out of DUV photoresist does not show strong temperature dependency.

Table 1 is obtained from the polymer solution containing radioactive tracers by combining aqueous and microlithographic material to give a mixture. The water content in the radioactive photoresist is higher than that in the unadulterated photoresist. According to the above-proposed diffusion mechanism, the values of the diffusion ratios appearing in Table 1 may be underestimated. The contamination effect in practical microlithography could be more serious and needs to be considered more carefully.

2.3. Numerical method on diffusion model

A diffusion model is proposed herein for describing the behavior of metallic impurities from DUV photoresist into the underlying substrate, being a modification of the model reported previously (Wang et al., 1999). The diffusion equation for the metallic species in the photoresist layer and the underlying substrate at time (t) and location (x) can be expressed as follows (Crank, 1976):

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2}, \quad (1)$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2}, \quad (2)$$

where C_1 and C_2 denote the concentrations of metallic impurity in the photoresist layer and the underlying

substrate, respectively, and D_1, D_2 are the diffusion coefficients for the DUV photoresist layer ($x > 0$) and the substrate ($x < 0$), respectively. Theoretically, the distribution of metallic impurity is homogeneous in the photoresist layer at the beginning. Therefore, the initial condition can be given as

$$C_1 = C_0, \quad 0 < x < L \quad t = 0, \tag{3}$$

$$C_2 = C_0, \quad x < 0 \quad t = 0, \tag{4}$$

where L is the photoresist thickness. The boundary conditions are

$$\frac{\partial C_1}{\partial x} \Big|_{x=L} = 0, \tag{5}$$

$$C_2 \Big|_{x \rightarrow -\infty} = 0. \tag{6}$$

The interface conditions at $x = 0$ are

$$C_2 / C_1 = k, \tag{7}$$

$$J = -D_1 \frac{\partial C_1}{\partial x} \Big|_{x=0} = -D_2 \frac{\partial C_2}{\partial x} \Big|_{x=0}, \tag{8}$$

where k (i.e., the impurity segregation coefficient at the interface) is the ratio of the concentration in the substrate to that in the photoresist at the interface when the final equilibrium is achieved. Eq. (8) expresses the fact that there is no accumulation of diffusing substrate at the interface.

The analytical solutions for these equations are difficult to get, instead, numerical analysis is performed in this work on a personal computer. The above partial-differential equations are first changed to the form of difference equations. Then, both space and time are divided into discrete intervals. The succeeding difference replaces the time derivative, and central difference replaces the space derivative. These relations can be described as (Gerald and Wheatley, 1994)

$$\frac{\partial C}{\partial t} \Big|_{x=x_j, t=t_j} = \frac{C_i^{j+1} - C_i^j}{\Delta t} + O(\Delta t), \tag{9}$$

$$\frac{\partial^2 C}{\partial x^2} \Big|_{x=x_j, t=t_j} = \frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{\Delta x^2} + O(\Delta x)^2. \tag{10}$$

Combining Eqs. (9) and (10),

$$C_i^{j+1} = \frac{D\Delta t}{(\Delta x)^2} (C_{i+1}^j + C_{i-1}^j) + \left(1 - \frac{2D\Delta t}{(\Delta x)^2} \right) C_i^j.$$

With the values of D_1, D_2 and k known a priori, the solution of concentration in the above equation can be achieved at each space and time interval. Unfortunately, reliable values of D_1, D_2 and k , for the metals, materials and temperature conditions used in this work, are not available from the literature. However, some numerical

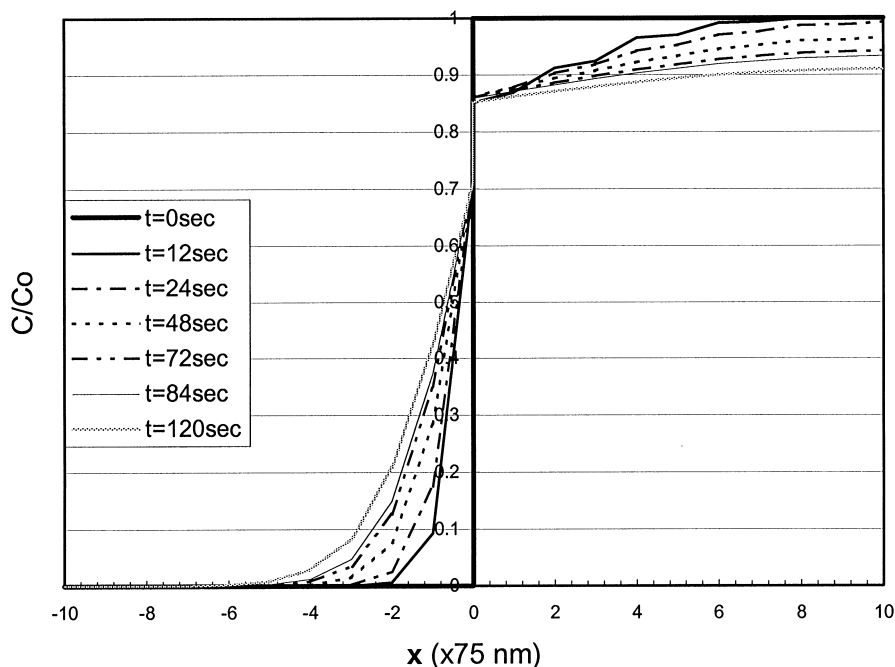


Fig. 1. The change of concentration gradient in the photoresist layer ($x > 0$) and the underlying substrate ($x < 0$) as a function of time. (total baking time = 120 s, assuming that equilibrium is attained after 1.0 s).

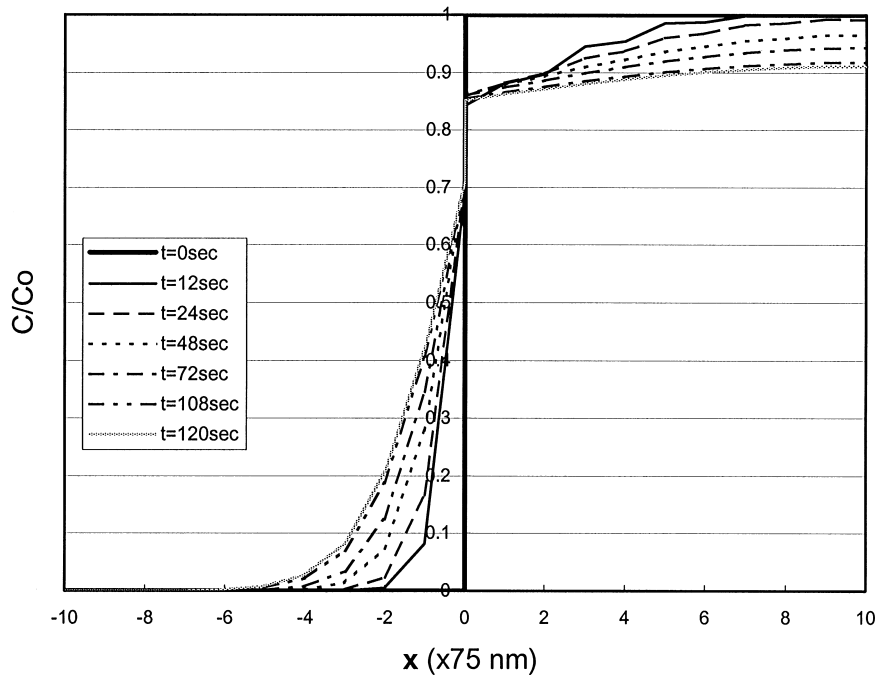


Fig. 2. The change of concentration gradient in the photoresist layer ($x > 0$) and the underlying substrate ($x < 0$) as a function of time. (total baking time = 120 s, assuming that equilibrium is attained after 20 s).

calculation results are still presented as follows for demonstrative and explanatory purposes.

Taking the out-diffusion of Fe from SEPR-401H photoresist to bare silicon substrate, baked at 100°C for 2 min, as an example, computational results are illustrated in Figs. 1–3. In the calculation, diffusion coefficients D_1 and D_2 were assigned semi-artificially. The values of D_1 was assumed to be $2.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ based on an engineering judgement, D_2 was assumed to be $8.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ as extrapolated from published data at high temperature. Iterative processes were used to determine the values of k based on the experimentally determined diffusion ratio (Table 1). These three figures were obtained at three assumed levels of equilibrium time (i.e., 1, 20 and 80 s). It can be found that the impurity concentrations are convergent at the interface after equilibrium is attained.

Although the above examples are based on assumed D_1 , D_2 and k values, it does demonstrate the capability of using the numerical calculation for studying the impurity diffusion behavior. Furthermore, if any two of the three parameters (i.e., D_1 , D_2 and k) are available, the third parameter can be obtained by the above numerical method using the experimentally determined diffusion ratios as a check criterion. To satisfy this criterion, the ratio of the integrated concentration at $x < 0$ (ref. Figs. 1–3) to the total initial concentration

should match the corresponding measured diffusion ratio (ref. Table 1).

3. Effectiveness of various wet cleaning recipes

To achieve better performance and reliability in device manufacturing, the silicon surface needs to be kept clean. Understanding the type and origin of contaminant and the mechanism of cleaning is very important. The essential functions of cleaning solutions are to dissolve the contaminants out of wafer surfaces and to prevent re-adsorption of contaminants from the cleaning solution (Morinaga et al., 1994). In this work, emphasis is laid on the discussion of the effectiveness of various wet cleaning solutions on metal contamination using radioactive tracers Cu, Fe and Co.

3.1. Experimental

To understand the effectiveness of wet cleaning recipes, various popular wet cleaning solutions, e.g., SC1, H_2O , SC2, DHF, SPM and BOE, were studied in this work. Radioactive tracer solution was spiked onto the test wafer samples on a 50°C hot plate. The radioactivity was counted by the same gamma-ray spectrometry system as mentioned in Section 2.1.

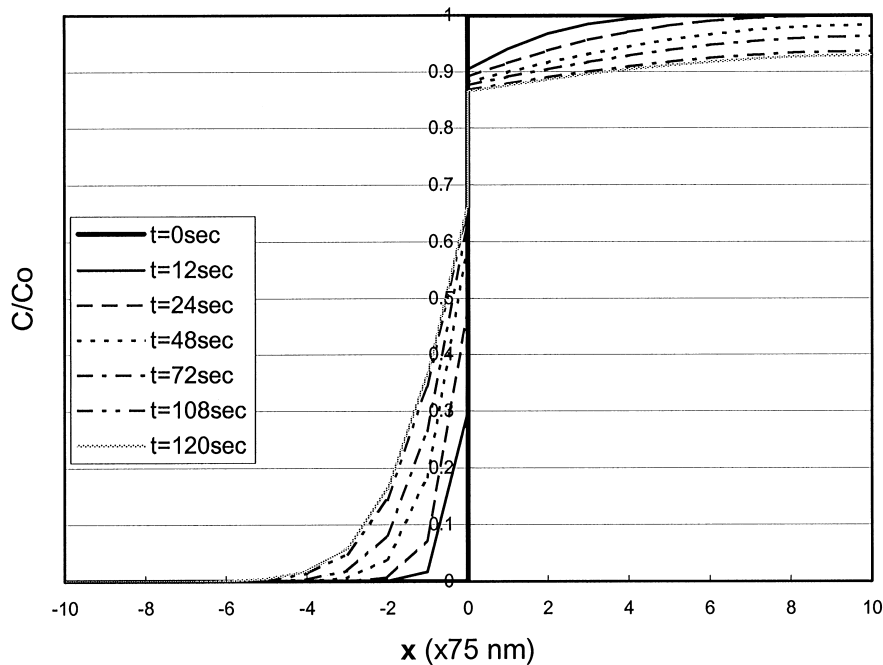


Fig. 3. The change of concentration gradient in the photoresist layer ($x > 0$) and the underlying substrate ($x < 0$) as a function of time. (total baking time = 120 s, assuming that equilibrium is attained after 80 s).

Afterwards, test samples were immersed in various wet cleaning solutions at various temperatures for 5 min, to dissolve or desorb the tracers. After cleaning, samples were immersed into room-temperature water solution to remove the residual chemical. The radioactivity emitted from the residual impurities was measured again. The effectiveness of various wet cleaning recipes was then assessed based on the ratio of the radioactivity counted after and before the cleaning process.

3.2. Results and discussion

Basically, the tracers of Cu, Fe and Co are deliberately applied onto wafer surface. The reaction of metallic ions onto silicon surface can be considered with the following mechanisms (Ohmi et al., 1992; Norga and Kimerling, 1995; Ohmi et al., 1993; Anttila and Tilli, 1992). The first mechanism is related to the difference of the electronegativity between metal and silicon. The electronegativity of Cu, Fe and Co is 1.90, 1.83 and 1.88 on the Pauling scale, respectively, compared with 1.90 for silicon (Lide, 1998). If the electronegativity of metal is higher than that of silicon, the metal ion tends to be neutralized by taking an electron from silicon and precipitates on the surface. The second mechanism is related to the difference in the enthalpy of oxide formation between metals and silicon substrate. Table 2 lists the relevant formation enthalpy of metal oxides. A

Table 2
Standard molar enthalpy of oxide formation at 25°C in kJ/mol

Formula	ΔH
SiO ₂	-910.7
CuO (II)	-157.3
Cu ₂ O (I)	-168.6
CoO (II)	-237.9
Co ₃ O ₄ (II, III)	-891.0
FeO (II)	-272.0
Fe ₂ O ₃ (III)	-824.2
Fe ₃ O ₄ (II, III)	-1118.4

negative enthalpy indicates that oxide formation is a heat-releasing process. The third mechanism considers the effect of surface adsorption of metal ions. This effect depends on not only the concentration of the metals but also the electrochemical potential and solution pH value.

Tables 3–5 show the remaining ratios of radioactive tracers of Cu, Fe and Co after 5 min treatment in various cleaning recipes with the temperatures of 25, 47 and 82°C, respectively. It shows that SC2 and SPM solutions are the most effective in metallic impurity removal, irrespective of the substrate types, while SC1 and H₂O are the least effective ones.

Note that the remaining ratios of Fe are exceptionally high after SC1 cleaning. This indicates that SC1, a

Table 3

The percentage remaining ratio of radioactive tracer after 5 min dipping in various cleaning recipes at 25°C

	SC1	H ₂ O	SC2	DHF	SPM	BOE
Bare-Si						
Cu	0.0	66.8 ± 1.19	0.0	71.8 ± 1.25	0.0	78.6 ± 1.42
Fe	95.7 ± 0.91	87.2 ± 0.86	4.3 ± 0.14	0.0	1.5 ± 0.08	0.2 ± 0.03
Co	9.4 ± 0.21	2.3 ± 0.08	0.0	0.0	0.0	1.1 ± 0.06
Poly-Si						
Cu	0.4 ± 0.07	80.0 ± 1.43	0.0	61.5 ± 1.15	0.0	81.5 ± 1.43
Fe	90.4 ± 0.84	73.6 ± 0.69	2.4 ± 0.14	0.0	1.2 ± 0.12	0.7 ± 0.08
Co	12.0 ± 0.18	0.6 ± 0.04	0.0	0.0	0.0	0.0
SiO₂						
Cu	0.3 ± 0.07	35.1 ± 0.79	0.0	2.0 ± 0.17	0.0	0.9 ± 0.11
Fe	86.9 ± 0.78	89.8 ± 0.88	0.0	0.0	0.0	0.0
Co	5.4 ± 0.12	0.0	0.0	0.0	0.0	5.0 ± 0.11
Si₃N₄						
Cu	0.0	53.7 ± 1.12	0.0	5.9 ± 0.31	0.0	2.9 ± 0.23
Fe	93.5 ± 0.86	92.8 ± 0.94	0.0	0.7 ± 0.05	0.0	0.8 ± 0.06
Co	4.2 ± 0.09	0.0	0.0	0.0	2.6 ± 0.08	0.8 ± 0.05

Table 4

The percentage remaining ratio of radioactive tracer after 5 min dipping in various cleaning recipes at 47°C

	SC1	H ₂ O	SC2	DHF	SPM	BOE
Bare-Si						
Cu	0.0	94.4 ± 0.67	0.0	81.6 ± 0.61	0.1 ± 0.01	94.2 ± 0.64
Fe	75.5 ± 0.34	64.6 ± 0.31	0.0	0.2 ± 0.02	0.5 ± 0.04	0.2 ± 0.02
Co	0.9 ± 0.06	22.1 ± 0.28	0.0	0.0	0.1 ± 0.02	0.8 ± 0.05
Poly-Si						
Cu	4.1 ± 0.11	76.5 ± 0.59	0.0	96.2 ± 0.66	0.5 ± 0.03	98.5 ± 0.71
Fe	85.4 ± 0.38	71.1 ± 0.33	0.0	0.0	0.7 ± 0.06	0.2 ± 0.02
Co	0.5 ± 0.04	12.9 ± 0.21	0.0	0.0	0.0	1.0 ± 0.05
SiO₂						
Cu	2.6 ± 0.08	45.9 ± 0.44	0.0	2.9 ± 0.09	0.1 ± 0.01	14.6 ± 0.21
Fe	74.8 ± 0.33	60.0 ± 0.27	0.0	0.0	0.0	0.0
Co	0.8 ± 0.05	0.4 ± 0.03	0.0	0.0	0.0	0.0
Si₃N₄						
Cu	1.8 ± 0.7	56.3 ± 0.48	0.0	4.2 ± 0.11	0.0	1.4 ± 0.06
Fe	77.2 ± 0.33	88.0 ± 0.38	0.0	0.0	0.0	0.2 ± 0.02
Co	0.5 ± 0.04	1.3 ± 0.06	0.0	0.0	0.0	0.0

well-known recipe for particle removal, is inefficient in removing Fe from the wafer surface, regardless of the substrate types and solution temperatures. This phenomenon could be explained by the mechanisms of metal oxide formation and the effect of surface adsorption.

Water is usually used to rinse off chemicals from previous cleaning steps in manufacturing process. Our results indicate that H₂O is not effective in removing Fe and Cu impurities. Conversely, the fact that the Co residual becomes zero for all the underlying substrates at 82°C, indicates that hot water immersion is very effective in dissolving Co impurity away from the wafer surface.

It is noted that the diffusion length of Co into substrate is very small, and therefore can easily be dissolved away by hot water.

The SC2 solution is very effective in removing Cu, Fe and Co contamination. The remaining ratios are practically zero for all of the cases studied in this work. This can be explained by the chemical behavior of SC2 solution; its strong acid (H⁺) competition effectively replaces the metallic ions (i.e. Cu²⁺, Co⁺, Fe⁺) on the wafer surface (Gilles et al., 1990).

After DHF or BOE treatment, the Cu residual is still high for underlying substrate of bare silicon and poly silicon. This might be due to the fact that the main

Table 5

The percentage remaining ratio of radioactive tracer after 5 min dipping in various cleaning recipes at 82°C

	SC1	H ₂ O	SC2	DHF	SPM	BOE
Bare-Si						
Cu	0.2 ± 0.03	39.3 ± 0.54	0.0	57.0 ± 0.69	0.1 ± 0.02	28.9 ± 0.50
Fe	81.0 ± 0.35	65.6 ± 0.32	0.0	0.0	0.0	0.0
Co	4.2 ± 0.12	0.0	0.0	0.0	0.0	0.0
Poly-Si						
Cu	33.4 ± 0.50	63.9 ± 0.73	0.0	85.3 ± 0.93	0.0	8.3 ± 0.23
Fe	74.2 ± 0.33	83.0 ± 0.36	0.0	0.4 ± 0.02	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0	0.0
SiO₂						
Cu	11.1 ± 0.26	13.8 ± 0.32	0.0	0.6 ± 0.06	0.0	25.3 ± 0.59
Fe	70.0 ± 0.34	44.8 ± 0.25	0.0	0.0	0.0	0.0
Co	0.5 ± 0.04	0.0	0.0	0.0	0.0	0.0
Si₃N₄						
Cu	30.2 ± 0.49	0.6 ± 0.06	0.0	1.8 ± 0.10	0.0	7.6 ± 0.21
Fe	46.7 ± 0.25	37.1 ± 0.21	0.0	0.0	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0	0.0

purpose of these two solutions is to remove metal oxides from wafer surface, whereas due to its large electro-negativity values, Cu tends to deposit on the Si wafer as atom clusters instead of oxides (Morinaga and Ohmi, 1995). On the other hand, the residuals of Fe and Co are near zero. This indicates that Fe and Co may appear as native oxide; the metal oxides can be removed by DHF and BOE solutions.

The SC1 solution is not satisfactory in removing residual metallic impurities from the wafer surface as can be seen from the tables. Succeeding acidic solution is needed to further remove metallic contamination. In most of the cases, the formation of metal oxides is enhanced at high pH, while the extent of dissolution is favorable at low pH (SC2, DHF or BOE). At high pH (SC1 or H₂O), metal oxide can be formed and adsorbed onto the substrate surface with even little metal in the cleaning solution (Kern, 1970). This may give rise to surface contamination.

3.3. A model for substrate metal redistribution after cleaning

A diffusion equation for the description of the pathway of metallic impurities from silicon substrates into the cleaning solution is proposed as follows:

$$\frac{\partial C_{sub}}{\partial t} = D \frac{\partial^2 C_{sub}}{\partial x^2}, \quad (12)$$

where $C_{sub}(x,t)$ is the impurity concentration, as a function of space x and time t , and D the diffusion coefficient in a semi-infinite substrate.

If the surface of a contaminated wafer is dipped in the cleaning solution, the metal in the thin interface region can be removed. The above process drives the out-diffusion of substrate metal to the interface region. Similarly, if the metal impurity is spiking into the cleaning chemical, leading to higher metal concentration, the concentration gradient drives the metal to diffuse into the thin interface region. In each case the rate of exchange of impurity at any instant depends on the difference between the concentration in the cleaning chemical and that in the interface region of wafer surface. A simple but reasonable assumption is that the rate of exchange is directly proportional to the difference between $C_{sub}(0,t)$ (the metal concentration at the interface of wafer surface at any time) and C_{sol} (the metal concentration in the cleaning chemical, which can be assumed to be zero in most cases). The relevant mathematical equation at the boundary condition ($x=0$) is

$$-D \frac{\partial C_{sub}}{\partial x} = \alpha(C_{sol} - C_{sub}) \quad \text{at } x = 0, \quad (13)$$

where α is a proportionality constant. This constant does not depend on dipping time, but depends on metal types, the constitution of cleaning chemical and the temperature of cleaning solution.

A solution to the above diffusion equation can be achieved by combining the semi-infinite substrate and the boundary condition. The solution is (Crank, 1976)

$$\frac{C_{sub}(x,t) - C_{sub}(x,0)}{C_{sol} - C_{sub}(x,0)} = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right)$$

$$= -\exp(hx + h^2Dt) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) + h\sqrt{Dt}, \quad (14)$$

where h is the cleaning coefficient, representing α/D , and $C_{sub}(x,0)$ is the initial concentration in a semi-infinite substrate. The $(C_{sub}(x,t) - C_{sub}(x,0))/(C_{sol} - C_{sub}(x,0))$ term is plotted against the function of distance (x) in Fig. 4(a). A high h value implies the condition of high cleaning efficiency. The rate of change of the total metal amount (M_t) per unit wafer cross-sectional area can be given by

$$\frac{dM_t}{dt} = -\left(D \frac{\partial C_{sub}}{\partial x}\right)_{x=0} = \alpha(C_{sol} - C_{sub}(0, t)). \quad (15)$$

Combining Eqs. (14) and (15) at the boundary ($x=0$), the total amount of metal (M_t) diffused for unit area of wafer surface, at any time t , can be obtained by integrating the above equation (Crank, 1976):

$$M_t = \frac{(C_{sol} - C_{sub}(x,0))}{h} \{ \exp(h^2Dt) \operatorname{erfc}(h\sqrt{Dt}) - 1 + \frac{2}{\sqrt{\pi}} h\sqrt{Dt} \}. \quad (16)$$

The relationship between the diffusing metal and $h(Dt)^{1/2}$ is illustrated in Fig. 4(b). The amount of diffused metal increases with the $h(Dt)^{1/2}$ term.

To describe the effect of temperature on D and α , the following equation is considered:

$$h(T) = \frac{\alpha(T)}{D(T)} = \frac{\alpha(T)}{D_0 e^{-E/k_B T}}, \quad (17)$$

where $\alpha(T)$ is dependent on metal type, cleaning reaction type and solution temperature, T is the solution temperature in Kelvin, k_B the Boltzmann constant, E the impurity activation energy in the lattice or interstitial sites and D_0 the pre-exponential factor which depends on the vibration frequency of atoms at such sites. Eq. (17) implies that $h(T)$ does not have to increase or decrease with cleaning temperature. Therefore, the experimental results appearing in Tables 3–5 as discussed in Section 3.2 can be realized.

4. Conclusion

This study employed the radioactive tracer technique to study the diffusion of metallic impurity from photoresist into substrate and the cleaning efficiency of the wet chemical process. Results indicate that the tracer technique is a useful tool for evaluating the behavior of metallic contamination in modern semiconductor manufacturing process.

In the diffusion of metal impurity from DUV photoresist into substrate, it is found that Cu and Fe have significantly higher diffusion ratios than Co, regardless of baking temperature and substrate type. This diffusion behavior can be explained with the net

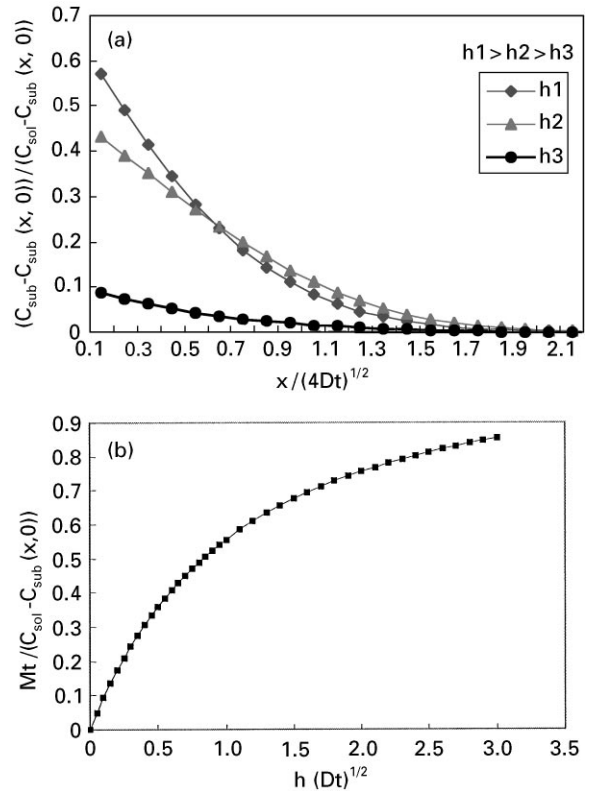


Fig. 4. (a) Concentration distribution $(C_{sub}(x,t) - C_{sub}(x,0)) / (C_{sol} - C_{sub}(x,0))$ as a function of $x / (4Dt)^{1/2}$ for various h values (b) the amount of impurity removed from the surface as a function of $h(Dt)^{1/2}$.

driving force of impurity diffusion and the mechanism of solvent evaporation. A diffusion model was proposed; this model, together with its numerical solution, can simulate the variation in the metal concentration profile in photoresist and underlying substrate.

In the cleaning efficiency study, it is found that SC2 and SPM solutions are the most effective in Cu, Fe and Co impurity removal, while H₂O and SC1 solutions are the least effective. The electronegativity, the enthalpy of oxide formation and the effect of surface adsorption are the possible mechanisms concerning Cu, Fe and Co removal. An out-diffusion cleaning model is proposed to describe the cleaning process. The proposed cleaning coefficient in the cleaning model, which is dependent on the types of metal, the constitution of cleaning chemical and the temperature of cleaning solution, can explain the tracer results.

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