Surface Deposition of Ionic Contaminants on Silicon Wafers in a Cleanroom Environment

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***Abstract*—The adsorption and desorption behaviors of ionic micro-contaminants on the silicon wafers in a cleanroom environment were investigated in this study. The experimental measurements showed that the surface density of ionic contaminants was significantly affected by both the exposure time and the properties of contaminants. The rate parameters of a kinetic model for surface deposition were determined by numerical optimization of fitting the experimental data on surface and ambient concentrations of airborne molecular contaminants (AMCs). Subsequently, the time-dependent deposition velocity and sticking coefficient of ionic species were obtained. The results showed that F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, and Mg^{2+} were the major ionic microcontamination species on the wafer surfaces, with the adsorption rate constant and the sticking coefficient of K^+ ion being larger than those of other ionic contaminants. After the determination of sticking coefficients, the allowable wafer exposure durations and the maximum ambient concentrations of ionic species were exemplified based on the guideline recommended by the International Technology Roadmap for Semiconductors (ITRS).**

***Index Terms*—Adsorption and desorption, airborne molecular contaminants (AMCs), cleanroom, microcontamination, sticking coefficient, wafer deposition.**

I. Introduction

THE airborne molecular contaminants (AMCs) are major challenges for present and future production of integrated circuit. Although wafers are handled under particle free in conventional mini-environment systems or front open unified pod (FOUP), however possible chemical contamination has still been overlooked. When wafers are waiting in the loading zone in the tool to be loaded one by one into the process zone, ion contaminants could possibly deposit on wafers during this pre-process time. Thus wafers and chemical contaminants could be kept together in the standard mechanical interface (SMIF) or FOUP. Wafer hazing and corrosion are some examples of inorganic AMCs-induced defects resulting in reduced yield [1]. Acidic anions cause etch rate shifts and metallization corrosion. Ammonia and other basic contaminants can affect the chemically-amplified photoresist at ppb levels causing T-topping [2]. Due to higher gas diffusivities, the surface arrival rate for inorganic gas phase species may greatly exceed those of particles with typical size of 0.01 to 1 μm [3]. The use of enclosures equipped with chemically-specific air filters and efficient purging of wafer boxes with inert gas are currently being used to reduce the level of contamination in sensitive production areas [4], [5]. Therefore, the strong needs to detect ever-shrinking critical defects have been reflected in the technical specification of Semiconductor Equipment and Materials International (SEMI) to recommend maximum allowable concentrations of airborne molecular contaminants [6].

There have been studies addressed on identifying the compositions of contaminating particles on the wafers. Uritsky *et al.* [7] investigated the appearance and composition of particles on the wafer surface using scanning electron microscope and energy dispersive X-ray spectroscopy (SEM/EDS) in a tungsten chemical vapor deposition process. Bai *et al.* [8] analyzed the particulate morphology and identified the elemental compositions of wafer contaminants as carbon, oxygen, sodium, magnesium, aluminum, phosphorus, sulfur, chlorine, potassium, calcium, and iron, etc.

The chemical contaminations on Si wafers are always complexly influenced by many factors. The AMCs concentrations in air and their thermal velocities will affect the surface arrival rate. The sticking coefficient, which depends on surface condition, will affect how much AMCs remained on the wafer [1]. In a number of recent studies, the deposition kinetics of several phthalate compounds on silicon wafers have been reported for long exposure periods up to several days [9]–[12]. Besides, the adsorption and desorption rate constants of several organic AMCs have been evaluated based on the actual data from cleanroom ambiences [10], [13], [14].

Literature data for the formation of time-dependent haze on silicon wafers and the deposition monitoring of inorganic ionic contaminants by capillary electrophoresis or ion chromatography have been published [15]–[18]. However, to the authors' knowledge the deposition rates of ionic contaminants on silicon wafer have not been studied and their adsorption/desorption behaviors on the silicon wafer have not been developed in the literature. Thus it leads to difficulty in establishing the relationship between the maximum allowable sit time of a wafer and the ambient concentration during exposure.

This study intends to analyze components of ionic contaminants and investigate their deposition rates on silicon wafers under various exposure times up to 24 h. The deposition rate parameters of ionic contaminants are determined by fitting the rate equation with the experimental data through an optimization algorithm. In addition, the sticking coefficients of the ionic species are derived based on the kinetic parameters. These adsorption parameters permit subsequent assessment of the maximum allowable wafer exposure time and the ambient concentration threshold.

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II. Surface Kinetics and Sticking Coefficient

When gas-phase molecules arrive within a few atomic distances of the target surface in stagnant air, they are invariably attracted to the surface by the van der Waals force [11]. A portion of the molecules striking the surface may still possess sufficient residual energy to instantaneously rebound from the surface. Other less energetic molecules may remain on the surface for an extended period of time via physisorption. This is generally considered as an equilibrium process between simultaneous adsorption and desorption. The surface contamination level is determined by the adsorption strength, which is a sensitive function of the interaction between the molecules and the surface. Assuming that there is no gradient in the gas composition, the kinetic equation for the rate of change in the surface density can be expressed as [11], [19], [20]

$$\frac{dC_s}{dt} = k_{\text{ads}} C_g - k_{\text{des}} C_s \tag{1}$$

where C_s represents the surface concentration (ng cm^{-2}), C_g is the ambient concentration (ng cm^{-3}), t is exposure time (min), and k_{ads} and k_{des} are the adsorption rate constant (cm min^{-1}) and desorption rate constant (min^{-1}), respectively. The boundary conditions for (1) are at $t = 0$, $C_s = 0$ and at $t = t$, $C_s = C_s(t)$.

For simplicity, the surface coverage is assumed to be so slow that the interaction among adsorbed molecules is negligible. It is also assumed that the gas phase concentration is a constant during the time period of interest. Solving the differential equation leads to [11]

$$C_s(t) = C_g \left(\frac{k_{\text{ads}}}{k_{\text{des}}}\right) \left[1 - e^{-k_{\text{des}} t}\right]. \tag{2}$$

As t is infinity, the asymptotic value of C_s can be shown as

$$C_s(\infty) = C_g \left(\frac{k_{\text{ads}}}{k_{\text{des}}}\right). \tag{3}$$

It is reported that airborne contaminants are adsorbed and desorbed depending on their molecular weight or their chemical nature [21]. This phenomenon is usually taken into account by the so-called sticking coefficient, E, which value is between 0 and 1. It indicates the probability of a molecule to be adsorbed on the surface after contact. The sticking coefficient can be calculated by the following formula [1]:

$$E = \frac{C_s}{\Delta t C_g u} \tag{4}$$

where u is vertical laminar flow velocity (cm min^{-1}).

By measuring the time-dependent surface density (C_s) and ambient concentration (C_g), the kinetic parameters such as adsorption and desorption rate constants can be established from (2) using a numerical algorithm based on the least-squares error method. A simple trial-and-error method was performed to acquire an initial set of solutions, and a heuristic algorithm known as the simulated annealing algorithm was employed to obtain the optimal values of K_{ads} and K_{des} [22]. Then, the calculated values of $C_s(t)$ were obtained from (2). The error between the given data set of calculated $C_s(t)$ and the measured C_s was then calculated and the procedure was repeated with different values of K_{ads} and K_{des} until the minimum squares of error was obtained. And the sticking coefficient can be determined based on (4) so that the relationship between the maximum allowable wafer sit time and its exposure concentration can be established.

III. Experiment

The measurements for the deposition of cleanroom ionic contaminants were conducted at a cleanroom photo area of a semiconductor fab in Taiwan. The relative humidity in the sampling area was $45 \pm 3\%$ and temperature was $22 \pm 1\ ^\circ\text{C}$. After standard Radio Corporation of America (RCA) cleaning, 200-mm silicon wafers with p doped in the (100) plane were used as the deposition "witness" wafers. To investigate the deposition of ionic contaminants on silicon wafers, the wafers are directly exposed in a cleanroom environment. The wafers were horizontally placed near the ASML Scanner PAS5500/500D system and exposed for various durations (30 min to 24 h) in a class 100 cleanroom environment. The backside of the test wafer was in full contact with an ultra-clean borosilicate-glass holder, thereby eliminating the possibility of deposition on the backside. After the cumulative exposure, these wafers were placed in clean containers, removed from the cleanroom and then analyzed by a high resolution focused ion beam (FIB) microscope (FIB-830, FEI Company, Hillsboro, OR) equipped with an energy dispersive X-ray spectroscopy (EDS) instrument. The image resolution of FIB was 5 nm, the depth resolution and the detection limit of EDS were $0.5\ \mu\text{m}$ and 1%, respectively. The ionic contaminants deposited on the wafer surface were extracted by deionized water [18], [23], [24]. The wafer extraction was agitated for approximately 30 min in the ultrasonic bath and the extracted contaminants were analyzed by a DIONEX DX-500 ion chromatography (DX-500, Dionex, USA) equipped with $\text{AS12A}+\text{AG12A}$ column for anions analysis and $\text{CS12A} + \text{CG12A}$ column for cations analysis. A micro laser particle counter (PMS, particle measuring systems) was also used to measure the concentration of particles larger than $0.01\ \mu\text{m}$ in the cleanroom environment.

The ambient inorganic concentration near the deposition "witness" wafers was monitored throughout each exposure experiment. Impingers were used to collect inorganic acids and bases. The impingers were filled with IC eluent absorbent ($2.7\ \text{mM Na}_2\text{CO}_3/0.3\ \text{mM NaHCO}_3$) for acid gases sampling, $0.01\text{N H}_2\text{SO}_4$ absorbent for basic gases sampling. The extracts of the acid and basic gases were also analyzed by DIONEX DX-500 ion chromatography. Detailed description of the ambient sampling and analysis condition can be referred to Lin *et al.* [25].

TABLE I
SURFACE CONCENTRATIONS AND DEPOSITION RATES OF THE IONIC AND ORGANIC CONTAMINANTS

	Contaminants	Measured ambient concentration (ng/cm^3), C_g Mean($\pm$SD[a]) $\times 10^{-3}$	Calculated adsorption rate constant (cm/min) K_{ads}	Calculated desorption rate constant (min^{-1}) K_{des}	Equation for time-dependent surface density (ng/cm^2), $C_s(t)$	Calculated asymptotic surface concentration, (ng/cm^2), C_s Mean($\pm$SD)
Anions	F^-	3.72($\pm$0.38)	3.6	4.8×10^{-3}	$C_g \times 750 \times [1-e^{-0.0048t}]$	2.79($\pm$0.28)
	Cl^-	2.15($\pm$0.24)	5.2	3.0×10^{-3}	$C_g \times 1733 \times [1-e^{-0.003t}]$	3.73($\pm$0.35)
	NO_2^-	1.96($\pm$0.23)	–	–	–	–
	NO_3^-	0.40($\pm$0.09)	10.4	7.5×10^{-3}	$C_g \times 1386 \times [1-e^{-0.0075t}]$	0.55($\pm$0.07)
	SO_4^{2-}	1.90($\pm$0.21)	2.1	4.4×10^{-3}	$C_g \times 477 \times [1-e^{-0.0044t}]$	0.90($\pm$0.10)
Cations	Na^+	1.90($\pm$0.27)	9.9	4.0×10^{-3}	$C_g \times 2475 \times [1-e^{-0.004t}]$	4.72($\pm$0.68)
	NH_4^+	8.20($\pm$1.24)	2.0	7.5×10^{-3}	$C_g \times 266 \times [1-e^{-0.0075t}]$	2.18($\pm$0.08)
	K^+	0.86($\pm$0.16)	28.8	3.3×10^{-3}	$C_g \times 8727 \times [1-e^{-0.0048t}]$	7.53($\pm$0.87)
	Mg^{2+}	0.28($\pm$0.07)	10.9	2.8×10^{-3}	$C_g \times 3892 \times [1-e^{-0.0028t}]$	1.12($\pm$0.18)
Organic	DEP[11]	20($\pm$5)	2.3×10^{-3}	1.9×10^{-2}	–	–

[a] SD : Standard Deviation

IV. RESULTS AND DISCUSSION

A. FIB/EDX Analysis

The wafer exposure time in the cleanroom environment was controlled from 30 min to 1 day to identify the effect of exposure time for the AMCs concentrations on the wafer surface. The results showed that hazing contaminants were most frequently observed for exposure time of 1 day. No hazing contaminants were found for exposure time of 30 min. The mean number concentration of particles in a cleanroom atmosphere was 1.84 ± 0.92 particles/cm^3 and the mass concentration of them was $17.25 \pm 2.62 \times 10^{-3}$ ng/cm^3 for 1 day exposure. Because the total mean mass concentration of inorganic AMCs, 21.37×10^{-3} ng/cm^3 as calculated from Table I, was similar to that of particles, thus it is reasonable to suspect that the hazing contaminants may be from both the airborne molecular contaminants and particles as well. Fig. 1 shows the FIB images of hazing contaminants and X-ray spectra of ionic contaminants. The morphology of hazing contaminants shows spherical shape. Small agglomerates of very fine primary particles are also observed. The contaminants were larger $(> 100 \times 100\ \mu m^2)$ than the wafer contaminating particles studied by Bai *et al.* [8], in which they reported that the sizes of organic + inorganic particulate contaminants varied form $3 \times 3\ \mu m^2$ to $25 \times 50\ \mu m^2$.

The EDS spectrum of the inspection point indicated in the FIB image is shown in Fig. 1(a), it reveals that the surface contaminants contain C, Cl, and K compounds. Thus the compounds causing wafer hazing might be both the organic and inorganic airborne molecular contaminants as well. Hazing contaminants of semi-void images containing C, K, O, Na, and S compounds are observed in Fig. 1(b). Because the appearance of hazing contaminant was obvious, the relative percentages of C and K elements were larger than that of Si element. It was found that the hazing chemical was also composed of organic and inorganic contaminants.

B. Determination of Adsorption Kinetics and Surface Concentrations On Silicon Wafers

Table I shows measured ambient concentrations and calculated wafer surface concentrations. In a cleanroom environment, the F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, and Mg^{2+} ions on the wafer surface can be analyzed by ion chromatography analysis. However, only the Cl, S, Na, and K elements were detected by the EDS for 1 day exposure time as shown previously in Fig. 1. This is mainly due to lower surface concentration of NO_3^- and Mg^{2+} ions on the wafer surface and less accurate analysis of F and N light elements via the EDS.

Workers through sweat and skin peeling have been identified as one of the major sources of Na^+ [17], while K^+ contamination could be due to potassium hydroxide (KOH) or water deep etching environment. And NH_4^+ commonly comes from the use of HMDS (Hexamethyldisilazane) and SC1 $(NH_4OH : H_2O_2 : H_2O)$ for wafer cleaning purposes. The F^- and Cl^- ions are most likely the residues during initial wafer preparation by SC2 $(HCl : H_2O_2 : H_2O)$ and HF cleaning processes, while the NO_3^- and SO_4^{2-} ions are from external environmental sources. These anions and cations may directly deposit on the wafer surface or from gaseous contaminants and distribute in the ambient air. It is also likely to be transmitted into particulate form and characterized as hazes found on wafers [8].

When all cations and anions were all taken into account, the detectable cation/anion molar ratios of $(Na^+ + NH_4^+ + K^+ + Mg^{2+})/(F^- + Cl^- + NO_3^- + SO_4^{2-})$ was around 2.58, indicating that cations were more than anions on the wafer surface. This was confirmed by that the total ionic species on the wafer were in basic state with pH value of the extracted solution to be 8.15. Thus, the cations might be combined with OH^- ions instead of forming salt particles.

The asymptotic curve described in (2) was employed to obtain the kinetic parameters of K_{ads} and K_{des} by a numerical algorithm based on the least-squares error method [11]. The optimal values of K_{ads} and K_{des} were listed in Table I along with measured average ambient concentration and the calculated asymptotic surface concentration. The maximum values of K_{ads} appeared to be those of NO_3^- and K^+ contaminants (10.4 and 28.8 cm/min), respectively for anions and cations. And those of K_{des} were NO_3^- and NH_4^+ contaminants (7.5×10^{-3} and $7.5 \times 10^{-3}\ min^{-1}$), respectively. Because the surface concentration of NO_2^- ion was lower than the instrument detection limit (IDL), Table I does not show their optimum values of K_{ads} and K_{des}. By comparing to our previously reported data for organic DEP (Diethyl Phthalate) [11], one can see that as compared to organic DEP, the adsorption rate constants (K_{ads}) of all ionic contaminants were higher than that of DEP [11] as shown in Table I. On the other hand, the desorption rate constants (K_{des}) of all ions were lower than that of DEP. This indicated that the deposition tendency of ions on wafer surfaces was higher than that of DEP even though the ambient concentration of DEP was higher.

After obtaining the kinetic constants, the time-dependent variation of surface concentrations of ionic contaminants can be simulated. The asymptotic shape of the simulated curves

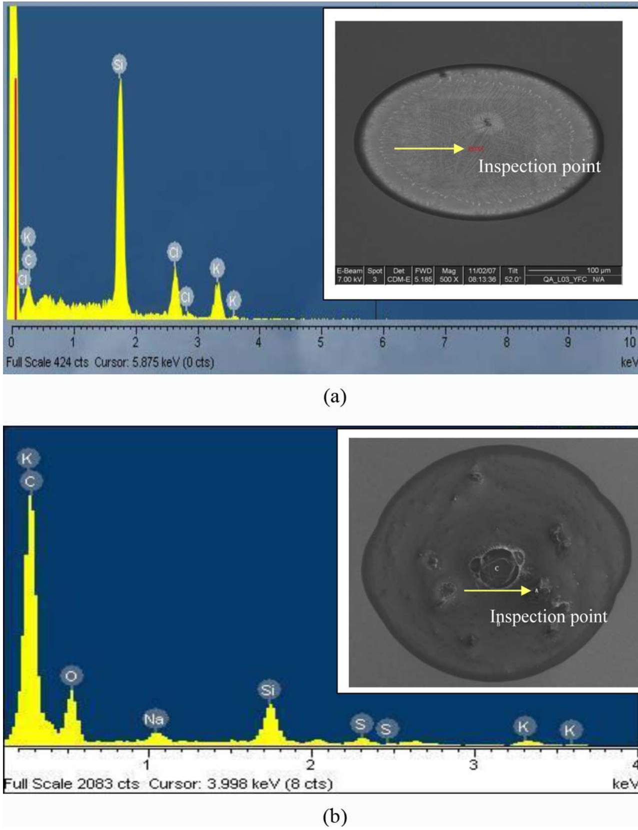

Fig. 1. FIB images and EDS spectrum of wafer surface contaminants in (a) General location and (b) Semi-hollow point of hazing contaminant for exposure time of 1 day.

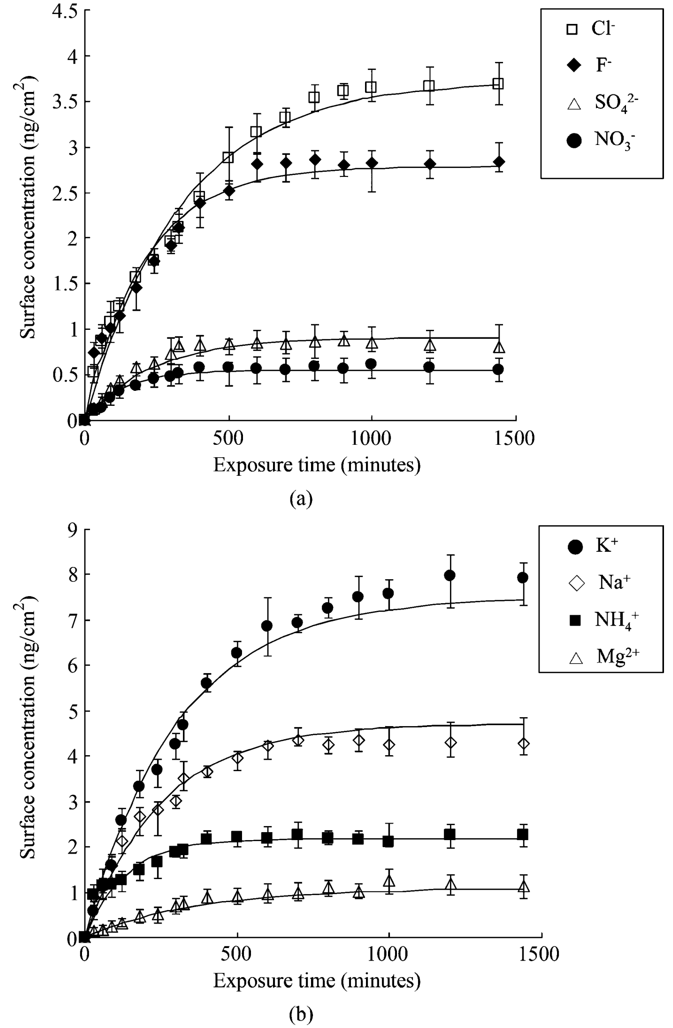

Fig. 2. Surface concentrations measured on the wafer surface as a function of exposure time for (a) Anions and (b) Cations. The ambient concentrations of each ionic species can be seen in Table I.

indicated that the wafer surface had a finite number of adsorption sites. And the simulated results are shown in Figs. 2(a) and 2(b) along with the experimental data. It was observed that the surface concentrations of all contaminants were increased with the exposure duration. The surface concentrations of NO_3^- and NH_4^+ reached quasi-steady-state at around 300 $\sim$ 500 min of exposure time, which were faster than those of F^-, Cl^-, SO_4^{2-}, Na^+, K^+, and Mg^{2+} ions. This observation can be interpreted by their larger values of K_{des}, reflecting that NO_3^- and NH_4^+ ions regained energy as they struck on the wafer surface and desorbed from it at much faster rates. On the other hand, although K^+ ions have the highest value of K_{ads}, its relatively low value of K_{des} implies that K^+ ions would reach equilibrium concentration at a much slower rate. The high value of K_{ads} also resulted in a higher surface concentration of K^+ as compared to those of other ions. For NH_4^+ cations, the difference in the values between K_{ads} and K_{des} were smaller than those of other cations and anions, which imply a faster equilibrium, thus the low adsorption rate of NH_4^+ ions leads to a lower surface concentration even though it has the highest ambient concentration.

C. Determination of Deposition Velocity and Sticking Coefficient

The deposition velocity, V_{dep}, of ionic contaminants onto wafer surface can be calculated from the contaminant's mass deposition flux and its gas-phase concentration, which was defined as the flux of a pollutant onto the wafer surface divided by the pollutant concentration in the environment [11].

$$V_{\text{dep}} = \frac{\text{Mass deposition flux}}{\text{Ambient concentration}} = \frac{\frac{C_S}{\Delta t}}{C_g} = Eu. \tag{5}$$

The vertical air flow velocity, u, in the cleanroom was $0.45\ \text{ms}^{-1}$. And the cumulative exposure time, Δt, ranged from 30 min to 24 h base on the sampling time. According to (5), the logarithmic trend of time-dependent deposition velocities and sticking coefficients of ionic contaminants are shown in Fig. 3(a) and (b). The deposition velocities and sticking coefficients of the ionic contaminants were much higher during initial adsorption time and declined rapidly with the exposure time. The deposition velocity and sticking coefficient of K^+ ions were the largest amongst all ionic species. This is expected since K^+ ions having the greatest surface adherence potential, i.e., the largest value of K_{ads}. The values of the rate of exponential decay of deposition velocity and sticking coefficient

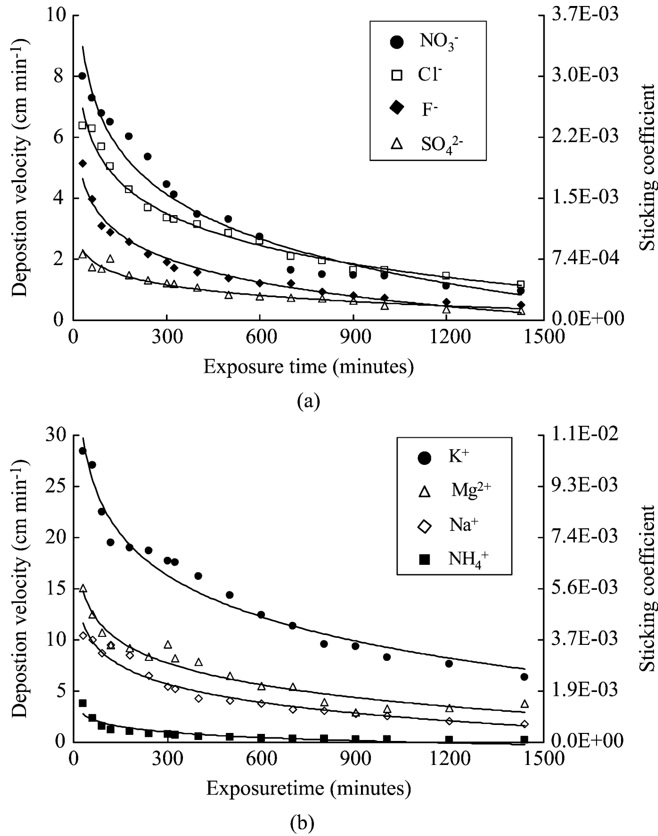

Fig. 3. Time-dependent function of the deposition velocity and sticking coefficient for (a) Anions and (b) Cations.

were in the sequence of $NO_3^- > Cl^- > F^- > SO_4^{2-}$ and $K^+ > Mg^{2+} > Na^+ > NH_4^+$, which had the same trend as K_{ads}.

Table II lists sticking coefficients of ionic contaminants based on the accumulative exposure time over 30 min, 1 h, 4 h, and 24 h of exposure. One can observe that values of the sticking coefficients calculated based on the different exposure times are quite different. The sticking coefficients obtained from 30 min exposure time were $4 \sim 19$ times higher than those from 24 h exposure time.

The comparison between ionic contaminants and organic DEP and DBP (Dibutyl Phthalate) on their sticking coefficients is also shown in Table II. The sticking coefficients over 1 h and 4 h of exposure ranged from 6.44×10^{-4} to 1.00×10^{-2} and 3.26×10^{-4} to 6.92×10^{-3} for ionic species, respectively. Kang *et al.* [12] estimated the values of E_{ave} for DEP and DBP to be $9.8(\pm 0.4) \times 10^{-6}$ and $1.4(\pm 0.1) \times 10^{-5}$, respectively, over 1 h of exposure under stagnant air, and $3.1(\pm 0.2) \times 10^{-6}$ and $5.7(\pm 0.6) \times 10^{-6}$, respectively, over 4 h of exposure under stagnant air. The sticking coefficients of DEP and DBP estimated by Kang *et al.* [12] are much smaller than those of ionic species. This can be explained by that the movement of a molecule under stagnant air was dominated by its thermal velocity. And the average thermal velocity of DEP and DBP used in Kang's study [12] were both nearly two orders of magnitude larger than the laminar velocity used in this study, thereby yielding much smaller values of E_{ave} in Kang's study [12].

TABLE II
COMPARISON OF THE STICKING COEFFICIENTS BETWEEN IONIC CONTAMINANTS AND ORGANIC DEP AND DBP

Contaminants		Sticking coefficient Mean(±SD[a])			
		0-30 minutes	0-1 hour	0-4 hours	0-24 hours
Anions	F^-	1.90×10^{-3}	1.47×10^{-3}	8.06×10^{-4}	1.88×10^{-4}
	Cl^-	2.36×10^{-3}	2.32×10^{-3}	1.36×10^{-3}	4.28×10^{-4}
	NO_3^-	2.96×10^{-3}	2.70×10^{-3}	1.98×10^{-3}	3.53×10^{-4}
	SO_4^{2-}	8.02×10^{-4}	6.44×10^{-4}	4.88×10^{-4}	1.13×10^{-4}
Cations	Na^+	3.86×10^{-3}	3.70×10^{-3}	2.41×10^{-3}	6.71×10^{-4}
	NH_4^+	1.39×10^{-3}	8.82×10^{-4}	3.26×10^{-4}	7.29×10^{-5}
	K^+	1.05×10^{-2}	1.00×10^{-2}	6.92×10^{-3}	2.36×10^{-3}
	Mg^{2+}	5.57×10^{-3}	4.62×10^{-3}	3.08×10^{-3}	1.39×10^{-3}
Organic[b]	DEP	—	$9.8(\pm0.4)\times10^{-6}$[12]	$3.1(\pm0.2)\times10^{-6}$[12]	$6.7(\pm2.8)\times10^{-5}$[14]
	DBP	—	$1.4(\pm0.1)\times10^{-5}$[12]	$5.7(\pm0.6)\times10^{-6}$[12]	$8.9(\pm2.7)\times10^{-5}$[14]

[a] SD：Standard Deviation

[b] The 0-4 hours average data on the sticking coefficients of DEP and DBP were from Kang et al. [12], while 0-24 hours of exposure on the sticking coefficients of DEP and DBP were from Veillerot et al. [14].

For 24 h of exposure time, the sticking coefficients ranged from 7.29×10^{-5} to 2.36×10^{-3} for ionic species. As compared to the results of Veillerot *et al.* [14] where the values of E_{ave} were $6.7(\pm 2.8) \times 10^{-5}$ and $8.9(\pm 2.7) \times 10^{-5}$ for DEP and DBP, respectively, for the exposure duration of 24 h under a vertical air flow velocity of $0.44\ \mathrm{ms}^{-1}$, these values were also smaller than most of the ionic contaminants except the NH_4^+ ions. Thus one can conclude that the surface deposition tendency of ionic contaminants is much stronger than that of organic contaminants.

D. Prediction of Critical Contamination Levels

As a guideline for wafer surface preparation technology, the ITRS recommends that the maximum allowable mobile ions impurity of less than 2.2–2.5 $\times 10^{10}$ atoms cm^{-2} be achieved for the 14–57-nm technology node by 2008–2020 [26]. This specification implies that devices could be damaged if the amount of mobile ion contaminants adhering to the wafer surface exceeds the level recommended by the ITRS. Therefore, silicon wafers are stored and conveyed by a protective box in the cleanroom to avoid damage to devices. However, there is still possibility that wafer could be contaminated during any manufacturing on transportation procedures. Thus process engineers are of particular interest to have knowledge on the maximum exposure time and the concentration threshold of mobile ions in local environments. Based on the ITRS recommended level,

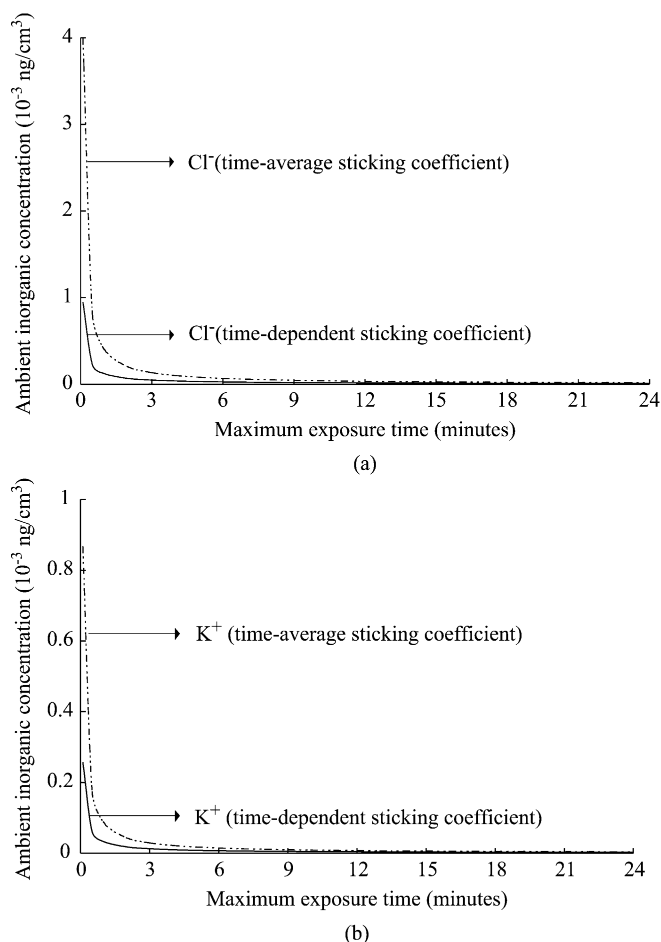

Fig. 4. Relationship between the maximum sit-time and the ambient ionic concentrations of (a) Cl^- and (b) K^+ contaminants under the 4 h time-average and time-dependent sticking coefficients. The profiles are generated based on the 2.5×10^{10} atoms cm^{-2} mobile ions threshold on wafer surfaces proposed by the ITRS.

the critical level of surface concentrations of F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, and Mg^{2+} ions are 6.5–7.4 $\times$ 10^{-4}, 1.2–1.4$\times 10^{-3}$, 2.2–2.5$\times 10^{-3}$, 3.5–3.9$\times 10^{-3}$, 8.4–9.5$\times 10^{-4}$, 6.5–7.4$\times 10^{-4}$, 1.4–1.6$\times 10^{-3}$, and 8.7–9.9$\times 10^{-4}$ $\mathrm{ng\ cm}^{-2}$, respectively. Thus based on the critical levels of surface concentration and their sticking coefficients, one can establish the relationship between maximum sit-time (t) and the ambient concentration (C_g) via rearrangement of (4):

$$tC_g = \frac{C_s}{Eu}. \tag{6}$$

Results on the relationship between maximum sit-time and threshold concentration based on the ITRS recommended level of 2.5×10^{10} atoms cm^{-2} on a wafer surface are shown in Fig. 4 using Cl^- and K^+ ions as example compounds. The time-average values of the sticking coefficient over 4 h of exposure were applied in the study of Kang *et al.* [11] to calculate the allowable maximum sit-time. But from Table II one can say that it is more reasonable to evaluate the relationship between maximum sit-time and threshold concentration based on the time-dependent sticking coefficient.

Based on Fig. 4(a), if wafers were to be exposed to 2.15×10^{-3} $\mathrm{ng\ cm}^{-3}$ of Cl^- contaminant in the environment as measured in this study (see Table I), the allowable sit-time were 11.1 and 2.4 s for the 4 h time-average and time-dependent sticking coefficients, respectively. Similarly from Fig. 4(b) one can see that if wafers were to be exposed to 0.86×10^{-3} $\mathrm{ng\ cm}^{-3}$ of K^+ contaminant in the environment, the allowable sit-time were 6.0 and 1.6 s for the 4 h time-average and time-dependent sticking coefficients, respectively. It indicated that even a few seconds of exposure to the cleanroom environment could incur damage to silicon wafer based on the time-dependent sticking coefficient. Thus the elimination of contamination sources is important to achieve control and ultraclean manufacturing.

V. Conclusion

Analytical monitoring of ultratrace amounts of inorganic cations and anions on the surface of a silicon wafer as well as in the cleanroom air has been conducted in this study. The results reveal that NO_3^- and NH_4^+ ions reach equilibrium concentration on the wafer surface at much faster rates than the other ions. The surface concentration of K^+ ion is relatively larger due to its higher value of adsorption rate constant (K_{ads}). Furthermore, a kinetic model was established to depict the time-dependent deposition for ionic contaminants. The model, validated by the experimental profiles, proved to be useful for the prediction of surface deposition quantity under various exposure times. The sticking coefficients of ionic contaminants were higher than those of DEP and DBP organic contaminants. By identifying the major ionic species and determining their sticking coefficients, it is possible to estimate the threshold limits for allowable wafer exposure times and maximum ambient concentrations according to the guideline recommended by the ITRS.

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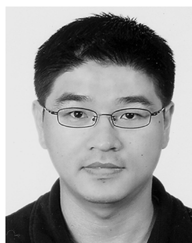

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