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Dimensional and Elemental Analysis of Particulate Contaminations on Silicon Wafers

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As the dimensions of semiconducting devices continue to shrink, microelectronic devices are becoming increasingly sensitive to micro-contamination on wafer surfaces. This investigation analyzes the particulate morphology, elemental composition and the particle sizes of wafer contaminants in the lithographic process area of a semiconductor plant. Scanning electron microscopic and energy dispersive X-ray spectroscopic analyses identified the elemental compositions of micro-contaminants of silicon wafers as silicon, carbon, oxygen, sodium, magnesium, aluminum, phosphorus, sulfur, chlorine, potassium, calcium, and iron. The organic contaminants on the surfaces of the wafers were approximately 1-2 μm and were the smallest of all the contaminants. Condensation by organic vapors was the likely source of organic contamination. Inorganic particles could also have contaminated the wafer surfaces by sticking onto them. The co-existence of organic and inorganic elements enlarges the wafer contaminants up to 30-50 μm. The particle sizes were not directly proportional to the period of exposure of the wafer.

Keywords: Silicon wafers, micro-contamination, airborne molecular contamination (AMC), clean room, lithographic process.

1. Introduction

As the dimensions of semiconducting devices continue to shrink to 0.13 μm and even lower, controlling micro-contamination has become increasingly important in their manufacturing procedure. Many sources of micro-contamination are present in a clean room environment, of which the deposition of airborne molecular contaminant (AMC) onto wafer surfaces is the most likely to affect product yield, as the arrival rates of AMC onto the wafer surfaces are several orders of magnitude higher than those of particles (Muller et al., 1994). Higley and Joffe (1996) considered the example of process-related AMC, and offered solutions that could be implemented in existing and future clean rooms. Recently, Barzaghi et al. (2001) demonstrated AMC control for DUV stepper lenses using purged gas purification. Because AMC adhering on wafer surfaces becomes more detrimental as feature geometries decrease to 0.13 μm and below, the chemical concentrations and compositions of wafer contaminants produced by AMC must be determined.

Many studies have addressed the identification of compositions of contaminating particles on the wafers. While studying how airborne organic contaminants affect a clean room, Saito (1995) and Tamaoki et al. (1995) developed methods for

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analyzing the contaminants adsorbed on wafer surfaces. Those methods involved gas chromatography / mass spectrometry (GC/MS), thermal desorption-gas chromatography / mass spectrometry (TD-GC/MS) and thermal desorption -atmospheric pressure ionization mass spectrometry (TD-APIMS). Many specific organic compounds adsorbed on silicon wafers were identified, including dioctyl-phthalate (DOP), other esters, and amines. Saga and Hattori (1996) analyzed organic contaminants on the surface of silicon wafers stored in various types of plastic box as well as volatile species out-gassing from the box materials to identify the source of the wafer organic contaminants. Tanishima and Abe (1998) examined the organic contamination of silicon wafer surfaces in processing equipment, and found that the wafer surfaces were contaminated in the fan filter unit (FFU) processing equipment, typically with organo-silicones and additives such as DOP.

Other studies have identified and quantified the contamination on wafer surfaces by metals. By applying vapor phase decomposition / total reflection X-ray fluorescence (VPD/TXRF), Liou et al. (1999) detected elemental metal concentrations on the wafer surfaces down to 10^8 atoms/cm^2. De Witte et al. (2000) considered the capability of time-of-flight secondary ion mass spectrometry (TOF-SIMS) in monitoring metal contamination on silicon wafer.

Uritsky et al. (1994) examined the appearance and compositions of wafer contaminants, using scanning electron microscope and energy dispersive X-ray spectroscopy (SEM/EDS) in a chemical vapor deposition process. However, wafer contamination problems were typically more significant in the lithographic process area of a fabrication plant than in other areas. Accordingly, this study analyzes particle contaminants on the wafer surfaces in the lithographic process area of an 8-inch integrated circuit (IC) plant by using an SEM/EDS instrument. Relationships between particle sizes and the chemical compositions and morphology of contaminants are also established to yield further information concerning the identity of possible micro-contamination sources.

2. Experimental Section

Blank silicon wafers were exposed in a lithographic process area of an 8-inch IC plant in Taiwan for 0, 12, 24 hrs and 2-3 days before coating. The wafers were then analyzed by a high resolution SEM/EDS (S-4700I+S-570 / XA-8800M, Hitachi/Jeol, Japan) instrument, to obtain a photo image and X-ray spectrum of the particle contaminants. A total of 34 SEM/EDS analyses of particles on silicon wafers were performed. A condensation particle counter (CPC, TSI model 3010, USA) was also used to measure the concentration of particles larger than 0.01 μm in the clean room environment.

The morphology and sizes of particle contaminants were determined by visual analyses of the SEM photo images. Most of the particles were non-spherical; therefore, the longest and shortest lengths of the contaminants were reported. When an SEM photo image showed more than one particle, the size of the largest particle was recorded. A cluster of several small particles was treated as a single large particle.

Elements with atomic sequences between B^5 and Se^{34} in the contaminants can be detected from the X-ray spectrum obtained using the EDS instrument. EDS yielded the relative percentages of each elemental compound. However, the X-ray spectrum determined the elemental compositions only at the single point where the X-ray penetrated, so information on the relative percentages of each compound is unreliable for particles with non-uniformly distributed chemicals. Consequently, this study reported only semi-quantitative analyses of the elements based on X-ray spectrum.
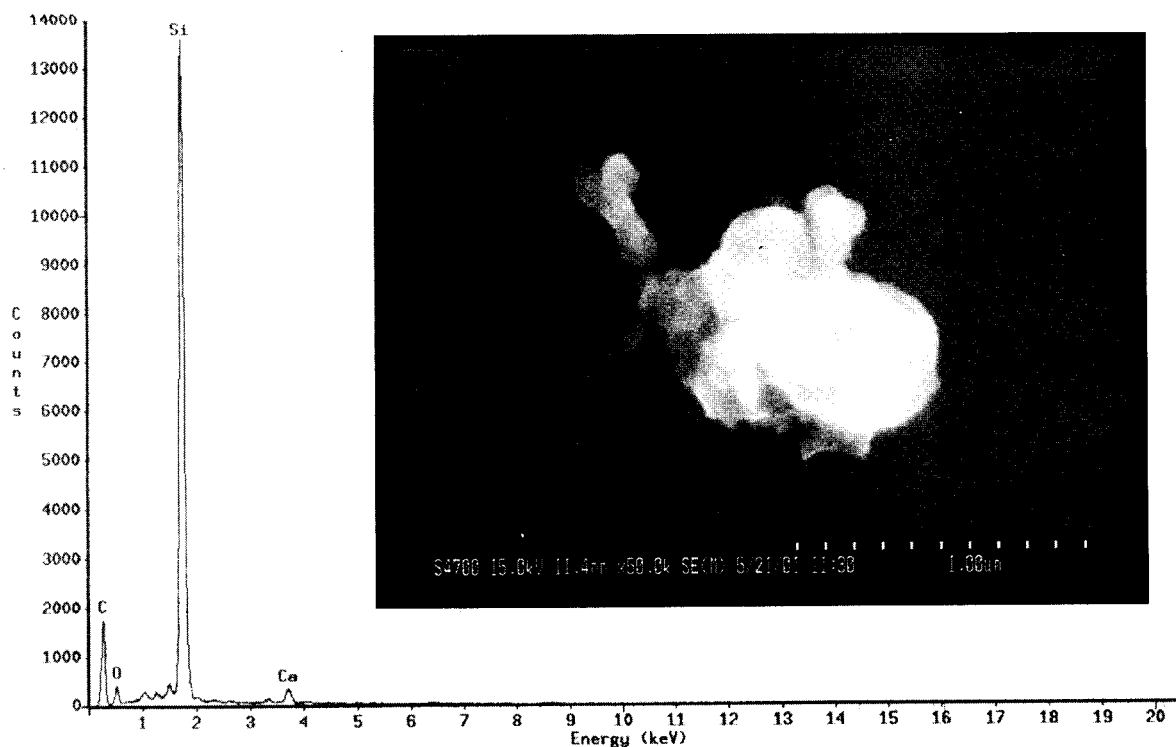
Figure 1. The SEM images and EDS spectrum of the type I (C-O) contaminants.

Table 1. Summary of SEM/EDS image and spectrum results of wafer contaminants.

Organic Particles		Inorganic Particles[a]	Organic+Inorganic Particles	
(I). C-O	(II). C-Cl-O	(III). Cl-K	(IV). C-O-K-P	(V). C-O-Na-Mg-Al-P-S-Cl-K-Ca-Fe
$1 \times 1\ \mu m^2$ $1 \times 2\ \mu m^2$ $2 \times 2\ \mu m^2$	$1 \times 3\ \mu m^2$ $1 \times 4\ \mu m^2$ $2 \times 2\ \mu m^2$ $4 \times 4\ \mu m^2$ $5 \times 7\ \mu m^2$	$1 \times 2\ \mu m^2$ $6 \times 5\ \mu m^2$ $7 \times 10\ \mu m^2$ $15 \times 20\ \mu m^2$ $20 \times 20\ \mu m^2$	$1 \times 2\ \mu m^2$ $1 \times 2\ \mu m^2$ $1 \times 3\ \mu m^2$ $2 \times 3\ \mu m^2$ $2 \times 4\ \mu m^2$ $3 \times 3\ \mu m^2$ $3 \times 4\ \mu m^2$ $3 \times 4\ \mu m^2$ $5 \times 10\ \mu m^2$ $6 \times 10\ \mu m^2$	$3 \times 3\ \mu m^2$ $3 \times 6\ \mu m^2$ $5 \times 5\ \mu m^2$ $6 \times 9\ \mu m^2$ $10 \times 15\ \mu m^2$ $15 \times 20\ \mu m^2$ $25 \times 35\ \mu m^2$ $30 \times 30\ \mu m^2$ $20 \times 50\ \mu m^2$ $30 \times 40\ \mu m^2$ $25 \times 50\ \mu m^2$

[a] Many small particles of $<1 \times 1\ \mu m^2$ were observed in all SEM images of Type III contaminants.

3. Results and Discussion

The particle concentrations in a class 1 clean room environment were investigated by condensation particle counter (CPC), while the wafers were exposed, to clarify the sources of wafer contaminants. The results of CPC indicated that the mean numerical concentrations of particles in a clean room atmosphere were 0.06 ± 0.02 particle/cm^3 and 0.07 ± 0.03 particle/cm^3, respectively, for 12 hours and 24 hours exposure. Thus it is reasonable to suspect that the wafer contaminants may be from the air borne molecular contaminants instead of directly from the particles in the clean room environment.

After the SEM analyses were completed, the particulate contaminants were classified according to their chemical composition into three categories--organic contaminants, inorganic contaminants and organic+inorganic contaminants. The organic contaminants were further grouped into carbon and oxygen (indicated by C-O)-containing particles, or carbon, chlorine, and oxygen (C-Cl-O)-containing particles. The organic+inorganic contaminants were further grouped into carbon, oxygen, potassium and phosphorus (C-O-K-P)-containing particles, or carbon, oxygen, sodium, magnesium, aluminum, phosphorus, sulfur, chlorine, potassium, calcium and iron (C-O-Na-Mg-Al-P-S-Cl-K-Ca-Fe)-containing particles. Table 1 summarizes the
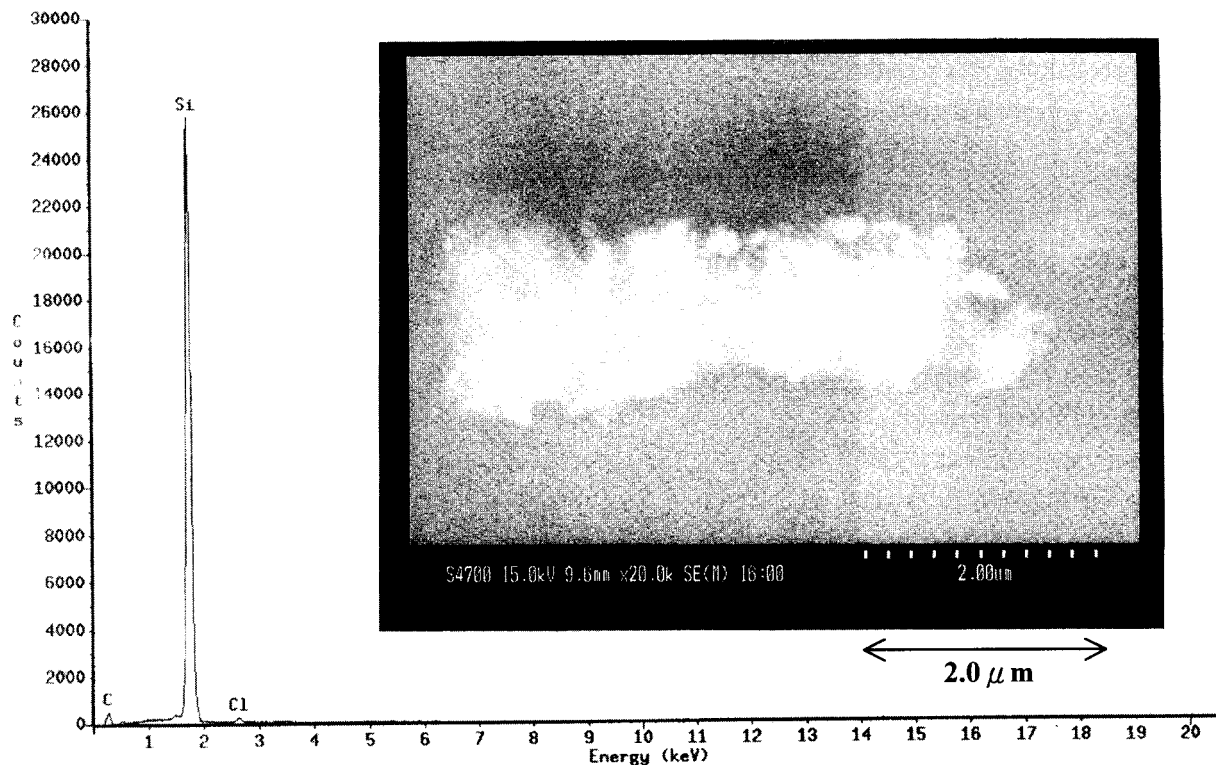
Figure 2. The SEM images and EDS spectrum of the type II (C-Cl-O) contaminants.

particle sizes of the five types of contaminants. The exact number of particles of each type of contaminant could not be counted because the SEM instrument provided photo images only. However, Table 1 shows that pure organic or inorganic particles (Types I to III) were less frequently observed than the co-existence of organic and inorganic particles (Types IV and V). The organic particles were smaller than the other types of particles.

Figures 1-5 show the SEM images and X-ray spectra of each type of particle contaminants. Notably, the silicon element (Si) dispersed significant energy in all figures. However, the X-ray source of EDS may have penetrated the particle contaminants and traveled into the silicon wafers, so the detected Si could be from the wafer itself.

The Type I particles consisted mainly of C and O compounds only. Consider the example of the SEM image shown in Fig.1: although Ca appears to have been detected, according to the EDS spectrum,

the elemental weight of C is 22 times of that of Ca. Therefore, the contamination on the wafer surfaces can be treated as organic. Table 1 indicates that the Type I particles were smaller ($<2\times2$ μ m^2) than the other types of wafer contaminating particles. As shown in Fig.1, the shape of the organic particles is irregular, with thin and smooth surfaces that may have been formed by vapor condensation. Hence, the condensation from the clean room air onto the wafer surfaces of organic vapors with high boiling points could be one of the initial sources of wafer contamination.

Table 1 reveals that Type II (C-Cl-O) organic particles were also smaller than the inorganic particles. As indicated by Fig.2, with the presence of the Cl element there seems to have tiny particles coalesced together to form a larger cluster particle.

The Type III inorganic particles include both K and Cl compounds. Their sizes varied from 1×2 μ m^2 to 20×20 μ m^2, indicating that inorganic compounds alone might have been the other source of wafer contaminants. Figure 3 shows the
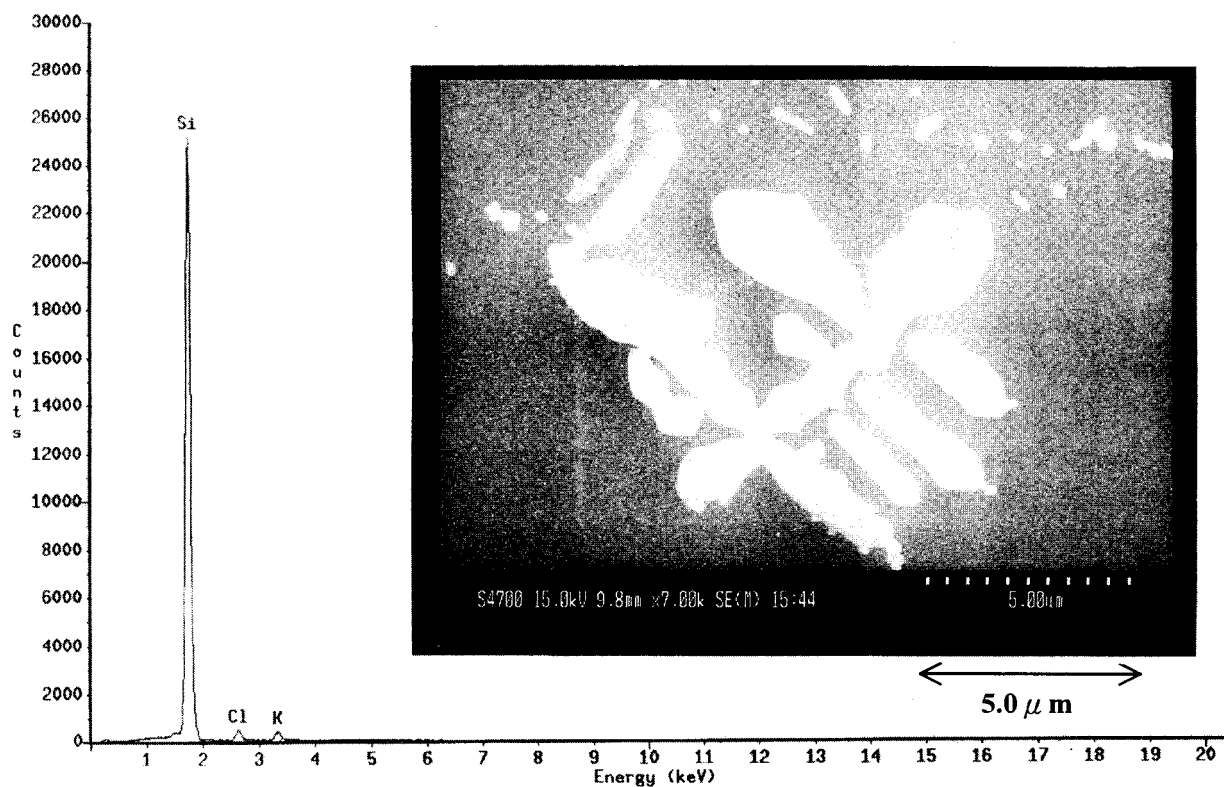
Figure 3. The SEM images and EDS spectrum of the type Ⅲ (Cl-K) contaminants.

morphology of inorganic particles. With respect to Type Ⅲ particles that contained both Cl and K compounds, the smaller particles that were loosely connected to each other exhibited a fractal geometry.

The Type Ⅲ particles were typically brighter than the other types of contaminants, and several single, small particles ($<1 \times 1 \mu m^2$) were always present around the large Cl-K particles. This phenomenon was observed less frequently for other types of contaminants. The presence of many small particles also revealed the high probability of coagulation of large Type Ⅲ contaminants from small particles.

Type Ⅳ (C-O-K-P) and Type Ⅴ (C-O-Na-Mg-Al-P-S-Cl-K-Ca-Fe) contaminants contained both organic and inorganic elements, but the elements contained in Type Ⅳ contaminants were much less than that in Type Ⅴ contaminants. As shown in Table 1, the particles of Type Ⅳ contaminants ($<6 \times 10 \mu m^2$) were typically smaller

than the particles of Type Ⅴ contaminants ($<25 \times 50 \mu m^2$). Particles that contained both organic and inorganic elements were the most frequently observed. A total of 34 SEM/EDS analyses yielded 22 observations of contaminants that contained both organic and inorganic elements.

Type Ⅳ particles contains potassium and phosphorus, as well as carbon and oxygen. Although all particles are porous, the morphology of Type Ⅳ particles does not show any fixed shape. Figure 4 shows near spherical morphology on the right side, but other Type Ⅳ particles were cylindrical, mushroom-shaped, or another irregular shape.

Type Ⅴ particles are the largest of all types of contaminants. The EDS analyses detected many elements and the relative percentage of each element were not the same. Therefore, neither the morphology nor the sizes of the particles were equal. Particles that contained many elemental compounds with significant peaks, as shown in
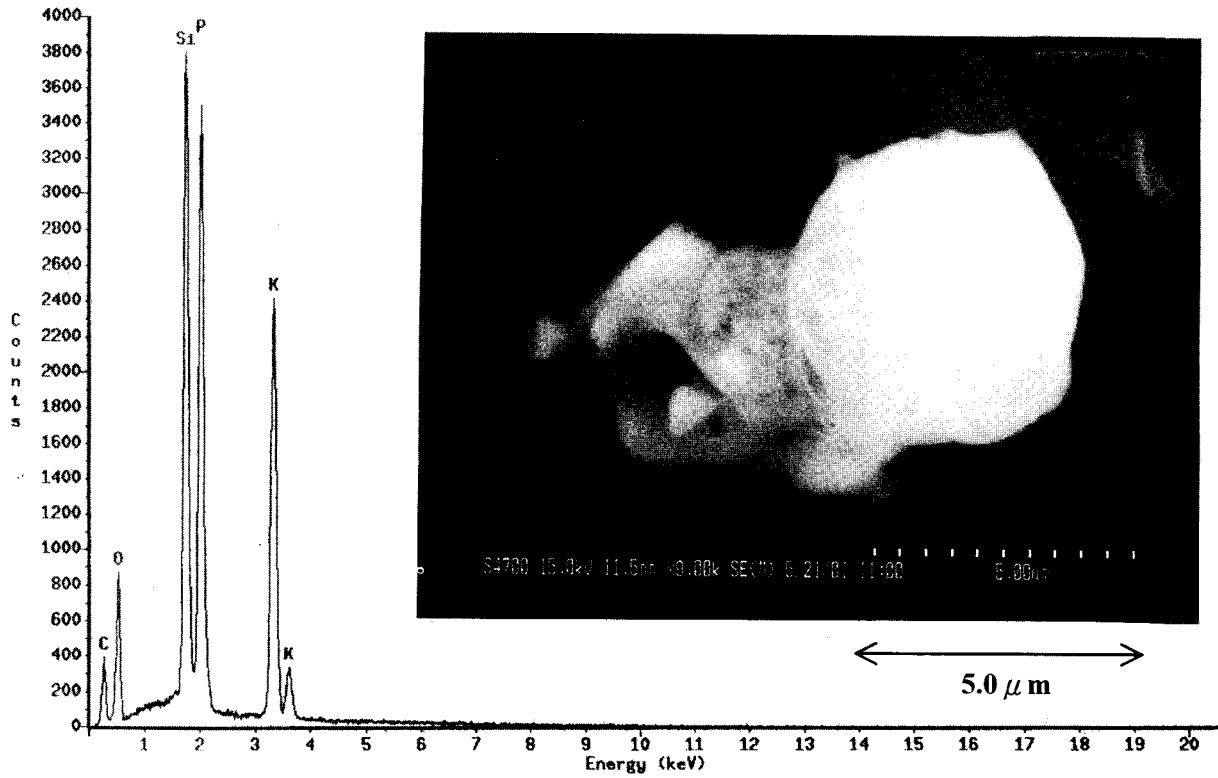
Figure 4. The SEM images and EDS spectrum of the type IV (C-O-K-P) contaminants.
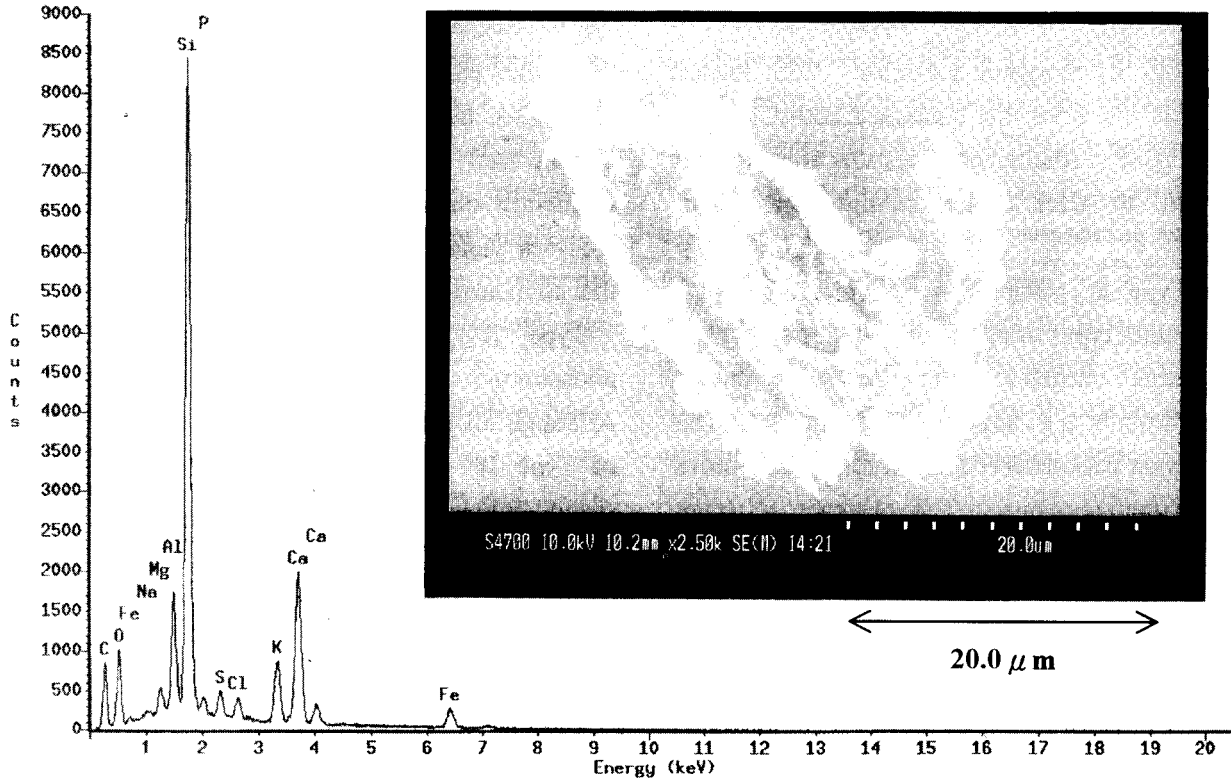

Figure 5. The SEM images and EDS spectrum of the type V (C-O-Na-Mg-Al-P-S-Cl-K-Ca-Fe) contaminants.

Fig.5, were usually irregularly shaped. For particles with significant energy dispersion, especially by Ca, the contaminants were composed of small, crystal-like particles. Exposure times of wafers in the clean room environment, before coating, were controlled from zero hours to three days to identify the effect of the period of exposure of the wafer to the clean room environment on the sizes of the contaminants.

The results showed that no contaminants were present on silicon wafers exposed for zero hours. The density of the particle contaminants on wafers exposed for 12 hours was approximately 10 particles/cm^2, and particles smaller than around 10 μm were most frequently observed. Increasing the wafer exposure time in the lithographic area increased the numerical density of wafer contaminants. The density rose to around 100 particles/cm^2 for three days of exposure time.

As specified by the International Technology Roadmap for Semiconductors (2001), the limitation for wafer contamination is < 2.6×10^{13} carbon/cm^2 for a 0.13 μm DRAM process. The atomic radii for elements detected in this study ranged from 0.5 to 2.5 Å, with a carbon radius of 0.77Å. Accordingly, a density of around 2×10^{13} ~ 2×10^{16} carbon/cm^2 can be estimated, with approximately ten spherical carbon particles of 1~10 μm diameter per cm^2 of wafer, which density is close to limit for a 0.13 μm DRAM process. Thus, even 12 hours of exposure to the clean room environment could incur damages to silicon wafers.

4. Conclusions

The micro-contamination on a wafer surface during the front-end process in a lithographic clean room area was investigated in this study. The elemental compositions of contaminants adsorbed on silicon wafers were also measured, and the contaminants were classified into five types, including C-O, C-Cl-O, Cl-K, C-O-K-P, and C-O-

Na-Mg-Al-P-S-Cl-K-Ca-Fe-containing particles. They could also be simply divided into three groups- organic, inorganic and organic+inorganic contaminants. The frequency of observation of organic/inorganic particles exceeded that of pure organic and the pure inorganic particles. Organic particles were smaller than the other types of wafer contaminants. The C-O-containing particles might have been formed by the condensation of organic vapors, and large C-Cl-O-containing particles might have been formed by the coalescence of small particles. The Cl-K -containing particles were typically brighter than the other types of contaminants, and their particles were loosely connected to each other. The C-O-K-P-containing particles were porous and were usually smaller than the C-O-Na-Mg-Al-P-S-Cl-K-Ca-Fe-containing particles. Both organic vapors and inorganic chemicals could be the initial sources of wafer contamination.

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