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Antistatic Protection in Wafer Drying Process by Spin-Drying

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Abstract—**The generation of static in the semiconductor manufacturing processes is an impediment which becomes increasingly grave with a rise in the degree of their integration [1]-[4]. The processes in which static trouble is now the greatest problem include wet processes and spin-drying.**

Antistatic technology is one of the key technologies in the manufacturing processing of semiconductors in the future. For antistatic protection of wafers, ionizers have been used in some instances. Conventional ionizers, however, have some vital disadvantages. The most serious defect is particle generation due to erosion and sputtering of the discharge electrode itsef and re-dispersion of deposits on the electrode surface. The sputtered particles consist of metallic materials from discharge electrode. The particle sizes are distributed between 0.01 μm and 0.1 μm in diameter. The re-dispersed particles consist mainly of SiO_2 including moisture (by X-ray analysis), and contain a small amount of $(NH_4)_2C_2O_4$ and R-COOH (R:hydrocarbon radical) (by Fourier transformation infrared rays spectroscopic analysis (FT-IR)). These compositions depend on the impurities in the atmosphere [5]. Another disadvantage is an ion imbalance, resulting in a high residual electric potential of tens to a few hundreds of volts (at 0.5 m below one electrode of a dc pulsed ionizer), which exposes devices to a high risk of destruction. Ionizers having these shortcomings can no longer be used for antistatic protection. Semiconductor manufacturing processes now require dust-free ionizers having a low residual potential after charge removal [4], [6]-[8].

We have developed a new ionizer for use with spin-dryers, and evaluated its charge removing and particle rejecting effects. It has proved very quick in charge removal, capable of keeping the residual potential at no more than 10 V, and also able to prevent statically induced particle deposition on wafers.

I. Introduction

CONCEIVABLY, static has mainly two impediments on semiconductor manufacturing processes. On one hand, the statically charged surface of an object is contaminated with drifting particles, which are drawn by the electrostatic force and deposit on the charged surface. On the other hand, the device is destroyed by static discharge.

Wafers are mainly dried by one of two methods, the spin-dryer process and the IPA vapor drying process. While the former is more often used at present, IPA drying is considered to be superior in terms of contamination with particles and the drop in yield due to device destruction. IPA is capable of complete static removal whether in a liquid or in a gaseous state, almost fully protecting wafers from static charging [9]. By contrast, when dried by a spin-dryer, wafers and wafer carriers are highly susceptible to charging by their friction with the fast air stream. Drying by spin-dryer, however, takes less time and accordingly is more suitable for use in mass production. Moreover, in IPA drying, IPA molecules themselves remain on the wafer surface though in no more than a single molecular layer [10]. Although this residual level is not yet high enough to affect the yield, it will make the process unusable in the future when the adsorption of gaseous impurities on the wafer surface will come to pose a problem.

Hence it is necessary to develop a static-free spin-dryer. It is in this context that the ionizer for use with spin-dryers has been developed. We have prevented particle generation due to sputtering of the discharge electrode themselves. The protection of its discharge electrodes with quartz glass completely prevents particle generation by ion and electron sputters, and the concentration of ozone generated is reduced to less than 1/10 of the usual level [4], [6]-[8]. This ionizer is excellent in charge removing performance, for instance, taking only about 1 second to reduce the wafer potential from ±5 kV to ±0.1 kV. The residual potential due to the imbalance of ion polarity is extremely low, only 10 V at the maximum. The ionizer's charge removing effect to prevent particle deposition was also evaluated, and almost complete success was achieved in preventing the statically induced deposition of particles to wafers while being dried by a spin-dryer.

II. Experimental

An external view of the ionizer developed for use with spin-dryers is shown in Fig. 1. The discharge electrode used herein is covered with dielectric ceramic material (quartz glass). A tungsten rod having a tapered needle at one end is in a tube of quartz glass. The ionizer consists of eight discharge electrodes covered with quartz glass positioned radially and three grounded metal rings arranged at same interval as their opposite conductors. A.C.11.5 kV is impressed on the discharge electrodes to generate positive and negative ions by corona discharge. The frequency is the same as the commercial frequency.

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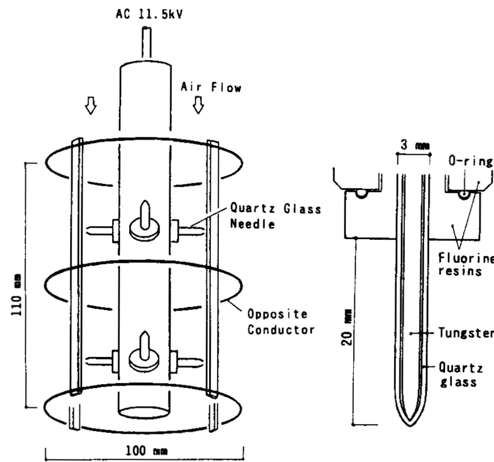

Fig. 1. The ionizer for use with spin-dryers.

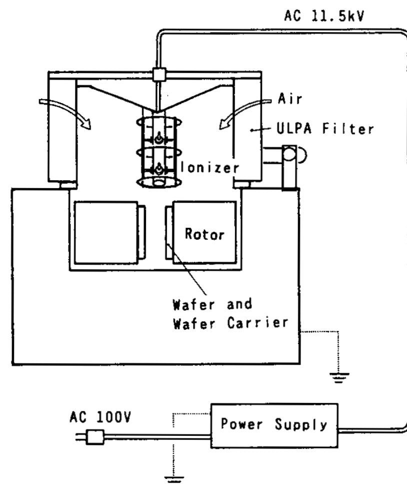

Fig. 2. Spin-dryer with a super clean ionizer.

The ionizer is fitted to a spin-dryer as illustrated in Fig. 2. When wafers are dried, clean air having passed an ULPA filter is supplied to the wafers, and the ionizer is positioned midway on the air flow path. The ionizer and rotor stop at the same time. The positive and negative ions generated by the ionizer are conveyed by this clean air flow to the wafers and wafer carriers to remove their charges.

In the experiment, first, the composition of the positive and negative ions generated by corona discharge was analyzed with an atmospheric pressure ionization mass spectrometer (APIMS). Then, to evaluate the ionizer's own performance, the ion concentration, the charge removal decay time required for the ± 5 kV charge of the plate to be attenuated to ± 0.1 kV, the residual potential after the attenuation, the concentration of particles generated from the discharge electrode and the ozone concentration were measured. The measurement procedure is roughly illustrated in Fig. 3. To simulate its processing in a spin-dryer,

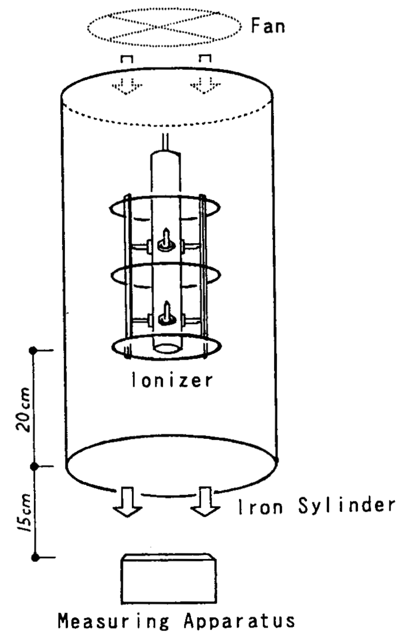

Fig. 3. Schematic diagram of measurement.

the ionizer was fixed within a grounded metal cylinder at its center. The ion concentration, the residual potential and the ozone concentration were measured at different speeds of an air blower placed at the top of the cylinder, varied stepwise from 0.24 to 3.0 m/s. The concentration of particles generated was measured at a 0.37 m/s velocity of the air flow having passed the ULPA filter. The measurement was carried out for about 150 consecutive hours with a condensation nucleus particle counter (CNC) capable of counting particles of 0.01 μm and above (counting efficienty: 50% for 0.01 μm particles and 100% for 0.05 μm particles).

Next, after the completion of the abovementioned evaluation of its own performance, the ionizer was fitted to a spin-dryer for overall evaluation. The items to be evaluated are the residual potential and the increase in particles depositing on the wafers after charge removal. For the sake of comparison, these items were also measured without charge removal, and the ionizer's effect to prevent contamination with particles was evaluated on the basis. The procedure of experiment is illustrted in Fig. 4.

First, the number of particles depositing on 5-inch wafer having native silicon oxide was counted with a surface laser-beam particle counter (particles on 0.5 μm and above and haze of 0.5 μm and below). After the counting, the native silicon oxide was removed with a diluted hydrofluoric acid solution, and the wafers were washed with ultra-pure water. After the washing, the wafers were set in the spin-dryer, and the surface potentials of the wafers and their carriers were measured with a surface voltage meter. We kept the air cleanliness in the cleanroom installed with the spin-dryer to be about 1000 counts/cf (>0.5 μm) to evaluate the effect of ionizer. The sources

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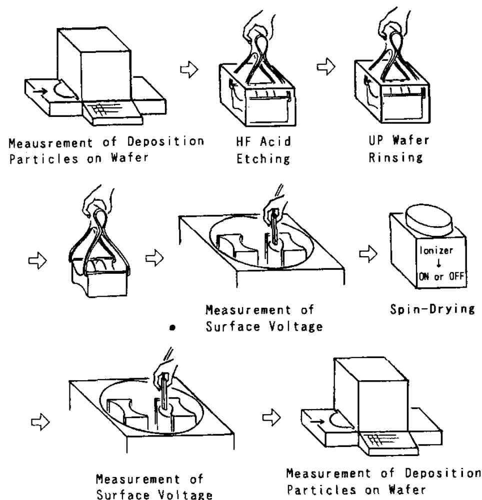

Fig. 4. The procedure of overall evaluation.

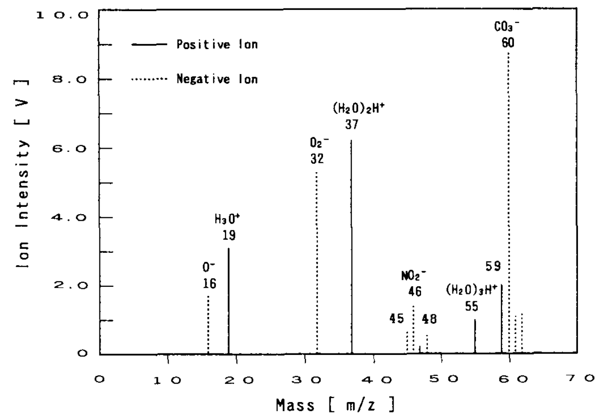

Fig. 5. APIMS spectra of air for positive and negative ion.

of the particles generation are human bodies and driving parts of machines. In this experiment, these particles adhere to inner surface of spin-dryer when the lid is opened, which disperse due to air flow turbulence and vibration at starting up. In both cases where charge removal was done and where it was not, the surface potentials were again measured after drying for three minutes, and finally the number of particles depositing on each wafer surface was counted. Since wafers were directly handled by human hands in this experiment, they were subject to contamination with particles generating from the human bodies. In view of this factor, the number of particles having deposited on each wafer by the time it was set in spin-dryer was also determined as the background level. The ionizer's effect to prevent particle deposition by charge removal during drying by the spin-dryer can be more accurately evaluated if the wafers are handled by a dust-free robot. Even in this case of human handling, however, the ionizer's effect can nevertheless be evaluated, though the measurement error would become more bigger, if the contamination with particles before wafers are set in the spin-dryer is deducted.

III. Results and Discussion

Fig. 5 shows the measurements of the composition of ions generated by the ionizer [7], [8]. Most of the positive ions were hydronium ions ($H^+(H_2O)_n$). Some hydrocarbonic ions (mass 59) were detected, seemingly attributable to the ionization of part of the chemical vapor used in the wet process or of what generated from human bodies. Among negative ions, CO_3^- ions accounted for the largest proportion, and O_2^-, O^-, NO_2^- and NO_3^- ions were also detected. Among them, however, O_2^- and O^- ions are likely to return soon (within 1 msec) to nuclear molecules (atoms) by secondary ionization reactions. In view of the fact that, although about 700 times more O_2 molecules are present in the atmosphere than CO_2 molecules, their negative ions are about equal in number, presumably collisions between molecules give rise to charge exchange reactions and finally there remain CO_3^- and NO_x^- ions which are more stable negative ions.

Incidentally, these ions are undesirable impurities for wafers. However, the ion deposition density roughly calculated*[1] from the quantity of ions required for charge removal is at most $10^9/cm^2$, so that the disturbance by these ions is negligible, compared with metallic contamination:

*[1] rough calculation:
Wafer: 5 inches (127 cm^2), 5000 V, 10 pF
$Q = 10 \times 10^{-12} \times 5000 = 5 \times 10^{-8}$ c
$N_{ions} = (5 \times 10^{-8})/(1.6 \times 10^{-19}) = 3.1 \times 10^{11}$
Density $= N_{ions}/(127 \times 2) = 1.2 \times 10^9$ ions$/cm^2$.

Fig. 6 shows ion concentrations at different air flow velocities, varied stepwise. The total concentration of positive and negative ions increased with a rise in air flow velocity because the rate of ion extinction changes due to the recombination of positive and negative ions. In the lower air flow velocity, packets of ions become smaller and the time required to rearch the neutralized targets is longer, resulting in lower ion concentration at the downstream. Numbers of researchers have measured air-ion mobilities in the atmosphere, which are 1 to 2.2 $cm^2/V/sec$ [11], and on the average, those of negative ions are larger than those of positive ions. The mobilities, however, depends greatly on the gaseous impurities which are ionized in the air. Moreover, negative ions including some electrons have greater mobility with increasing of electric field [5]. As regards the polarity of the ions, while positive ions were predominant in the slow air flow range, the difference narrowed with a rise in air flow velocity. The lower negative ion concentration at a slower air flow is likely to be due to the extinction of negative ions, which are more mobile, as they are absorbed by the conductive metal cylinder.

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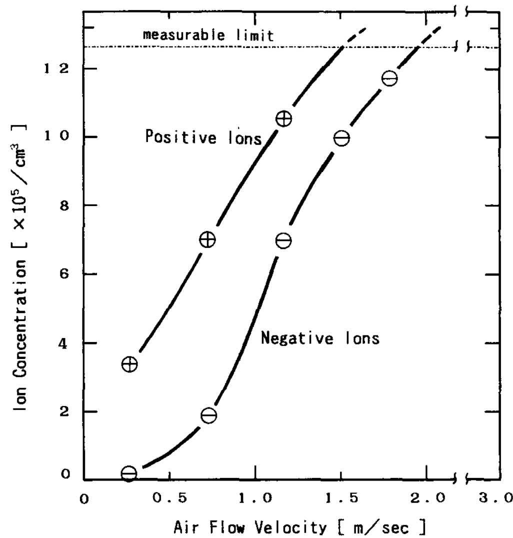

Fig. 6. The dependence of ion concentration on air flow velocity.

A. Charge Removal Decay Time and Residual Electric Potential

The charge removal decay time and the residual electric potential measured by charged plate moniter (CPM: with a capacitance of about 20 pF) when the air flow velocity was varied stepwise from 0.24 to 3.0 m/sec are shown in Fig. 7. The charge removal decay time here means the length of time required to reduce the potential of the CPM from ±5 kV to ±0.1 kV. The charge removal decay time significantly shortened with a rise in air flow velocity, shortening below 10 seconds at an air flow velocity of over 1 m/sec and below 1 second at 3 m/sec. Meanwhile, although the concentration of positive ions was higher than that of negative ions at an air flow velocity of 1.5 m/sec and above, the charge of the positively charged plate attenuated more quickly than that of the negatively charged one because of the greater mobility of negative ions [11]. The residual potential, though close to 100 V at an air flow velocity of 1 m/sec, decreased with a rise in air flow velocity, decreasing below 10 V at 3 m/sec.

Furthermore, we investigated the dependence of the capacitance of the wafer on the number of 5-inch wafers in a cassette and the neutralization capability of the ionizer. The measured values of the capacitance are shown in Fig. 8. For example, a full cassette (25 wafers) had capacitance of 17.3 pF and the decay time required to reduce the potential of the wafers from ±5 kV to ±0.1 kV was below 1 second.

Incidentally, since this ionizer, when fitted to a spin-dryer, is operated at an air flow velocity of about 3 m/sec, the charge removal decay time is expected to be 1 second or less and the residual potential, no more than +10 V. The residual potential will be discussed again with reference to data in the later section on overall evaluation.

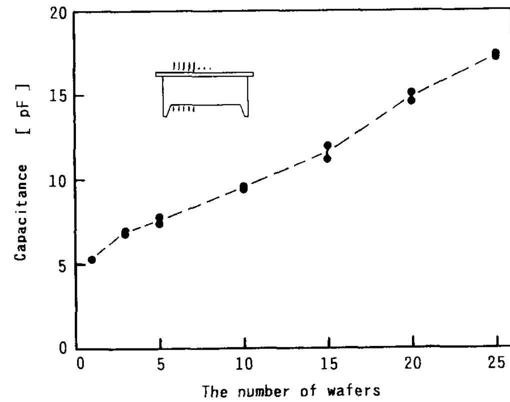

Fig. 8. The dependence of the static capacity on the number of wafers (5 inch per wafer).

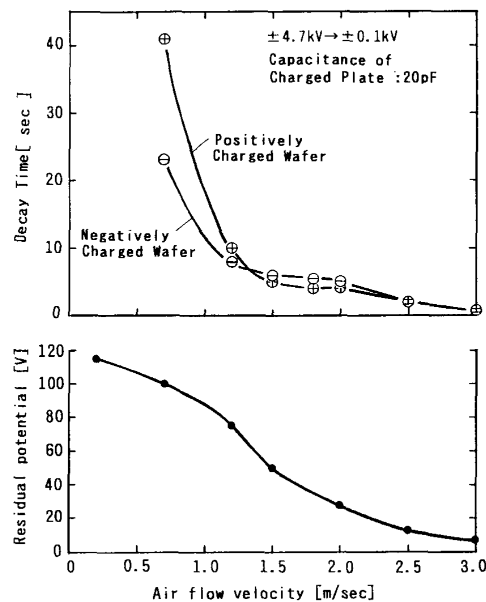

Fig. 7. The dependence of the neutralization capability on air flow velocity.

B. Particle Concentration

The result of measurement is shown in Fig. 9. The concentration of particles when the ionizer is at operating is substantially the same as the background level when it is not operating, indicating the virtual absence of particle generation. No deterioration of the electrode surface was observed after continuous five-month operation. It shows no particle generation due to erosion and sputtering of the electrode suffface.

Incidentally, although the result shown in Fig. 9 indicates that more than 20 particles were generated once, this is re-dispersion of the deposition on the electrode surface. The particles have a wide variety of sizes, such as 0.01 μm or greater than 0.1 μm. The main composition of the particles is SiO_2 including moisture (by X-ray analysis) [12]. The remains, however, depend on gaseous im-

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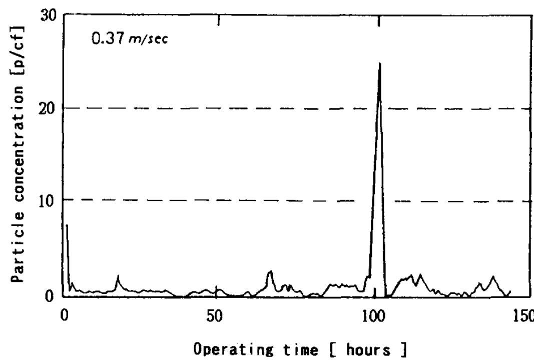

Fig. 9. Particle concentration.

purities which are ionized in air [5]. The particle generation, e.g. a few tens of days and the generation rate depends on relative humidity. Fig. 10 shows the dependence of particle generation on relative humidity after about 1800 hours of continuous operating. The ionizer used herein is designed to be installed under cleanroom ceilings, which consists of 24 discharge electrodes covered with quartz glass. It is obvious that particle generation depends on relative humidity. More particles generated at higher relative humidity; the particle concentration exceeded 1000 c/cf when relative humidity reached 75%. This reason is considered that the main composition of the particles is SiO_2 including moisture. SiO_2 deposit contains more moisture and becomes more flagile with an increase in relative humidity. The deposit with more moisture is more easily sputtered by air ions or electrons. Hence, we can prevent the particle generation by controlling the relative humidity. It may be effective to flow gases such as dry air or nitrogen-gas through the corona discharge area round of electrodes [13].

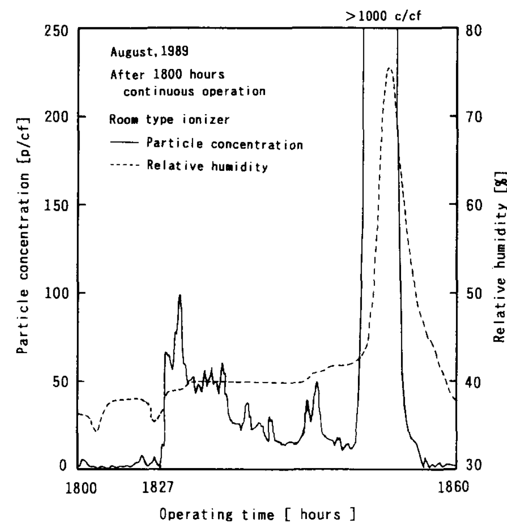

Fig. 10. The dependence of the particle generation on relative humidity.

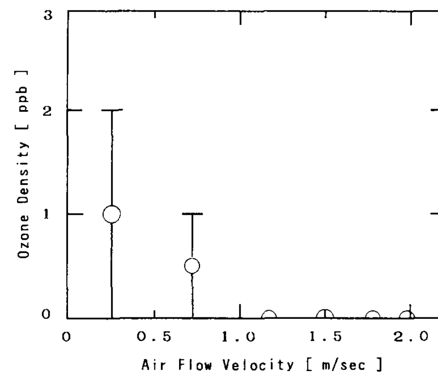

Fig. 11. Ozone generation from ionizer.

C. Concentration of Ozone Generated

Fig. 11 shows how the ozone concentration changed when the air flow velocity was varied stepwise. Although 1 to 2 ppb of ozone was occasionally detected at an air flow velocity of less than 1 m/sec, the concentration was below the measurable limit (1 ppb) of the ozone meter at over 1 m/sec. There is no problem about the generation of ozone.

D. Overall Evaluation

Fig. 12 shows the residual potential after charge removal by the ionizer, when it was actually fitted to a spin-dryer, and the number of particles depositing on wafers. The charge potential, measured at the time of setting in the spin-dryer after washing with ultrapure water, was found +5 kV or more for wafers and −5 kV or less for wafer carriers, both very high, beyond the measurable limit of the surface voltage meter. After the wafers and wafer carriers were dried by the spin-dryer with the ionizer off, the charge potential was −5 kV or less for the latter, while the polarity of the former had changed from positive to negative, and their absolute potentials were somewhat lower than before drying, down to between −400 and −800 V. Our measurement show that, in frictional charging between solid and gas, the solid side is apt to be charged negatively. As the absolute level of the wafer potential is close to 1 kV, however, the static disturbance would be too great to ignore. Meanwhile, when the ionizer was operating, the wafer' and the wafer carrier' potentials fell to very low levels of +10 V and +6 to +10 V, respectively. These finding indicate a sufficient charge removing effect of this ionizer.

The number of particles depositing on wafers did not change significantly from before to after drying by the spin-dryer with the ionizer turned on, indicating that particles had hardly deposited on the wafers while they were dried by the spin-dryer. In this case, the number of particles was found greater before drying by the spin-dryer. This is due to the change of the number of particles depositing in the course of handling and further to the small number of samples, which invite large measurement errors. On the other hand, when wafers were dried by spin-

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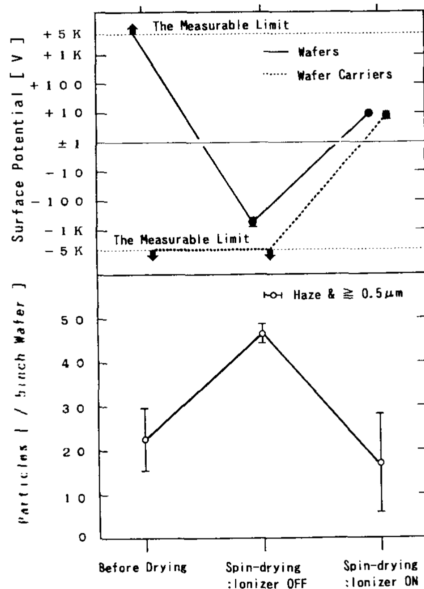

Fig. 12. Residual potential and the number of particles on wafers when the ionizer was actually fitted to a spin-dryer.

dryer with the ionizer off, the number of depositing particles almost doubled from before to after the drying, indicating statically induced deposition during the drying process. These finding demonstrate that the equipment of the spin-dryer with the ionizer can almost fully eliminate the deposition of particles, of which 10 or more had deposited in the conventional process.

IV. Conclusions

By equipping the spin-dryer with a new type of ionizer, which has overcome many disadvantages of conventional ionizers. the static charging of wafers during the drying process had been completely prevented. The ionizer is very quick in charge removal, and the residual electric potential due to the ion imbalance is only ± 10 V or less. As a further effect of charge removal, it has also been demonstrated that the statically induced deposition of particles on wafers during the drying process can be almost fully eliminated.

The generation of metallic particles, which are sputtered by air ions (or electrons) from discharge electrode, is completely prevented. The solid depositing on discharge electrode, however, is dispersed due to air ion or electron sputtering. Using dry clean gas will be effective to prevent this particle generation. From an economical point of view, periodical cleaning-up with wiper may be more convenient. The cleaning interval is sufficient to be half-year because an ionizer of spin-dryer is not operated continuously.

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He joined Takasago Thermal Engineering Co., Ltd. in 1966. Presently, he is General Manager of the Research and Development Center.

Tadahiro Ohmi (M'81), for a photograph and biography, see this issue, p. 233.

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