

Application of high purity ozone beam to charge compensation in surface analysis by AES/XPS

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The applicability of high purity ozone jet to the reduction of charging problems during surface analysis by AES/XPS was examined. A new compact ozone jet generator, which allows support free attachment to ICF-114 flange, was designed and fabricated for the purpose. It was shown that co-irradiation of high purity ozone jet with an electron beam considerably reduce charging problems in SiO₂ samples, but not so much with an X-ray beam. Possible mechanism for the reduction of charging was also discussed.

1. Introduction

Sample charging often causes serious problems in surface analysis of insulating materials by AES/XPS. Several practical methods have been proposed and applied to reduce problems associated with charging phenomena. For example, such methods as adjustment of primary electron-beam conditions, co-irradiation of an additional electron beam or an ion beam [1] have been applied to AES, and a flood gun method is most commonly used in XPS. Sample heating or sample coating with a conductive material have been also applied with considerable success in some cases. However, we often encounter different problems by adoption of those methods as briefly summarized in ref.1.

In the present study we have checked the applicability of a new method for the reduction of charging problem. That is, high purity ozone (O₃) jet was co-irradiated with an electron beam or an X-ray beam during AES/XPS analysis. The new method was applied to an oxide sample (crystal SiO₂) based on the idea that sample charging closely relates to the existence of defects, which can act as charge trapping sites. Since ozone is a powerful oxidizing reagent which can oxidize Si substrate even at a room temperature condition [2, 3], it is expected that ozone can repair effectively oxygen deficient defects (i.e., Si-Si bonding in the case of SiO₂ material). The reduction of sample charging in the AES analysis of an Al₂O₃ sample by exposure of O₂ gas was also reported recently [4].

For simultaneous exposure of ozone beam with an electron beam or an x-ray beam,

we have fabricated a compact ozone jet generator [5]. The performance of the new ozone generator and the effect of the ozone exposure are described in this paper.

2. Design and performance of the new ozone jet generator

Since ozone is toxic and decomposes explosively to molecular oxygen (O₂) by local heating and/or by the presence of catalytic materials, safe handling of high purity ozone gas is a key issue to construct a high purity ozone source. We have already fabricated an ozone jet generator, which can supply high purity ozone jet by evaporation of liquid ozone. The details of the ozone jet generator were described elsewhere [5,6], and usefulness of the generator was made clear through the application of it to oxidation of Si substrate [2, 3] and to cleaning of surface contamination on semiconductor/metallic samples [7, 8].

In the present study, we have fabricated another ozone jet generator. Fig.1 schematically shows the constitution of the new generator. The improved features of the generator are;

1) The main part of the generator, which is consisted of an ozone vessel made of stainless steel, a cold head of a cryocooler, a fracture valve for safety, etc, are made as small as possible. So the total weight of the part became 12 kg, and it allows support free attachment to ICF 114 flange.

2) Several operation menus such as accumulation of liquid ozone, supply of high purity ozone by vaporization of liquid ozone, and safe exhaustion of residual ozone by decomposition with an ozone killer are

prepared, and all valves of the vacuum system were automatically controlled for the menu operations.

3) A combination of a molecular drag pump and an oil-sealed rotary pump is used as the evacuation system instead of an oil-sealed rotary pump connected to a fore line trap. Although continuous supply of liquid N₂ to the fore line trap was necessary in the former system to prevent contamination of the ozone vessel by rotary pump oil, no care was required in the new system, leading to the automatic valve control mentioned above.

Other features of the high purity ozone generator are the same as the former one, though we need a little longer time for the accumulation of liquid ozone due to the adoption of a smaller size cold head (cooling power; 8W at 77 K). The performance of the generator based on the data taken through a long-term running is summarized in Table.1.

It should be emphasized that the flux of the pure ozone jet can be controlled steadily (fluctuation; <2.5%/1.5 hour), since it simply depends on the temperature of the ozone vessel (i.e., the equilibrium vapor pressure of ozone), which is precisely controlled with an accuracy of 0.1K by a combination of a cryocooler and a heater. Another important point is the purity

of ozone in the jet, and it is >80% at a sample position [2]. The residual component is oxygen molecules which are generated by dissociation from ozone in a beam pipe kept at room

Table 1 The performance of the ozone jet generator

Beam flux of the jet ^{a)}	>1x10 ¹⁶ molecules/s (T _E = 85K)
	>1x10 ¹⁷ molecules/s (T _E = 95K)
Purity of liquid ozone ^{b)}	~100% (T _L = 95K)
Purity of ozone jet	> 80 at% ^{c)}
Stability of the jet ^{d)}	< 2.5% / 1.5 h
Weight	12 kg

temperature.

T_E and T_L: ozone vessel temperature during vaporization (T_E) and accumulation (T_L) of liquid ozone.

a) The conductance of the gas line was 0.02 L/s.. b) It was found that higher the T_L, higher the purity. c) Other component was O₂. d) A change of 0.1 K in T_E results in the 2~3% change in the ozone vapor pressure.

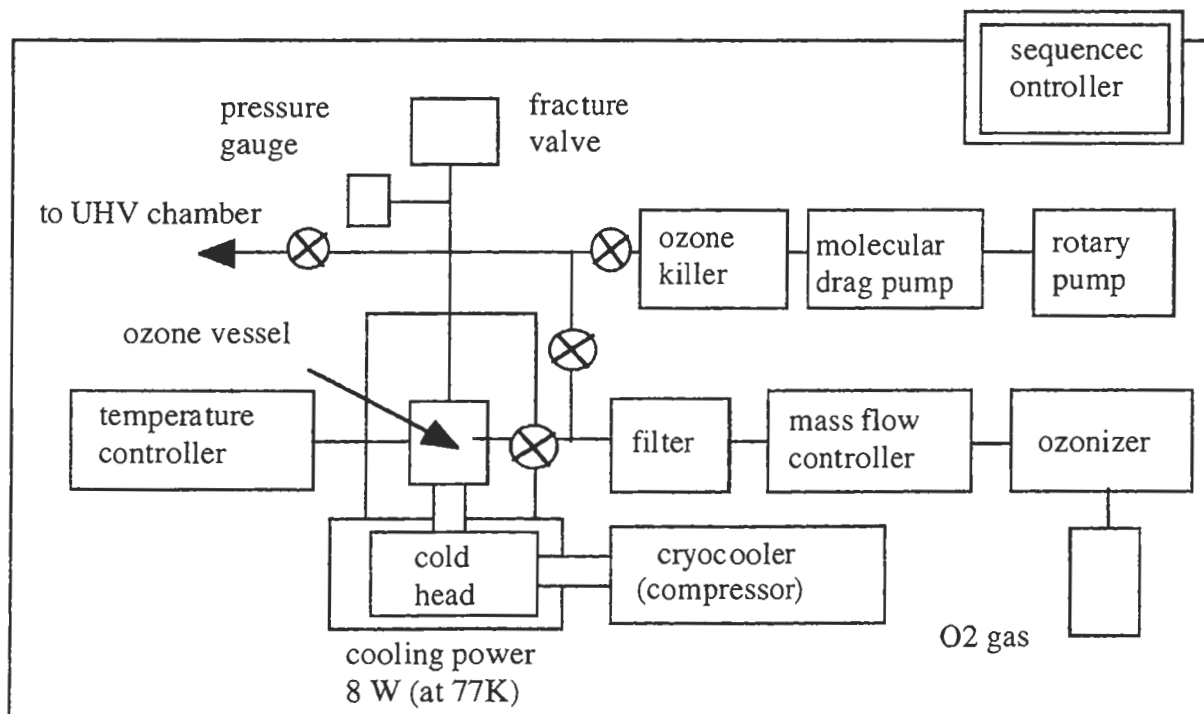


Fig. 1 Schema of the compact ozone jet generator

3. Results and discussions

3.1 Compensation of charging phenomena caused by e-beam irradiation

In AES analysis of insulating samples, severe charging often occurs especially when a primary beam voltage is higher than, e.g., 10 kV. It is because secondary electron yield is usually lower than one under such condition, and negative charge accumulation occurs in those samples. Compensation of accumulated negative charge is much more difficult than the compensation of positive charge, since we cannot supply slow electrons for charge compensation.

We were also hindered by strong charging from a RHEED analysis of SiO₂ single crystal (thickness; 0.5 mm) with a 30 kV primary beam; we could not observe a RHEED pattern at all. However, clear RHEED pattern was observed by co-irradiation of the high purity ozone jet (pressure; 10⁻⁴ Pa), and it allowed the surface analysis of the sample by RHEED excited AES, as is reported elsewhere [10].

For oxide samples, the accumulation of negative charge often relates to the existence of defects, which include extrinsic defects such as oxygen vacancy generated by irradiation of an electron beam [11]. Therefore, the results suggest that ozone could contribute to repair the oxygen deficient defects, leading to considerable reduction of sample charging caused by e-beam irradiation.

3.2 Compensation of charging phenomena caused by x-ray irradiation

In order to check the effect of ozone exposure on the reduction of charging problems during XPS analysis, we have attached the compact ozone jet generator to a home made XPS system equipped with a monochromatic Al X-ray source (PHI; model 10-410) and a hemispherical energy analyzer (PHI; model 10-360). Fig. 2 schematically shows the relative arrangement of them together with a sample position.

The angle between the X-ray axis and the analyzer axis is 70 deg. The sample can be rotated around the axis which is perpendicular to a plane formed by the X-ray axis and the analyzer axis. In the experiments, the effect of ozone exposure was investigated at sample positions of 90 deg. (normal) and 45 deg. to

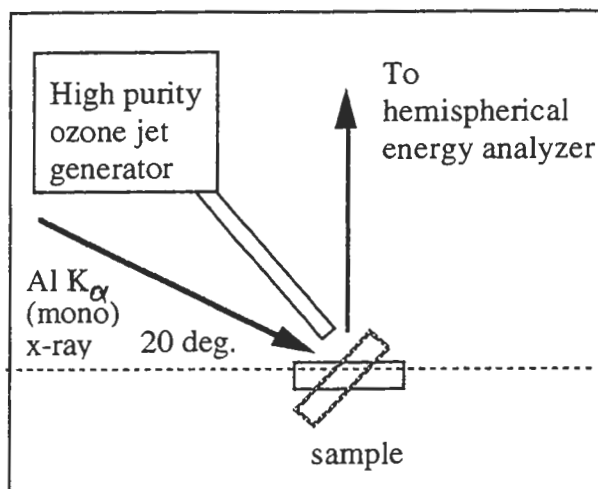


Fig. 2 Schema for the relative arrangement of X-ray source, energy analyzer, ozone jet supply, and sample.

the analyzer axis. The distance between the sample and a guide pipe (1/4 inch in diameter) of ozone jet was about 10 mm. The x-ray source was operated at a condition of 150 W. A crystal SiO₂ with a thickness of 0.4 mm was used as a sample. The sample was set in the measurement system without any pretreatment.

Fig. 3 shows an effect of ozone exposure on an XPS measurement of the sample at a sample position of 45 deg. to the analyzer axis. The pressure in the XPS chamber was 10⁻⁸ Pa before the measurement, which increased to low 10⁻⁷ Pa by x-ray irradiation. The observed sample charging was not so critical without exposure of ozone as shown in the figure with open square marks;

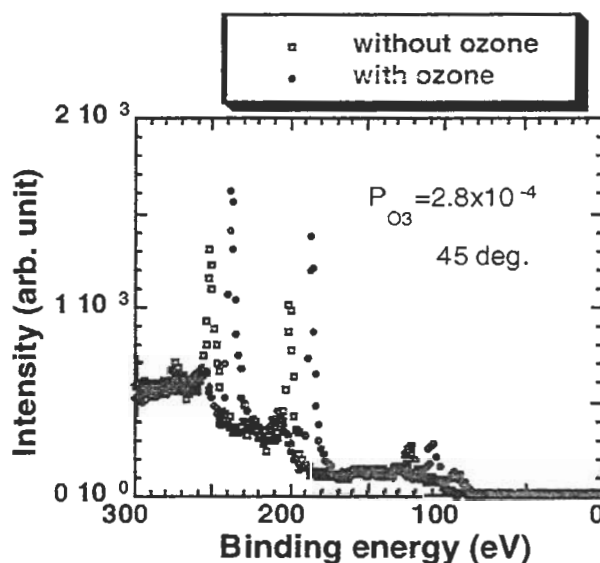


Fig. 3 Effect of ozone exposure during XPS analysis of a SiO₂ crystalsample. The angle between the analyzer axis and the sample was 45 deg.

we could notice the appearance of Si-2p and Si-2s peaks, though both peaks appeared at about 100 eV higher binding energy positions, suggesting positive charging of the sample.

When we exposed the sample to an ozone jet simultaneously with the irradiation of an x-ray beam, we could slightly reduce the charging phenomena; the peak shift due to charging reduced by about 10 eV from the case without ozone exposure, as shown with solid circles in Fig.3. The pressure of the XPS chamber during the ozone exposure was about 3×10^{-4} Pa, and other conditions were kept same. By supplying higher flux of ozone, we could reduce the peak shift due to charging phenomena slightly more than the case shown in Fig.3. However, we could not completely remove sample charging under the exposed ozone pressure lower than 1×10^{-3} Pa.

Fig.4 shows the results of ozone exposure during XPS measurement at a sample position normal to the analyzer axis. Heavier sample charging occurred under the condition than that observed in Fig.3, and we could not find any peak in an energy region below 1,000 eV. By exposing the same sample to a high purity ozone jet at a pressure of 7.5×10^{-4} Pa, the appearance of O-1s peak, Si-2s peak, and Si-2p peak is recognized as shown in Fig.4, although the spectrum still shows peak shifts by about 40 eV.

We tested the effect of a flood gun method on the sample under the same experimental condition as that used in Fig.4. The result showed that it worked quite

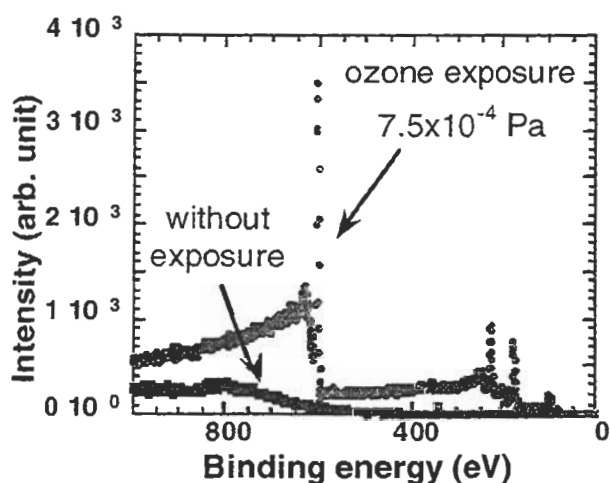


Fig. 4 Effect of ozone exposure during XPS analysis of a SiO₂ crystalsample. The angle between the analyzer axis and the sample was 90 deg.

effectively to the SiO₂ sample, and sample charging could be almost removed.

It is suggested from these results that the exposure of high purity ozone jet is not so powerful for XPS analysis as that for AES analysis.

5. Summary

The effects of ozone exposure on charge compensation during AES/XPS analysis was investigated using a crystal SiO₂ sample. Drastic positive effect was confirmed for AES, but the effect was not enough for XPS. The reason is not clear at present, and is left for further study. The introduced ozone pressure was still high compared to usual AES/XPS analysis condition. However, it will not be a problem from the view point of surface contamination, since ozone contributes to the elimination of adventitious carbon contamination [8, 9]. As ozone can easily oxidize a sample, the application of the ozone exposure method to charge compensation may be restricted to analysis of oxide samples.

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