

Synchrotron-radiation-induced formation of salt particles on an X-ray lithography mask

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The suppression and removal of contaminants on X-ray masks are required for the application of X-ray lithography to practical semiconductor production, because contamination is easily transferred to the replicated resist patterns and degrades the LSI patterns. In order to study contamination of a Ta/SiN X-ray mask, its growth process was investigated using an atmospheric reaction chamber and *in situ* observation apparatus for gases at atmospheric pressure. It was found that the contamination particles were ammonium sulfate and oxalate. The sources of the salt particle were also identified.

Keywords: hard X-ray; photochemical reaction; X-ray lithography; contamination; atmosphere.

1. Introduction

Recently, the dimensions of integrated circuit devices have become very small. Therefore, defects such as particle and chemical contamination must be removed from the lithography process since they fatally affect the performance of the device. In X-ray lithography, the suppression and removal of contaminants on X-ray masks (Okada *et al.*, 1996) are mandatory for application to practical semiconductor manufacturing, because contamination is easily transferred to the replicated resist patterns and degrades the LSI patterns. Capasso *et al.* (1996) reported that X-rays may induce photo-assisted processes that deposit salt-like films on the

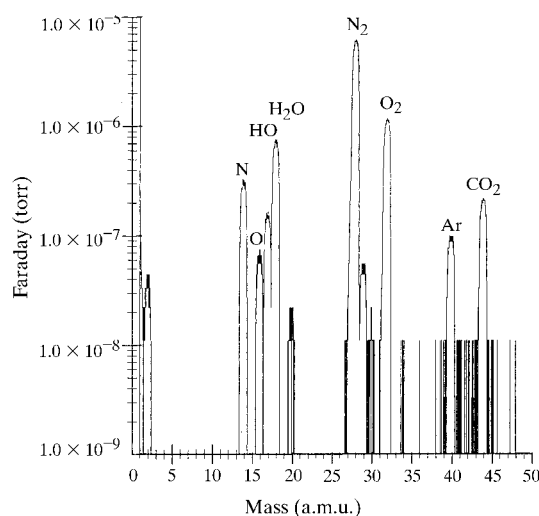


Figure 1
The mass-spectrum pattern of the air in the experiment room.

mask surface. The salt is extremely soluble in deionized water and the mask can be easily cleaned if the sources of growth cannot be eliminated. However, detailed analysis of the salt particles has not yet been performed and their formation remains unexplained. The aim of our study is to analyse the contamination elements and to clarify the mechanism of contamination formation.

In order to clarify the mechanism of contamination formation on Ta/SiN X-ray masks, we studied its growth process using an atmospheric reaction system and *in situ* observation apparatus for gases at atmospheric pressure. It is particularly important that the concentrations of the minor components of air are measured to identify the contamination sources. We measured their concentrations with a microanalyser using the chemiluminescence and pulsed fluorescence methods.

2. Experimental

The beamline has been designed and constructed for photochemical reactions occurring under atmospheric pressure in a normal conducting acceleration ring (NAR) at NTT's synchrotron radiation facility (Shibayama *et al.*, 1989). The beamline ABL-5C and the optical system are illustrated by Takahashi *et al.* (1998). Synchrotron radiation light from the NAR is extracted with a horizontal divergence angle of 30 mrad and focused using the first toroidal mirror at a 2.1° glancing angle. The reflected synchrotron radiation beam is focused on a point upstream. This beam is then collimated by the second toroidal mirror (incident angle 1.5°). The collimated beam passes through a He buffer chamber before entering the reaction chamber. The He buffer chamber is used to protect a Be window from oxidation induced by the synchrotron radiation. The beam enters the He buffer chamber through a Be bulk-head window (10 × 30 mm, 25 μm thickness), which separates the high vacuum of the storage ring from the He chamber. The synchrotron radiation beam is transported through the He buffer chamber without intensity attenuation. The buffer chamber and reaction chamber are separated by a silicon nitride window (20 × 20 mm, 2 μm thickness). The peak value and full width at half-maximum (FWHM) of the final synchrotron radiation spectrum are 1600 and 1800 eV, respectively (Takahashi *et al.*, 1998), after the Be and Si nitride windows.

The He buffer chamber and the atmospheric-pressure reaction chamber are described in detail by Takahashi *et al.* (1998). The gas flow is controlled by a high-accuracy mass-flow controller. The systems used to investigate the gas phase reactions were a quadruple mass spectrometer operated in a normal atmosphere (Hiden: DSMS), a stereoscopic microscope (Nikon: SMZ-2T) and a gas analyser using the chemiluminescence and pulsed fluorescence methods (Thermo Electron: model 43B, model 17). A micro-Fourier transform infrared spectrometer (FT-IR) was used to analyse the surface of the X-ray mask.

3. Results and discussion

Before producing contamination particles on the X-ray mask with the air in the experiment room, we analysed the main components of the air using the quadruple mass spectrometer operated under atmospheric pressure (Hiden: DSMS). Fig. 1 shows the mass-spectrum pattern of the air in our experiment room. It can be seen that the main components are nitrogen, oxygen, water and argon. The hydrogen peak comes from the hydrogen adsorbed on the manifold inner wall of the mass spectrometer. This quadruple

mass spectrometer was used for the identification of the reaction atmosphere in the reaction chamber. The minor components of air such as NH_3 , NO , NO_2 and SO_2 cannot be detected because of the lack of sensitivity of the quadruple mass spectrometer.

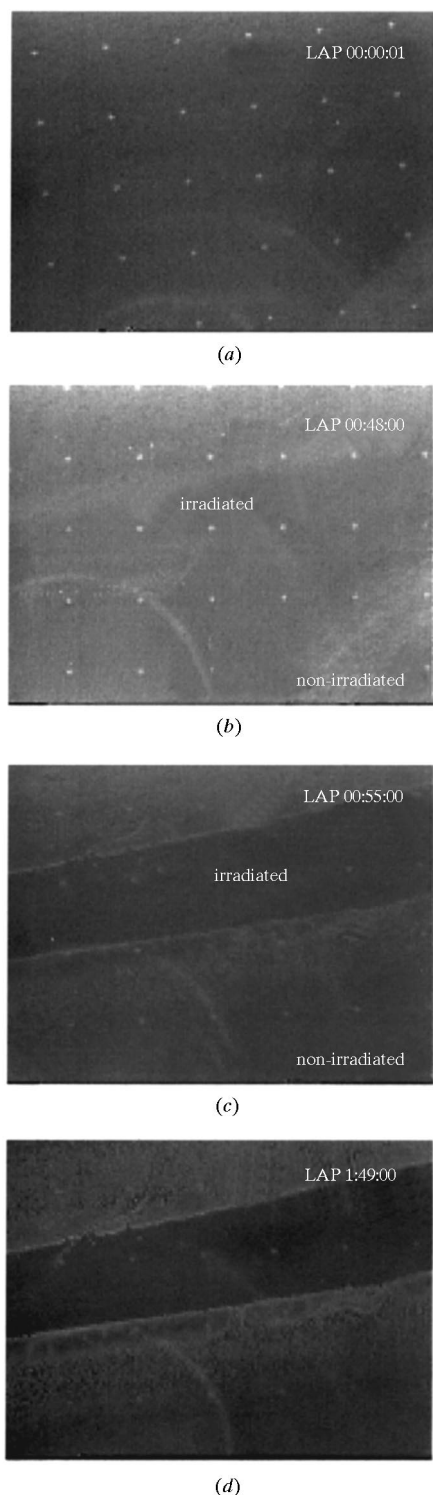


Figure 2

The time dependence of the stereoscopic microscope images of the contamination particles synthesized on the X-ray mask. (a) Before synchrotron radiation irradiation, (b) 72 h and 46 min after synchrotron radiation irradiation starts, (c) 6 min after synchrotron radiation irradiation and venting the chamber with air, (d) 60 min after venting.

The contamination particles were synthesized by irradiating, with synchrotron radiation, the X-ray mask in the reaction chamber with air introduced from the experiment room. The contamination formation process was monitored during exposure using a stereoscopic microscope (Nikon: SMZ-2T). Figs. 2(a)–2(d) show the time dependence of the stereoscopic microscope images of the contamination particles synthesized on the X-ray mask. The contamination formation did not depend on the substrate material and was found to be related to the air components. During irradiation a contamination film also grew outside the synchrotron-radiation-irradiated area. This indicates that the contamination growth is related to competition between synchrotron-radiation-induced desorption of the active species and adsorption of active species from the excited air components. The most notable feature is that growth proceeds for a finite time after irradiation. This suggests that the nuclei or adsorbed molecules for contamination growth have already been formed during irradiation.

Analysis of the mask contamination particles which grew in the irradiated and non-irradiated areas gave important information about the mechanism of the contamination growth. Figs. 3(a) and 3(b) show the infrared absorption spectra of the contamination particles grown in both synchrotron-radiation-irradiated and non-irradiated areas. Both spectra agree with the standard results for ammonium sulfate (NH_4) $_2$ SO_4 . This salt has also been observed in optical steppers (Roman, 1997), where it is formed by vapour phase reaction of the minor components in the air. We assume a similar mechanism is also possible in the case of synchrotron radiation irradiation. The origin of the salt is assumed to relate to minor components of the air. We suppose such minor components are NH_3 and SO_2 . In order to ascertain if this is correct, we measured the concentrations of NH_3 and SO_2 in the air of the experimental room with a microanalyser using the chemiluminescence and pulsed fluorescence methods (Thermo Electron: model 43B, model 17). The time dependence of the NH_3 , NO_2 and

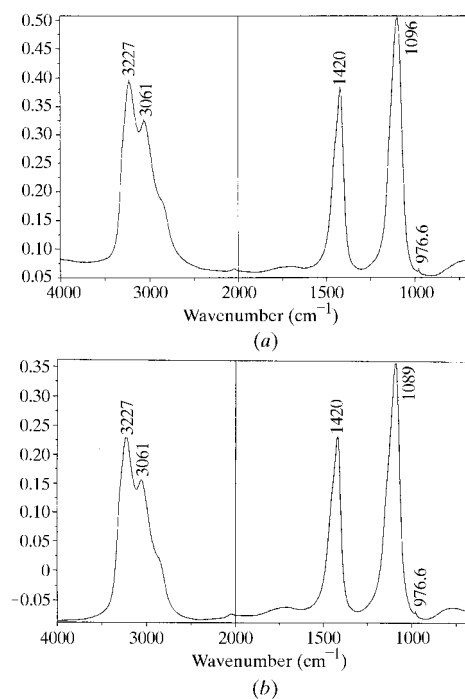


Figure 3

The infrared adsorption spectra of the contamination particles grown in both (a) synchrotron-radiation-irradiated and (b) non-irradiated areas.

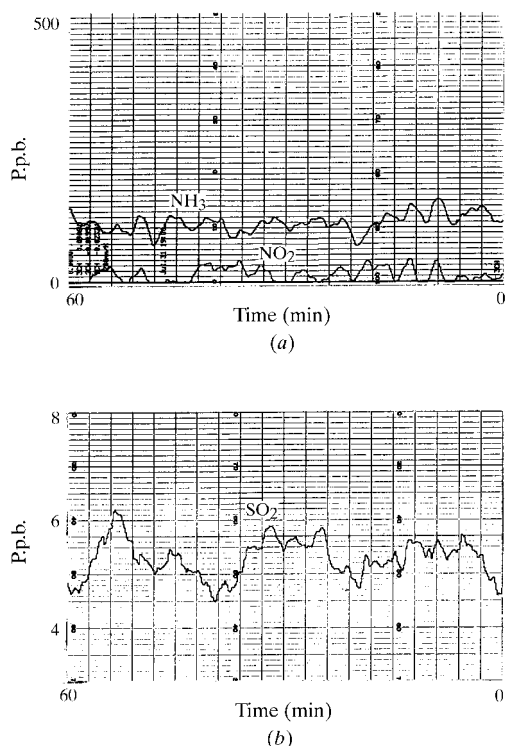


Figure 4

The concentrations and time dependence of NH_3 , NO_2 and SO_2 in the air of the experiment room. (a) NH_3 , NO_2 concentration, (b) SO_2 concentration.

SO_2 concentrations is shown in Figs. 4(a) and 4(b). The concentrations of NH_3 and NO_2 in the air of the experimental room were about 100 and 20 p.p.b., respectively, and 5.2 p.p.b. for SO_2 . The reason for the fluctuation in each time chart is not clear, but it is not noise since the chart level is fixed at zero during zero gas measurement. It may be due to the ventilation system in the experiment room. These quantities are obviously sufficient for contamination growth.

The next step was to confirm that contamination formation is due only to the minor components of the air, which are assumed to

be the sources of the contamination particles. Since contamination particles are not grown from air without the minor components, we conclude that the contamination is related to the minor components of the air. By using a controlled gas atmosphere and analysing the photo-dissociated products, we hope to gain a more detailed insight into the mechanisms of contamination formation.

4. Conclusions

The suppression and removal of contaminants on an X-ray mask are important for the application of X-ray lithography to semiconductor manufacturing, because contamination is easily transferred to the replicated resist patterns and degrades the LSI patterns. In order to explain the mechanism of contamination formation on a Ta/SiN X-ray mask, we investigated its growth process using an atmospheric reaction system and *in situ* observation apparatus for gases at atmospheric pressure. We found that the contamination particles were ammonium sulfate and oxalate. The contamination growth reaction is assumed to be due to the synchrotron-radiation-induced vapour phase reaction between the gas components of the air.

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