Volume and weight losses of PMMA by exposure to soft X-ray

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Abstract

The decomposition process of PMMA by X-ray was followed as a function of X-ray dose by examining its volume and weight changes. The volume change was determined from the surface height difference between exposed and non-exposed areas which were formed by using a punched metal mask. The height change was considered to be almost proportional to the volume change. The weight loss caused by the X-ray irradiation was determined for samples to which no mask was applied.

The PMMA's volume and weight losses are due to the decomposition of its constituent polymer by the X-ray. Evaporation of its fragments generated by the X-ray is the main cause for the volume and weight losses. There should also be other kinds of fragments that are not volatile at the ambient temperature because the PMMA's weight decreases further by annealing after the irradiation.

The mechanism of the X-ray decomposition process is different from that of the plasma ashing process which is one of the important semiconductor technologies, since PMMA cannot be completely removed from the substrate by using only the X-ray irradiation. This might be suggesting that the X-ray decomposes PMMA and generates some non-volatile species, i.e. anti-X-ray materials. And they leaved on the substrate.

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Introduction

The LIGA process consists of lithography, plating and mold technologies. The first step, X-ray lithography (and development) is the most important part in the entire process for which PMMA is selected as a resist material most popularly. The PMMA's polymer structure is decomposed by X-ray on the molecular level, then this polymer can be easily dissolved in solvents. The decomposition of polymer changes its physical properties. The knowledge on the change in physical property of PMMA as a result of the X-ray exposure is very important to improve the LIGA process to make finer patterns. Though PMMA has been an important material and used routinely for the LIGA process, it has been used without rigorous inspection on its decomposition mechanism and products.

In this report, the PMMA's molecular decomposition will be discussed from the view points of weight and volume changes.

Experiments

(1) The measurement of volume change

Using a punched metal plate as an X-ray mask, PMMA was exposed to X-ray. After the exposure the height difference between exposed and non-exposed areas was measured. The height difference, or step height, is considered to be proportional to the volume change.

Two kinds of PMMA samples were prepared. One was a 400 μm thick sheet commercially obtained. The other was a film of about 1 μm thick formed on a silicon wafer. The PMMA dissolved in anisole was spread by using a spin coater and then annealed at 160℃ for 2 hr to remove anisole completely.

The samples were exposed to soft X-ray in He gas atmosphere at 1 atm. At the BL-6 of Ritsumeikan SR center was performed the X-ray irradiation experiments. The BL-6 has only a single thin Be foil (200 μm) window which isolates the irradiation experiment chamber from the SR ring. Low energy light is absorbed by the Be window and thus 1 ~ 7 keV light reaches the sample.

The dose value used in this report is the accumulated current of SR ring multiplied by the exposed time.

(2) The measurement of weight change

The sample glass plates were prepared by coating with PMMA dissolved in anisole (0.5 g). They were annealed at 160℃ for 2 hr. Thickness of the PMMA film was about 3 μm. The weight of PMMA film on a glass plate was measured by using a balance before the exposure to the soft X-ray irradiation. And after the exposure the weight was measured again. The weight change between before and after the irradiation process and the dose of the exposure was examined.

Results and Discussion

Some physical properties of PMMA change after the X-ray exposure. Even its visual observation with a microscope provides some important information concerning the change in its physical properties. It is possible to confirm the boundary between the exposed and non-exposed area, even if the height difference or the step between them is very small.

(1) The volume change by X-ray exposure: PMMA sheet (400 μm thick)

Samples were prepared from commercial PMMA sheet (400 μm thick). They were exposed to X-ray by certain amount of dose through an X-ray metal mask punched a 1 mm diameter hole in it. The difference in height was measured after the exposure and the result is given in Fig.1. It is clear that the height difference or the depth of the 1 mm hole is proportional to the dose value. The increase in depth indicates the gradual increase of decomposed PMMA by X-ray. There are two issues to be considered now. One is the vaporization of fragments generated from PMMA by the X-ray decomposition process and another is the reorganization of the polymer structure after the X-ray exposure.

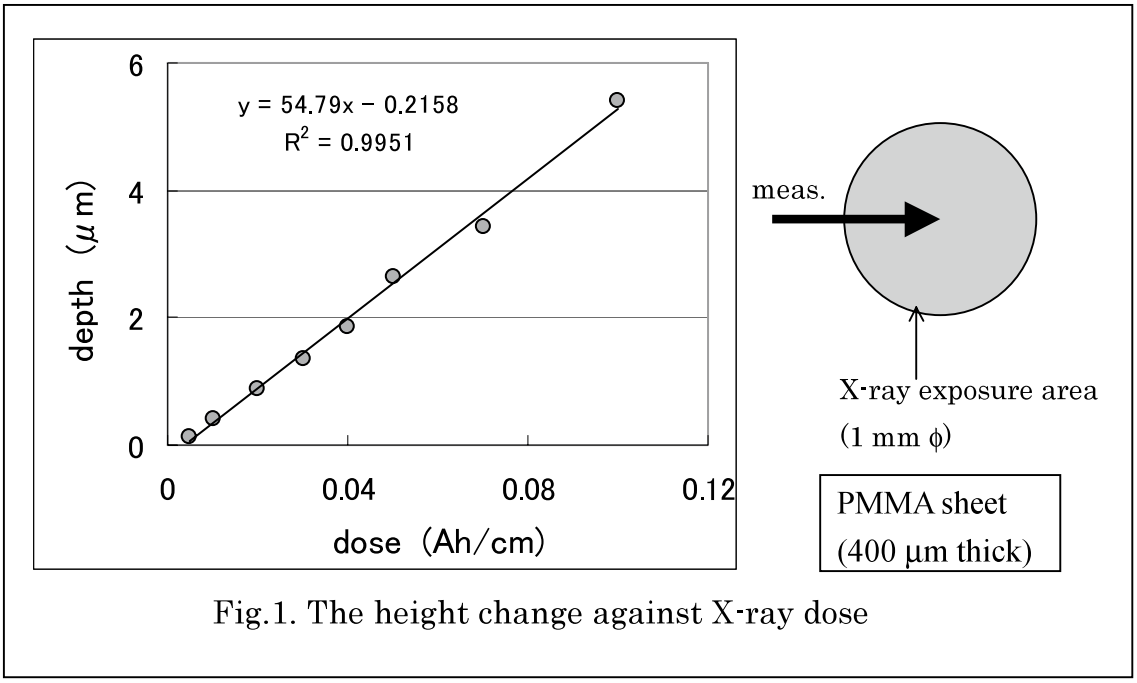

Fig.1. The height change against X-ray dose

(2) The weight change by X-ray exposure

The samples of PMMA film (about 3μm thick) on glass plates were used. They were exposed to X-ray directly by certain amount of X-ray dose. The X-ray metal mask was not used. The weights before and after exposure were measured. Then the weight loss due to the decomposition by the X-ray irradiation was obtained and shown in Fig.2. It is clear that the weight change is proportional to the dose value. This indicates that the vaporization of

fragments generated from the PMMA decomposition is in proportion to the dose value.

The exposed PMMA samples were further studied concerning the annealing effect on them. Their weights were measured after the annealing process. It was observed that their weights decreased after annealing and the amount of weight loss depended on the annealing conditions, i.e. temperature and duration, etc. This must be due to the fact that the generated fragments are composed of some different kinds of molecules with different vaporization temperatures. The result on this subject will be reported in detail later.

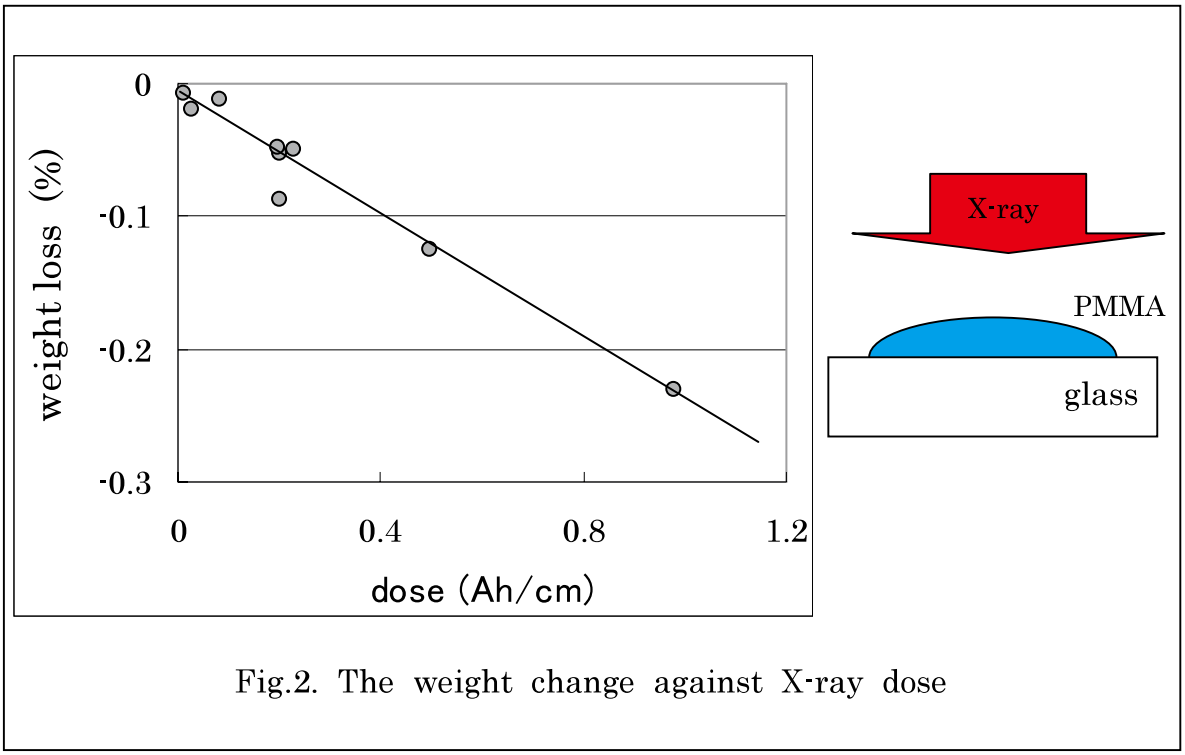

Fig.2. The weight change against X-ray dose

(3) The volume change by X-ray exposure: for the case of thin film (1 μm)

The samples of 1 μm thick film on Si were prepared by the spin coat method. They were exposed to X-ray using the metal mask and the height difference was measured in the same way as experiment (1). The result is shown in Fig.3. The height difference increases as the dose increases but levels off at the higher dose region. The amount of vaporization is limited. This experiment is different from that of (1) in the thickness of PMMA film. In the case of experiment (1), the PMMA sheet is very thick and its amount is large enough compared with the dose of X-ray. However, in experiment (3) the amount of X-ray dose must be almost enough in order to decompose the thin film completely. This fact suggests the generation of X-ray-proof-materials. It is true that the method of X-ray decomposition at room temperature cannot completely remove polymeric or organic film on a substrate, unlike the ashing method used for semiconductor industry.

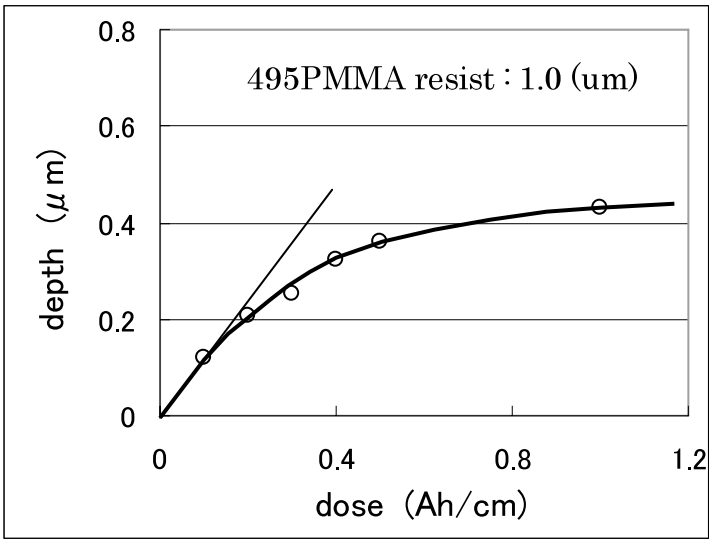

Fig.3. The height change against dose: 1 μm film

Summary

From the measurements of volume and weight changes with the dose of X-ray exposure, it was concluded that the PMMA molecules were decomposed by X-ray to generate smaller molecular fragments and that some of them vaporized from PMMA. There must be several kinds of the fragments which vaporize at deferent temperatures. The decomposition mechanism by X-ray is different from that of the plasma ashing of semiconductor technology. Because the PMMA film cannot be completely removed by X-ray, the X-ray decomposition products may include a kind of anti-X-ray material.