

Hardness change of a PMMA resist polymer by X-ray exposure

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1. Introduction

PMMA (poly-methyl methacrylate) is widely used for the resist materials of X-ray lithography. It is important to understand how the PMMA changes by the X-ray exposure to make a fine structure. Basic process of X-ray radiation must be the destruction of chemical bonds of a PMMA resist, but full understanding of the process is still unknown. At a glance, we can recognize that the X-ray exposure causes shrinkage, yellowing, and brittleness.

So far, I have studied the effects of X-rays on the PMMA resist by liquid chromatography, IR and XAFS [1, 2, 3]. In this short note, I focus on the hardness by the X-ray exposure. It is known that the PMMA exposed by X-ray becomes fragile, suggesting that it becomes harder. To confirm this expectation, I measured the Vickers hardness of a PMMA resist after X-ray exposure.

2. Experiments and Results

A 20 mm × 20 mm × 1mm sized sheet of PMMA was prepared, on which synchrotron X-rays exposed in an area of 10mm ϕ . The Vickers hardness was measured with the instrument (DUH-211) (Shimadzu Ltd). This instrument can also provide thin film hardness, as is called 'the micro Vickers hardness'. The pyramidal diamond indenter press was 2(mN). Figure 1 shows the Vickers hardness of the PMMA sheet from a non-exposed to the exposed area at every 0.2 mm step. X-ray dose was 0.1 (A·hr/cm). Since it is difficult to discuss the absolute hardness, we focus the difference between the non-exposed and exposed areas, by using the hardness on the non-exposed area as a standard. The vertical axis shows the Vickers hardness, and the crossing arrow indicates the position measured. The experimental error was about 4%, which was not due to the sample heterogeneity, but due to the measurement condition. It is distinct that the PMMA sheet was softened after X-ray exposure.

Next, the X-ray exposure dose dependence was studied. It was hard to measure a high dose

sample, because babbles generated during the X-ray exposure and cracks happened during the Vickers hardness measurement by the PMMA brittleness. Figure 2 shows the X-ray dose dependence of the hardness. The Vickers hardness of non-exposed PMMA was 206.4 ± 2.9 . The points above 200 were non-exposed area PMMA, and the lower points were exposed area. It is clear that PMMA softens more according to the X-ray exposure dose. At high dose, the hardness decreases linearly. At low dose, it is not clear whether it is linear or not, because of large experimental error.

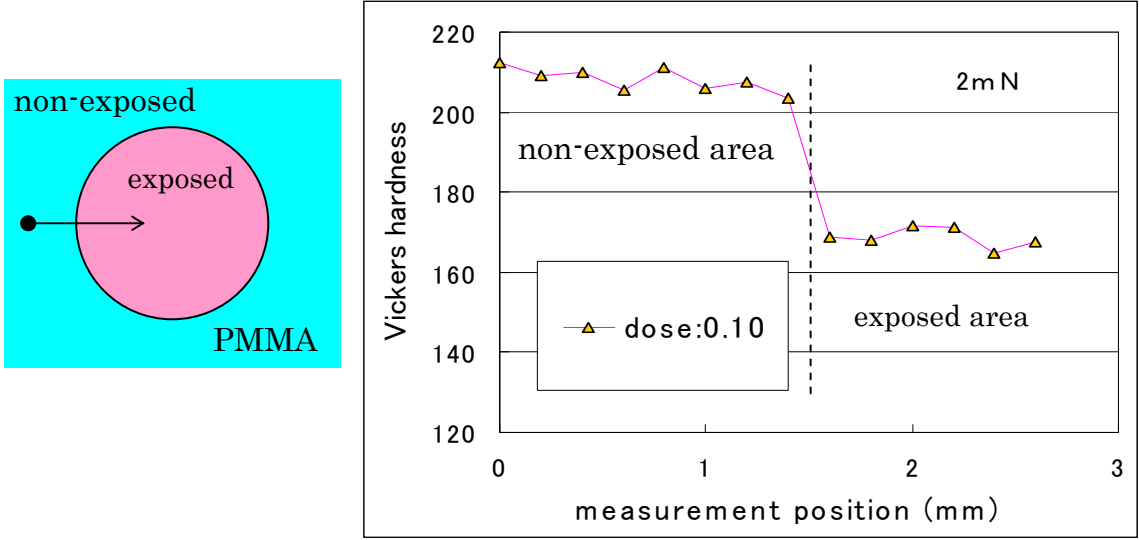


Fig.1. The Vickers hardness measurement of PMMA

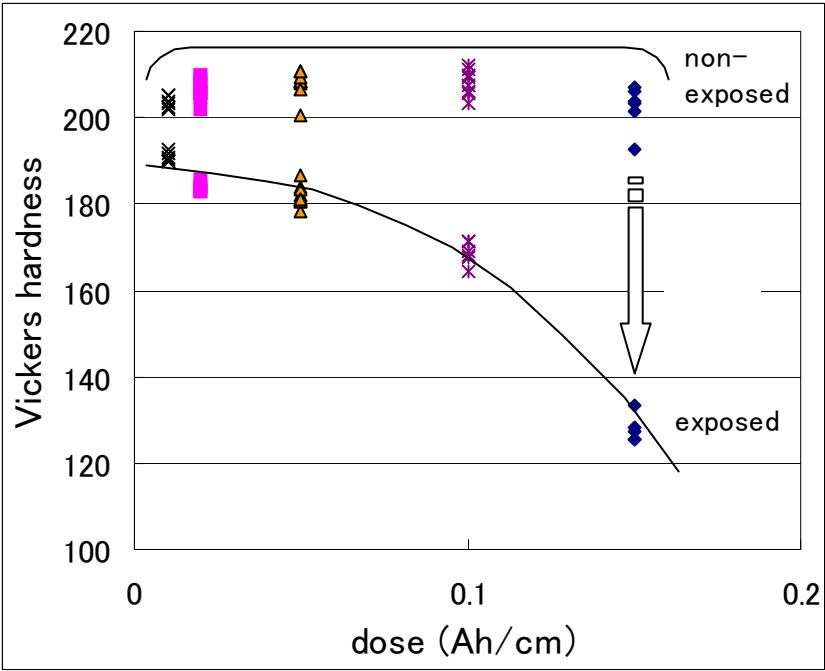


Fig.2. The X-ray exposure dose dependence

Third, I studied the hardness under low dose in more detail. In this experiment it was hard to find the border of the non- and the exposed area, since the amount of change by the exposure was too small. To cancel the other factors of the unevenness, the measured values were standardized by non-exposure one. This result is shown in Fig.3. It is clear that the relationship between the hardness and dose is linear.

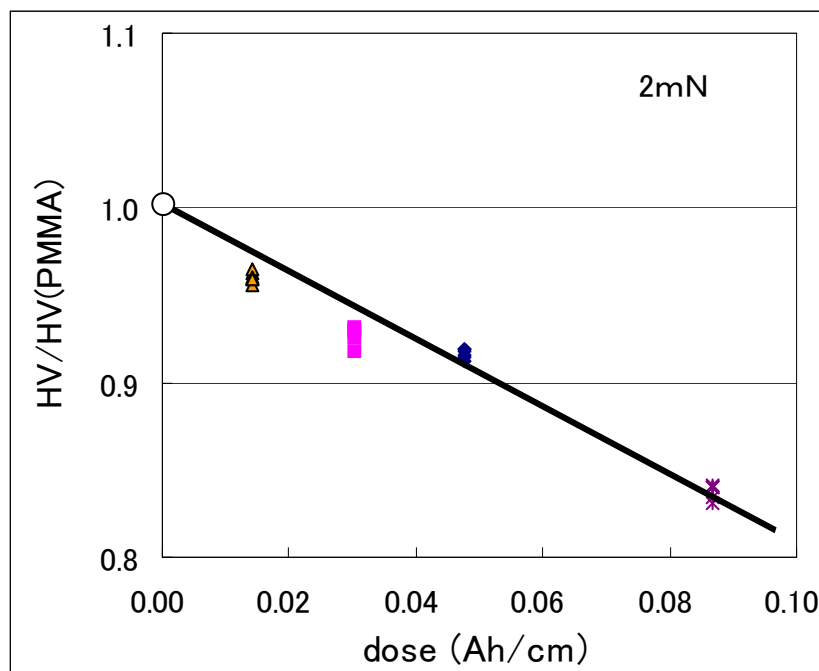


Fig.3. The X-ray exposure dose dependence at low dose

Summary

Results obtained clear shows that the PMMA sheet is softened after X-ray exposure, unexpectedly. At low dose the hardness decreases linearly, and at high dose it decreases more the straight line. The indenter press was selected to 2 mN, which is so small that the depth obtained may be less than 0.1 (mm) under surface. The decreasing linearly is reasonable. At high dose other mechanisms must happen to decrease more, such as bubble generation.

References

- [1] H.Ikeda : *Memoirs of the SR Center, Ritsumeikan University, 2009, No.11, pp.41-45*
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- [3] H.Ikeda : *Memoirs of the SR Center, Ritsumeikan University, 2009, No.11, pp.51-55*