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In-situ X-ray diffraction studies of evaporation induced self-assembly process of mesostructured silica films

Hidenosuke ITOH[1], Takashi NOMA*[1], Hirokatsu MIYATA[1], Kazuhiro TAKADA[1], Yasuhiro KAWASHIMA[1], Atsuo IIDA[2]
[1]Canon Research Center, Canon Inc., Ohta-ku, Tokyo 146-8501, Japan
[2]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

Mesoporous silica films have been widely investigated in view points of synthesis, characterization and application. Recently, our group reported [1] that a mesoporous silica film with highly aligned porous structure was fabricated by dip-coating using a rubbing-treated polyimide film as an alignment layer. The initial stage of the dip-coating process is the key to solve the formation mechanism of mesostructured silica. Our group has performed micro X-ray diffraction experiments of mesostructured silica films under static conditions [2]. In this report, we show our in-situ X-ray diffraction results of the formation of the mesostructured silica films with aligned porous structure .

Experimental

The mesostructured film was formed on a silica glass substrate with a rubbing treated polyimide by evaporation induced self-assembly (EISA) process. Figure 1 shows our experimental setting for the substrate dipping into a precursor solution. For the film formation, a reservoir was moved downward instead of pulling up the substrate to observe the structural changes in a fixed area. The rubbing direction was set to be parallel to the movement of the reservoir. The composition the precursor solution is Brij56 0.08: TEOS 1.0: Isopropyl alcohol 22: H_2O 5: HCl 0.004. In-situ micro beam XRD has been performed under a reflection geometry at beam-line 4A of the Photon factory, KEK. The beam size was 4.0 x 4.0 μm and the energy 8 KeV. Two-dimensional (2D) XRD patterns were collected by a high-speed CCD detector with a time-resolution of 0.15 s.

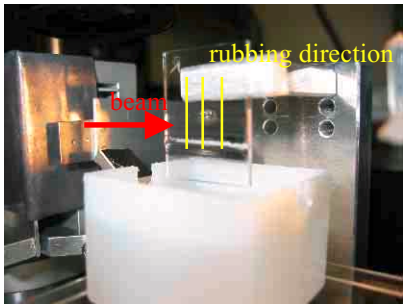
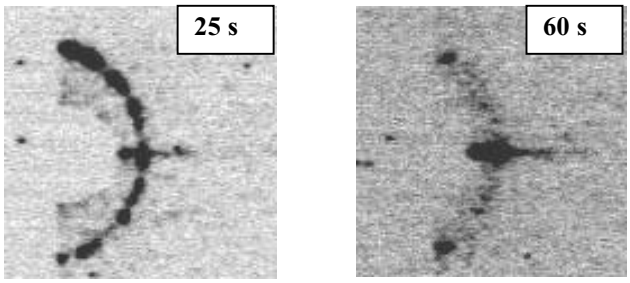


Figure 1 Experimental setting for dipping the substrate into a precursor solution.

Results and discussion

The formation of mesostructure has been achieved in a very short period. Figure 1 shows the 2-D XRD patterns recorded, with the incident beam perpendicular to the rubbing direction, after 25 s, 55 s, and 60 s from when the measured area was apart from the solution surface. Initially, no diffraction was observed, showing the lack of any structural regularity. As shown in Fig. 2(a), a Debye ring with high intensity was observed at 25 s, which reveals the formation of a regular structure with polycrystalline features. Interestingly, this Debye ring disappeared once and weak spots suggesting the aligned cylindrical micelle structure perpendicular to the rubbing direction were obtained around 55 s. The diffraction spots increase their intensity and the distance between them became narrower with expansion of the structural period as shown in Fig. 2(b). The alignment has been completed around 60 s. From these results it is considered that (i) the initially formed micelle structure is rearranged to the aligned cylindrical micelle structure in a short time scale. (ii) the alignment is completed via the shrinkage of the structural period.



(a) (b)

Figure 2 Two-dimensional X-ray diffraction patterns from the silica glass substrate with dipping speed of 100 μm/s. The time indicated at the upper right of each figure is the time from when the measured area was apart from the solution surface.

References

[1] H. Miyata et al., *Chem. Mater.*, *17*, 5323 (2005).
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* noma.takashi@canon.co.jp