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2D XRD study of a silica film with a zigzag mesoporous structure

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Introduction

Mesoporous silica, prepared through self-assembly of surfactant can be formed on a substrate as continuous films. We have found that the in-plane orientation of the mesopores in the mesoporous silica films can be controlled using a substrate with a rubbing-treated polyimide (PI) coating[1,2]. This substrate with a rubbed PI allows the formation of mesoporous silica films in which the cylindrical mesopores are aligned along two distinct in-plane directions under optimum preparation conditions. The two alignment directions are symmetric with respect to the normal of the rubbing direction, and we assume a controlled in-plane zigzag mesoporous structure for this film. Here, we report the 2-dimensional X-ray diffraction (2D-XRD) study of the film, which results are consistent with the proposed in-plane zigzag structure.

Experimental

Preparation of the film

A silica glass substrate was coated with a PI with a hexamethylene group in the repeating unit. This substrate undergoes a rubbing treatment, and then, it is kept in a reactant solution containing a surfactant and a silica precursor at 80 °C for 5 days for the mesoporous silica film formation. The composition of the solution is as follows: Brij56 0.0088: tetraethoxysilane 0.1: H_2O 100: HCl 3. The film was washed with pure water and air-dried.

2D-XRD measurement

The 2D-XRD patterns were recorded under a reflection geometry using a 3 μm × 3 μm X-ray microbeam with 8 keV at the Photon Factory, KEK on beam-line 4A. An X-ray CCD detector with an image intensifier was used as a detector. The patterns were recorded in three sample directions; 75 °, 90 °, and 105 ° with respect to the rubbing direction. Here, 75 ° and 105 ° are the two alignment directions of the mesopores (Figure 1).

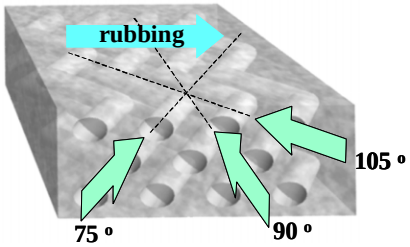

Figure 1. Schematic of the zigzag mesoporous structure and three directions for recording 2D-XRD patterns.

Results and discussion

The recorded 2D-XRD patterns are shown in Figure 2. At 90 °, that is, when the projection of the incident x-rays is perpendicular to the rubbing direction, the diffraction spots on the left and right sides are of comparable intensity. However, when the sample is rotated by +15 ° (at 105 °), the diffraction intensity of the spots on the left side becomes larger than that on the right side. On the contrary, when the sample is rotated by –15 ° (at 75 °), the spots on the right side become more intense than those of the left spots.

The observed change in the diffraction patterns can be explained by the relative positions of the reciprocal lattice points of the zigzag-structured film with respect to the Ewald sphere. The TEM and SEM images of the zigzag structured film show the curved structure at the kink positions, that is, the in-plane orientation of the mesopores is continuously changed between the two directions. For such zigzag structure, the reciprocal lattice points have dumbbell-like shape. Depending on the direction of the incident X-rays with respect to the orientation directions of the mesopores, the cross-section of the dumbbell-like reciprocal lattice points on the Ewald sphere changes. Consequently, the diffraction patterns of the zigzag-structured film become asymmetric unless the direction of the X-rays is evenly deviated from the two orientation directions of the mesopores.

These 2D-XRD results are consistent with the proposed in-plane zigzag mesoporous structure of the film.

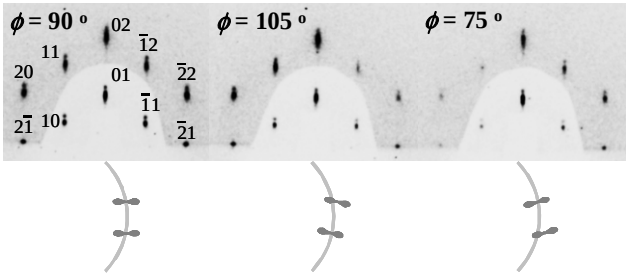

Figure 2. 2D-XRD patterns recorded at different angles (above), and relationship between the reciprocal lattice points and the Ewald sphere for each geometry (below).

References

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