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Pure-Silica Zeolite Films Prepared by a Vapor Phase Transport Method

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1. Introduction

Much attention has recently been paid to pure-silica zeolite films as a candidate for low dielectric constant (low-k) materials. Zeolite films are expected to have a lower k value and higher mechanical strength than conventional silica films due to their microporous crystalline structure. In researches on zeolite low-k films, the synthesis has so far only been performed by conventional hydrothermal methods [1, 2]. In this paper, pure silica ZSM-48 zeolite films on Si substrates were formed by a vapor-phase transport (VPT) method [3] and were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR).

2. Experimental

Fig. 1 shows the framework view of ZSM-48 zeolite. It has a one-dimensional 10-membered ring channels with a diameter of 5.6 Å × 5.3 Å [4]. The preparation procedure for a sol-gel precursor and the schematic diagram of the VPT method for the zeolite films were shown in Fig. 2. The precursor solution was prepared using ethanol (EtOH), tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl) and water. A surfactant template (Brij78) and the precursor solution were mixed [5]. TEOS, HCl and EtOH were semiconductor grades. The mixture solution was dropped onto a Si (100) substrate by a spin-coating method. The Si wafer was cut into 3cm×3cm pieces. For VPT crystallization, the piece was placed in the center of an autoclave after a mixture of ethylenediamine (EDA), triethylamine (Et_3N) and water was poured into the bottom of the autoclave to produce vapor. Synthesis for the zeolite films was performed at 200 ℃ under an autogenous steam pressure. The experimental conditions for the VPT method were summarized in Table 1. As-synthesized films were rinsed with acetone and were calcined in nitrogen at 500 ℃ for 10 h. A heating rate of 0.1 ℃ was adopted in the range of 200-500 ℃.

The crystallite morphology and structure of the products were analyzed by SEM (Hitachi S4700) at an acceleration voltage of 15 kV, XRD (Rigaku RINT 2000) with Cu Kα radiation (λ=1.5418 Å) and FTIR (JEOL FTIR-660 Plus ST(V)) at 2cm^{-1} resolutions.

3. Results and Discussion

Fig. 3 shows the time-course of SEM pictures (top view) of the zeolite crystals on the Si wafers (sample 1, 2, and 3). In Fig. 3(a), the morphology of the crystal forms thin needles (about 45μm in length, about 0.3μm in diameter) and the crystals are randomly oriented across the surface on the Si wafer. The form of the crystals changed from thin needles to stick-like morphology (about 1.5 μm in diameter) with crystallization time shown in Fig. 3 (b) and (c).

Fig. 4 presents the time-course of the XRD patterns of the zeolites crystals formed on the Si substrates (sample 1, 2 and 3). The diffraction peaks of the zeolite crystals were coincident with those of ZSM-48 zeolite. It is known that ZSM-48 zeolite is not a code for one material but for a family of materials and have two groups of the polytypes: monoclinic unit cells and orthorhombic unit cells [4]. The XRD patterns of the two groups show many similarities with the exception that at a low angle the monoclinic polytypes have two peaks at 2θ = 7.5° and 8.7°, while the orthorhombic polytypes show three peaks at 2θ = 7.15°, 7.6°, and 8.1°. The experimental XRD patterns showed only two peaks at 7.54° and 8.74° at low angle. For this reason the XRD patterns were the orthorhombic patterns of unit cell parameters with a = 24.66 Å, b = 8.4 Å, c = 24.66 Å and β = 109.47°. Fig. 4(a) shows that the diffraction peaks for the crystal faces of ZSM-48 zeolite emerged during the first 4 days. The intensity for (020) crystal face increased after 6 days as shown in Fig. 4 (b) and (c).

Fig. 5 shows the XRD patterns (sample 4 and 5) when the volume ratio of $EDA/Et_3N/H_2O$ was changed. The intensities of the diffraction peaks of sample 4 and 5 were weak compared with that of sample 3. This suggests that the mixture ratio is important for the crystallization of the zeolite in the VPT method.

Fig. 6 shows the FTIR spectrum of sample 3. The absorption peak was observed around 550 cm^{-1}, which is assigned to the presence of the 5-membered ring of tetrahedral in the framework and characteristic for the structure of ZSM-48 zeolite [6]. The other two peaks around 800 and 470 cm^{-1} are attributed to the Si-O symmetric stretch and bend, respectively, and are not structure sensitive.

4. Summary

Pure silica zeolite films on Si substrates were synthesizes by the VPT method. SEM images showed that the forms of the crystals are needles and changed to stick-like morphology with crystallization time. XRD patterns suggested that the crystal is ZSM-48 zeolite of the unit cell parameters with a = 24.66 Å, b = 8.4 Å, c = 24.66 Å and β =109.47°. FTIR spectrum showed the characteristic for the structure of ZSM-48 zeolite. For crystallization of the zeolite the mixture ratio of $EDA/Et_3N/H_2O$ is important in the VPT method.

References

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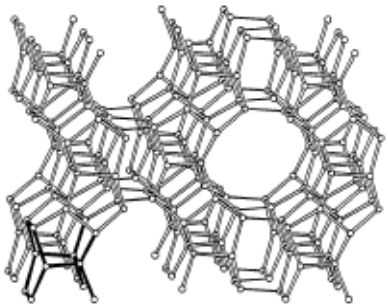

Fig. 1. ZSM-48 zeolite framework

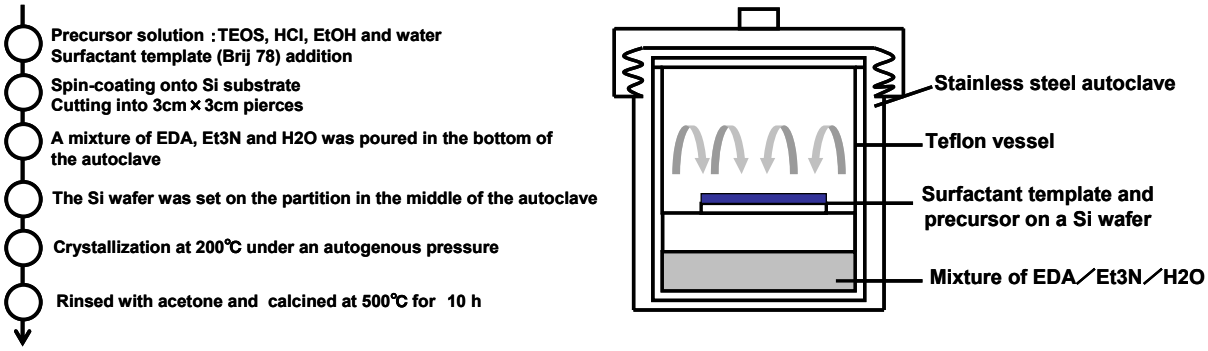

Fig. 2. Preparation procedure and schematic diagram of a vapor phase transport method for pure-silica zeolite films

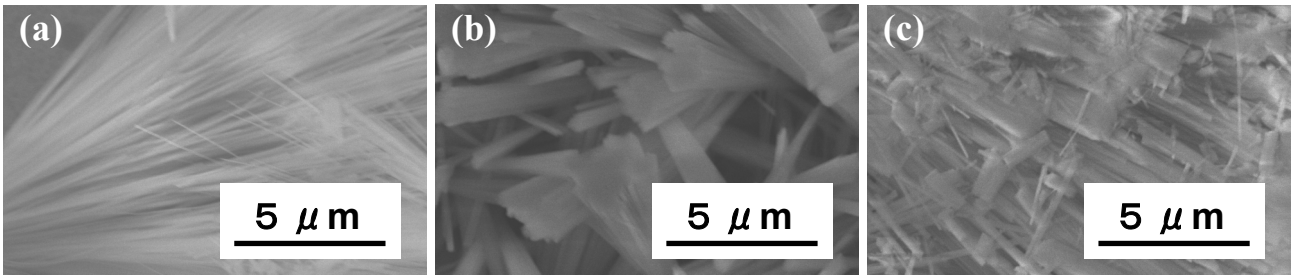

Fig. 3. SEM images (top view) of the crystals formed on Si wafers. (a) sample 1 (b) sample 2 (c) sample 3.

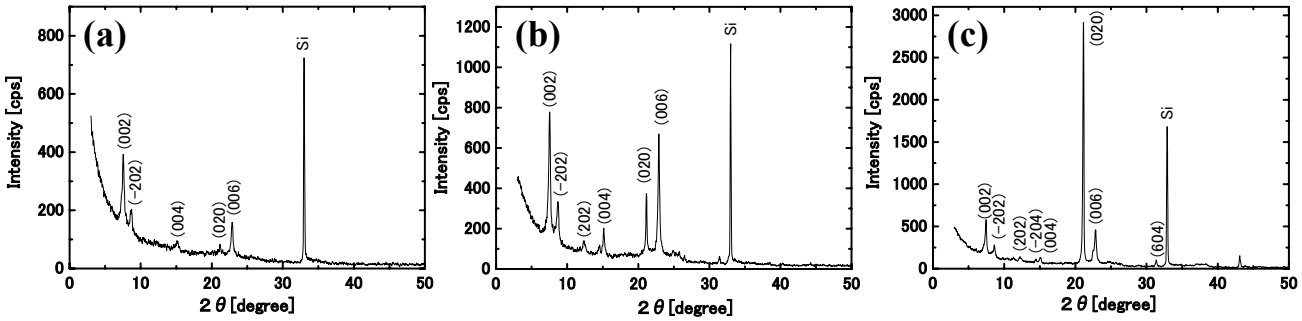

Fig. 4. XRD patterns of MTW zeolite films formed on Si substrates. (a) sample 1 (b) sample 2 (c) sample 3.

Table 1. Experimental conditions for a vapor phase transport method

Sample No.	EDA/Et3N/H2O (volume ratio)	Crystallization time/day
1	1/2/1	4
2	1/2/1	6
3	1/2/1	8
4	2/1/1	6
5	1/1/2	6

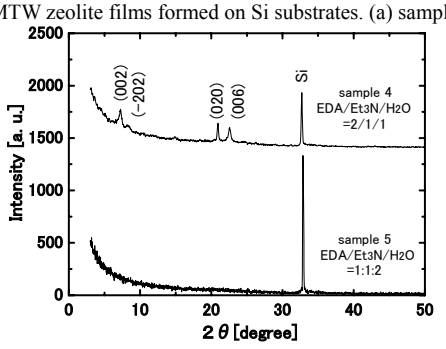

Fig. 5. XRD patterns of sample 4 and 5.

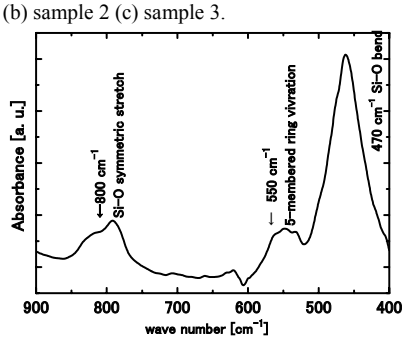

Fig. 6. FTIR spectrum of sample 3