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Pure silica MFI zeolite films as antireflection coatings

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Densely packed thin films of pure silica MFI (Mordenite Framework Inverted) type zeolites nanocrystals (35 nm) are deposited by spin coating method. The influence of coating suspension suspensions and spin-on rotation conditions on films thickness is investigated. The optical constant and thickness of the films are defined from the reflection spectra using nonlinear curve fitting method. It is demonstrated that the MFI thin films with appropriate thickness deposited on both sides of glass substrate operate as an antireflection coating in the visible spectral range. An increase of transmission with 6% and decrease of reflection with 7.5 % are observed.

Keywords: zeolite nanocrystals, films, optical properties, antireflection coatings.

INTRODUCTION

Zeolites (molecular sieves) are crystalline materials with framework-type structure built of regular and uniform pores of molecular dimensions [1]. The zeolites are classified according to their framework type, pore dimension and the Si/Al ratio of the frameworks.

The high crystalline zeolites have found wide application in catalysis, separation, and ion exchange processes [2,3]. In addition to the traditional uses, advanced applications of these materials have also been explored [4] including low dielectric constant (low-k) zeolite film used as insulator for future generation computer chips [5,6], single zeolite layer antireflective coatings [7], various sensor devices [8,9], etc. Besides, the unique combination of chemical and optical properties of zeolites opened up the possibility of using them as a part of tunable Bragg stacks [10,11]. A number of novel applications of zeolites depend on the ability to create thin, adhesive films on various substrates [4]. Among various techniques for fabrication of zeolite-based films, the spin coating method is widely used because it is simple, fast and offers operating precision, flexibility and high uniformity over the surface [9,12,13].

Reliable and non-destructive measurements of zeolite film characteristics such as the film thickness and refractive index (or dielectric constant) are beneficial for estimating the performance of zeolite films in the above-mentioned applications. If the optical properties of zeolite films can be controlled and optimized then the opportunity for variety of practical applications is opened up.

In this paper we study the optical properties of zeolite films obtained by spin coating of aqueous zeolite dispersion consisting of pure silica crystals with MFI type structure (Si-MFI) and small sizes (35 nm). Besides, the possibility of controlling the optical thickness of the zeolite films through variation of concentration or spin-on deposition rate is investigated. The preparation of single layer antireflection coating consisting of Si-MFI nanocrystals is demonstrated.

EXPERIMENTAL DETAILS

Pure silica MFI-type zeolite (Si-MFI) was synthesized according to the procedure described in [14]. After completing the synthesis, the crystalline suspension was purified by high-speed centrifugation in three subsequent cycles and redispersed in water. The size of the nanoparticles was measured by Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano. Additionally, the size and crystalinity of nanosized particles were confirmed by Transmission Electron Microscopy

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(TEM) using a JEOL 2010 FEG operating at 200 kV.

The zeolite thin films were prepared by spin coating approach: 0.25 ml of aqueous colloidal suspension with a constant concentration (1-7 wt. %) was mixed with 0.05 ml of methylcellulose and the mixture was dropped onto preliminarily cleaned Si-substrate according to the procedure described in [15]. The speed and duration of rotation were 1000 - 2500 min^{-1} and 30 s, respectively. The layers were annealed from room temperature to 320 °C with temperature accelerating speed of 10 °C / min and then held at this temperature for 30 minutes. The zeolite layers with a thickness in the range 40-200 nm were subjected to further characterization.

The surface roughness and thickness of zeolite films were studied by Scanning Electron Microscopy (SEM) using JEOL JSM6700F SEM at an accelerating voltage 30.0 kV. Reflection spectra (*R*) of zeolite films were measured in the spectral range 400 – 900 nm using UV-VIS-NIR spectrophotometer (Cary 5E, Varian) with an accuracy of 0.3 %. The refractive index (*n*), extinction coefficient (*k*), and thickness (*d*), of the films were determined simultaneously from the reflection measurements using non-linear curve fitting method described in details elsewhere [16]. The experimental errors for *n*, *k* and *d* are 0.005, 0.003 and 2 nm, respectively.

RESULTS AND DISCUSSION

The DLS and TEM results for zeolite suspensions with Si-MFI nanocrystals are presented in Fig. 1. As can be seen, the mean hydrodynamic diameter of the zeolites is 35 nm and the crystals exhibit almost plate-like morphology.

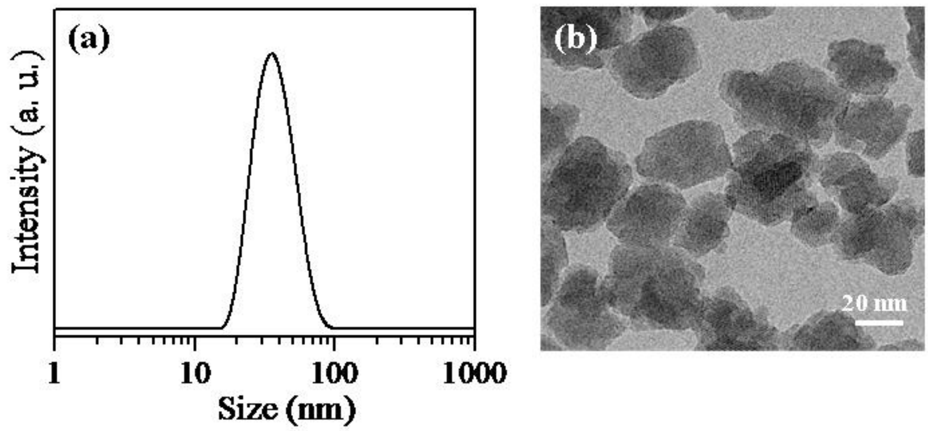

Fig. 1. (a) DLS curves for colloidal suspensions containing Si-MFI type zeolites; (b) TEM images of Si-MFI zeolites.

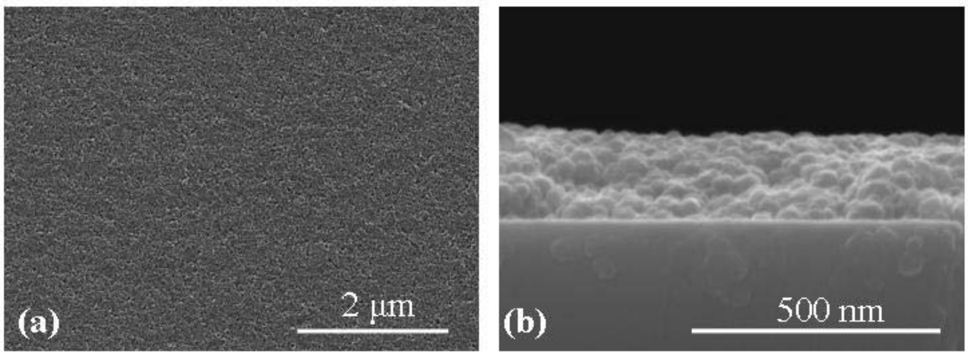

Fig. 2. SEM images of Si-MFI film: (a) surface and (b) cross-sectional view.

The zeolite nanocrystals are deposited in the films (thickness of 40-200 nm) by spin coating with different deposition conditions (concentrations from 1 to 7 wt.%; deposition rates from 1000 to 2500 min^{-1}). The surface and cross sectional views of the films with thickness of 150 nm are presented in Fig. 2. As shown, the zeolite nanocrystals are closely packed and form continuous cracks free films along the silicon substrate. The quality of the zeolite films (surface roughness and homogeneity) is preserved under annealing at 320 °C.

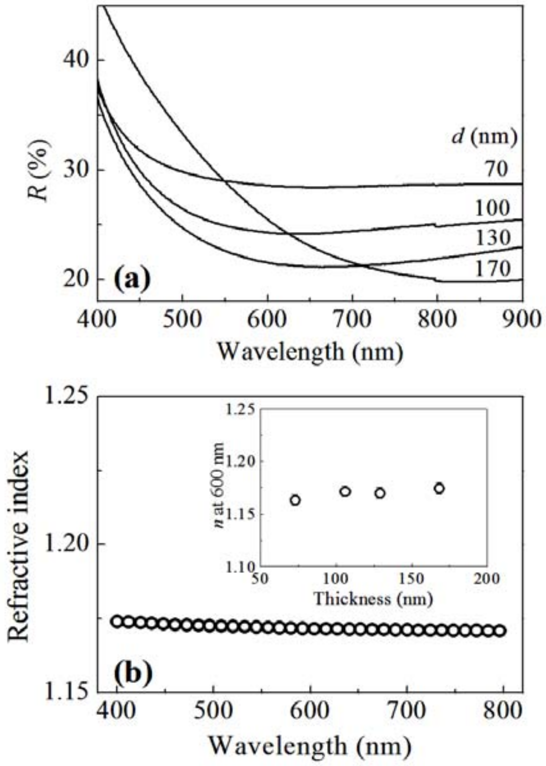

Fig. 3. a) Reflection spectra of thin Si-MFI films with denoted thicknesses deposited on Si-substrate; b) Refractive index of Si-MFI thin films as a function of wavelength and thickness (inset).

The reflection spectra (R) of Si-MFI zeolite films with a thickness from 70 to 170 nm are shown in Fig. 3(a). A decrease of reflection with increasing the films thickness is observed: when the thickness of the films increases from 70 nm to 170 nm, the R-value at wavelength of 900 nm decreases with 12 %. Using the reflection spectra, the refractive index, extinction coefficient and thickness of the films are calculated [16].

Fig. 3(b) presents the calculated values of the refractive index of zeolite film with a thickness of 100 nm as a function of the wavelength (i.e. the dispersion curves of n). As can be seen, the dispersion of n is very weak that is not surprising considering that the MFI-zeolite film is transparent in the studied spectral range. The n values of 1.174 and 1.171 at wavelengths of 400 and 800 nm are measured, respectively. The thickness dependence of refractive index is shown in the inset of Fig. 3 (b). As can be seen the influence of the films thickness on the n value is negligible: n changes from 1.164 to 1.175 for films with thicknesses of 70 and 170 nm, respectively.

For many applications the precise control of the film thickness is essential for the right performance of the device. In the current work, two approaches are applied to tune the thickness of zeolite films. In one case the concentration of the coating suspension is varied and in the other case the conditions of film preparation (spinning rate). Figure 4(a) shows the change of the film thickness with variation of the concentration of the coating zeolite suspension. It is seen that the film thickness increases linearly with an increase of the concentration. Thus, films with thicknesses in the range 20-200 nm were prepared by changing the concentration from 0.5 to 7 wt.%. The dependence of film thickness as a function of the deposition rate at two constant concentrations of the suspensions is shown in Figure 4(b). The variation of spinning rate from 1000 to 2500 min^{-1} leads to the formation of films with a thickness from 220 to 120 nm (5 wt.% zeolite suspension) and from 90 to 50 nm (2 wt.% zeolite suspension). However the results show that the quality of films obtained at lower spinning rates (1000 min^{-1}) are slightly deteriorated.

Another way for varying the film thickness is by increasing the number of consecutive steps of deposition. After each deposition step the samples were subjected to annealing at 320 $^{\circ}$C for 30 min in order to increase the mechanical stability of the zeolite films.

The ability of the MFI-type zeolite nanocrystals to form compact thin films with good adhesion along with suitable optical properties can be used for design and fabrication of single layer antireflective (AR) coating on glass substrate. This is the simplest AR coating and consists of a film with quarter-wave thickness ($n\lambda_c/4$, n is refractive index, λ_c is the wavelength of minimum reflection) whose refractive index is the square root of the substrate's refractive index. Thus waves reflected from the top and bottom boundaries of the film interfere destructively and as a result the overall reflection is zero for λ_c. Considering that the refractive index of glass substrate is 1.51 in the visible range the n value of AR coating should be 1.23. As seen from Fig. 3(b) the Si- MFI zeolite films have refractive index of 1.17 that is very close to the targeted value of 1.23. Hence, the MFI-zeolite films are very suitable for AR coating. Besides, the thickness of the film can be precisely controlled (Fig. 4(a)) that is essential for the reflection suppression.

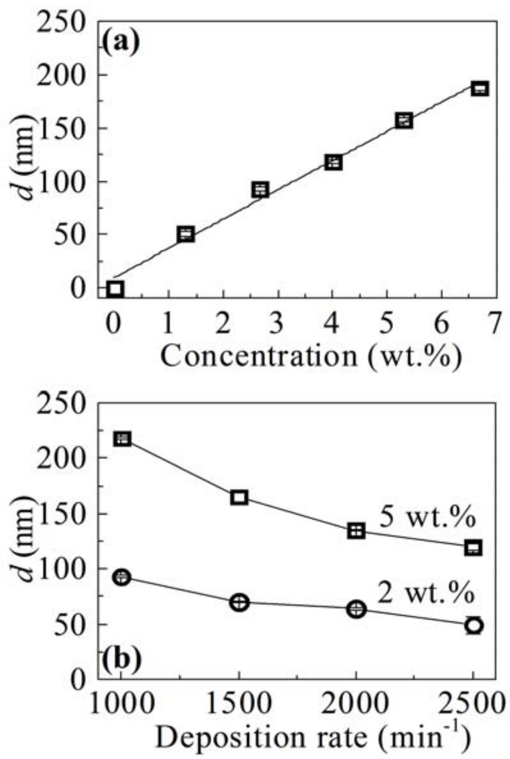

Fig. 4. Dependence of thickness of Si-MFI films on the concentration of the colloidal solution (a) and on deposition rate (b).

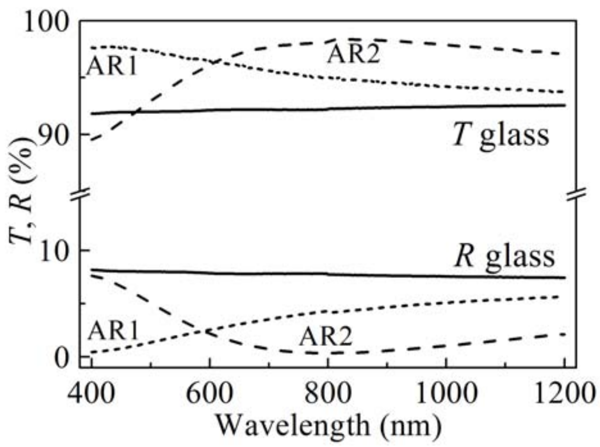

Fig. 5. Transmittance and reflection spectra of single layer antireflection coatings with thicknesses of 85 nm (AR1-dotted curve) and 170 nm (AR2-dashed curve) deposited on both sides of glass substrate (solid curve).

Figure 5 presents two AR coatings for the visible and near infrared spectral range. For quarter wave optical thickness of 400 nm, (i.e $4nd$ = 400 nm) the thickness of AR coating should be 85.5 nm, while for 800 nm, the d value should be 171 nm. For the deposition of films with the desired thicknesses, colloidal solutions of Si-MFI nanocrystals with concentrations of 2.7 and 5.8 wt.% respectively are prepared. The films are deposited on both sides of the glass substrate. The films transmission and reflection spectra are presented in Fig.5 along with the spectra of the bare glass substrate. It is seen that both films (AR1 and AR2) operate as antireflection coatings: a decrease of R and increase of T are observed in the whole studied spectral range. Besides minimum reflection of 0.36 % has been reached (see AR2 curve). The mean value of R in broad spectral range (600-1200 nm) is below 1%. Simultaneously an increase in transmission with 6 % is observed.

CONCLUSIONS

The optical properties of zeolite films obtained by spin coating of aqueous suspension of Si-MFI nanocrystals are investigated. It is demonstrated that zeolite nanocrystals are closely packed and form continuous films that cover the entire surface of the substrate. The optical characterization revealed that the Si-MFI film exhibits refractive index from 1.164 to 1.175 depending on the film thickness. Besides, two ways for controlling the films thickness are presented: variation of the concentration of coating suspension and spinning rate during deposition process. The potential of Si-MFI zeolite films for broadband antireflection (AR) application is demonstrated by fabrication of AR coating on both side of glass substrate.

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SI-MFI ЗЕОЛИТНИ ФИЛМИ КАТО АНТИОТРАЖАТЕЛНИ ПОКРИТИЯ

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(Резюме)

Si-MFI зеолитни нанокристали (35 nm) са отложени като тънки слоеве посредством метода на центрофужното нанасяне. Показателите на пречупване и поглъщане, както и дебелината са определени от измерените спектри на отражение чрез нелинейно фитване. Дебелината на отложените слоеве е калибрирана като функция на концентрацията на суспензията и скоростта на отлагане. Показано е, че Si-MFI слоеве с подходяща дебелина, отложени върху двете повърхности на стъклена подложка могат да се използват като антиотражателни покрития. Наблюдавано е намаляване на отражението във видимата област на спектъра с 7.5 %, като едновременно с това пропускането нараства с 6%.