

Stability of oriented silicalite-1 films in view of zeolite membrane preparation

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Silicalite-1 is grown as *b*- and (*a*, *b*)-oriented monolayers on silicon wafers and on silicon wafers containing low-stress silicon nitride windows, aiming at two new membrane systems. The orientation of crystals determines the stability (crack formation), due to tensile or compressive stress, imposed on the layer after removal of the organic template. By application of etching procedures, the nitride support can be removed, leaving the crystal layer undamaged. The latter makes preparation of oriented and nonsupported thin layers for gas separation purposes possible. © Elsevier Science Inc. 1997

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INTRODUCTION

Zeolite-support composites can be applied as catalysts in reactors, as sensors for detection and/or controlling, and as membrane devices for the separation of gases and liquids. Combining catalysis and separation techniques allows the engineering of catalytic membranes and membrane reactors.

In the last decade, the interest in zeolite-on-support configurations has grown worldwide.¹⁻³ Research on the formation of supported zeolite layers has been mainly focused thus far on the medium-pore (10-membered oxygen ring) tectosilicate MFI (silicalite-1/ZSM-5). This zeolite is known to grow relatively easily on various surfaces, whereas its growth is characterized by a broad range of concentrations, pH, and temperature without the formation of other zeolites, allowing thorough investigations on its growth behavior.

The growth of MFI^{1,4-16} on porous supports like alumina or stainless steel generally results in a random orientation of crystals, due to the roughness of the supports applied. Until now, *oriented* films have only been prepared on nonporous silicon wafers.^{17,18} For permeation studies, continuous layers without pinholes are essential to allow selective passage of gas molecules through the zeolite pores only. To obtain defect-free MFI layers on porous supports, relatively thick layers are required. As a result, fluxes through the membrane

decrease. For a full understanding of the observed transport through zeolite layers, uniformity of the layer is essential. In modelling studies¹⁹ on permeation behavior, exact values of the open area of the support and the (uniform) thickness of the zeolite layer are required.

A new preparation method will be reported for the synthesis of oriented MFI layers on silicon wafers. Crystal orientation on trenches and pores, etched in the wafers, will be discussed. As an extension of this work, crystal growth over silicon nitride windows inside the wafers while, by selective etching procedures, the nitride windows are removed to form an oriented and locally nonsupported layer of MFI will be discussed. Such layers make investigation of stress created only by the zeolite crystals possible. It will be shown that the removal of the organic template causes stress in the obtained layer, depending on the crystal orientation.

EXPERIMENTAL

Silicon wafers (prepared at DIMES, The Netherlands) were placed in 50-cm³ autoclaves in a preheated hot-air oven under static conditions under a small angle to prevent crystals, nucleated in the solution, to drop on the surface. The side facing upward was coated with vacuum grease (Dow Corning, high vacuum grease) to prevent crystallization from occurring at both sides.

The following chemicals were used: tetrapropylammonium hydroxide (TPAOH, 40%, CFZ Zaltbommel, The Netherlands), demineralized water, and tetraethoxysilane (Janssen Chimica). The applied molar

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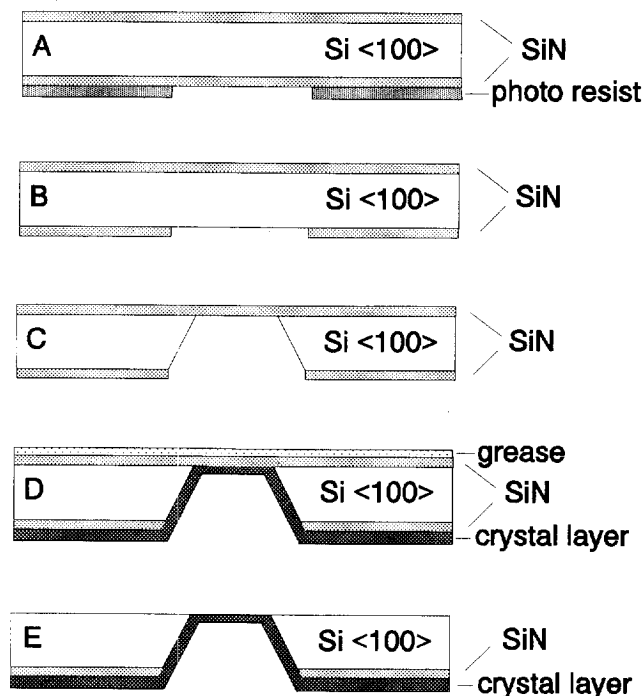


Figure 1 Principles of thin-layer preparation in silicon/silicon nitride composites.

composition for obtaining a *b*-oriented crystal layer was as follows:

$$\text{H}_2\text{O} : \text{TPAOH} : \text{TEOS} = 99.0 : 0.23 : 0.84$$

The obtained synthesis mixture was then aged at ambient temperature for 1 h under vigorous shaking before being placed in the autoclaves (filling: 2/3 of its volume). After synthesis, the autoclaves were rapidly cooled with cold water and the wafers were washed with demineralized water and dried at 80°C.

Silicon as well as silicon nitride can be obtained as thin layers. In the latter case, thin layers of nitride can be prepared as windows inside the silicon wafer. These window-containing wafers were prepared using semiconductor technology. *Figure 1, A-E*, shows the sequence of preparation steps to obtain the substrates.

On both sides of the $\langle 100 \rangle$ wafer a silicon nitride layer is grown by low-pressure chemical vapor deposition at 846°C, and a pressure (*P*) of 150 mtorr using dichlorosilane and ammonia ($\text{DCS}/\text{NH}_3 = 170/30$ standard cm^3/min [sccm]) is obtained. On stoichiometric silicon nitride a tensile stress is imposed due to the silicon substrate. Therefore low-stress nitride (SiN) was used. Such a stress-free behavior is limited to thin layers only, thus nitride layers of 500 nm were grown. A mask was made in a photoresist film, covering one side of the substrate (*Figure 1A*), using a lithographic process. The uncovered nitride parts are removed by means of plasma etching (Drytek 384 T, RF-power = 400 Watts, $\text{SF}_6 = 100$ sccm, $P = 250$ mtorr), and the photoresist was removed in an oxygen plasma (*Figure 1B*). Next, the uncovered silicon is removed by etching in a 9 M KOH-solution at 83°C for 5.5–6 h (*Figure 1C*). Due to differences in etching rates for the $\langle 100 \rangle$ and $\langle 111 \rangle$ direction

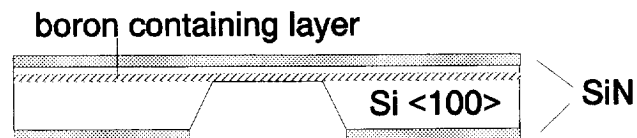


Figure 2 Preparation method for thin silicon layers.

(approximately 100 times faster in the $\langle 100 \rangle$ direction), windows are formed under an angle of 54.74°. The etching stops at the nitride layer due to the rate difference in etching for silicon (100 $\mu\text{m}/\text{h}$) and nitride (0.02 $\mu\text{m}/\text{h}$), resulting in a selectivity ratio of 5,000 to 1. The obtained substrates were placed in the autoclaves with the silicon side facing slightly downward. On this side crystals of silicalite-1 are grown. The side, facing upward, is shielded from the synthesis mixture with a layer of vacuum grease (*Figure 1D*). After crystallization, the grease is removed by boiling in refined petroleum ether and subsequent washing in HNO_3 (100%). Next, the remaining nitride is removed in boiling H_3PO_4 (85%)²⁰ at a temperature not exceeding 157°C (etch rate $\text{SiN} = 1,500 \text{ \AA}/\text{h}$, selectivity $\text{SiN}/\text{SiO}_2 = 32$, selectivity $\text{SiN}/\text{Si} = > 100$) to obtain a nonsupported zeolite film (*Figure 1E*).

A second method of preparing thin layers is based on the difference in etching rate between pure silicon and silicon containing high concentrations of boron (see *Figure 2*). Such layers either can be epitaxially grown on silicon substrates or can be obtained by the implantation of boron in silicon containing small amounts of boron. At a concentration of boron of 1×10^{20} atoms/ cm^3 (2 0/00), the etching rate of KOH (11.5 M at 65°C) is 20 times lower than at a concentration of 10^{15} atoms/ cm^3 , although a concentration of 4×10^{19} boron atoms/ cm^3 results in a three times lower etching rate²¹.

The obtained SiN layers can be perforated using a lithographic process on the nitride side of the substrate. After plasma etching (Alcatel 300 GIR) and removal of the photoresist, holes limited to a size of $4 \times 4 \mu\text{m}^2$ and a total open area of 24% can be obtained.

The obtained crystal layers were investigated with light microscopy, scanning electron microscopy, and XRD analysis (Siemens Kristalloflex D5000), using $\text{CuK}\alpha$ -radiation without α_2 -stripping. The thickness of the crystal layer was determined using a surface profiler (TENCOR 500). The removal of the organic template was monitored using FT i.r. spectroscopy (Bruker IFS 66).

RESULTS AND DISCUSSION

Synthesis on silicon/silicon nitride substrates.

b-Oriented silicalite-1 layers

The following model describes the growth of the crystal layer under the synthesis conditions applied: under aging, the silicon source is hydrolyzed and small sol particles are formed. These silicon oxide sol particles try to lower surface energy by precipitation on the support surface (*Figure 3*) and form a thin gel layer during synthesis.

This tendency increases due to a pH drop, resulting

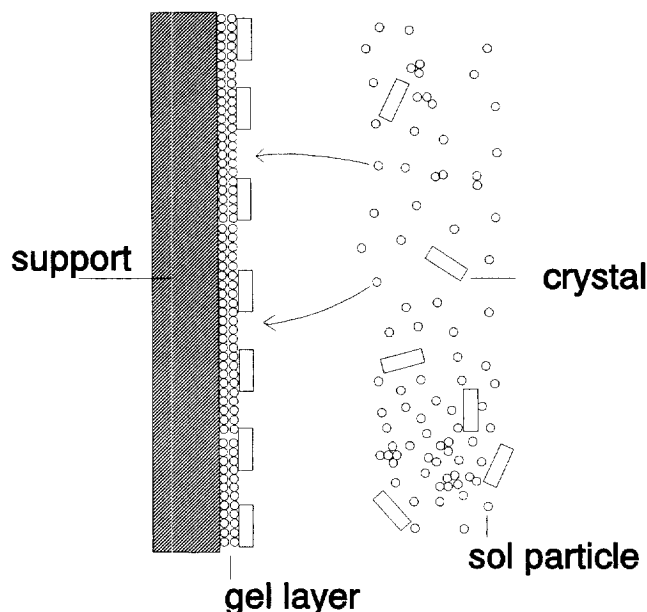


Figure 3 Schematic principle of gel formation and crystal growth on a surface.

from Hofmann degradation of TPA, causing a decrease in solubility of the silicon species. Crystals start nucleating on the interface of the gel and liquid where the gel supplies the silicon and the liquid supplies the template for zeolite growth. The crystals consume the gel until they reach the support surface. In the mother liquid sol particles form larger units by coagulation and move to lower parts in the autoclave due to gravitational forces, forming a thicker gel. In the mother liquid liquid crystals nucleate as well. To form a uniform gel layer, no cations should be present in the synthesis mixture. Metal ions (including sodium) stimulate gel formation in the entire synthesis volume rather than selectively on the surface of the support. For that reason, a sodium-free synthesis is used while the initial pH and TPA concentration is high, so as to stimulate the pH drop while maintaining enough template for the actual growth of the zeolite.

This procedure, resulting in a *a b*-oriented crystal layer, was applied on a 1-cm² silicon substrate containing silicon nitride windows, according to the method described in *Figure 1*, with 12 small holes with a diameter of 4 μm lithographically created in the nitride layer. The synthesis was carried out under static conditions at 165°C for 2 h. *Figure 4* shows an SEM image of the obtained layer. As can be seen from the figure, the 10 pores remain uncovered. Gel formation is apparently limited inside these pores, probably due to poor wetting by the synthesis mixture and the relatively high viscosity of that mixture. The crystals on the flat surface consume the gel film underneath but cannot grow over the pores, as gel is lacking there. Silicon has to be supplied from the liquid by diffusing toward the pinhole, a relatively slow process, to make further growth of the crystals possible. An increase in synthesis time results in two phenomena: (1) Due to the high pH, the silicon support starts to dissolve; and (2) silicon is con-

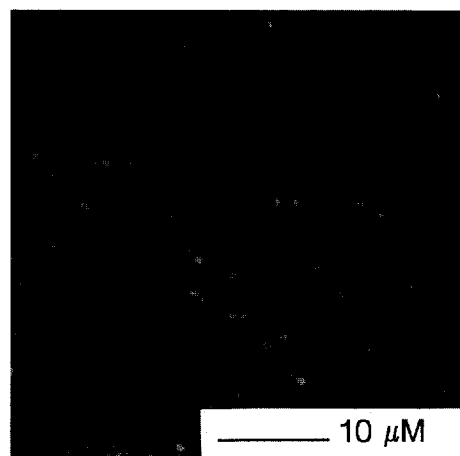


Figure 4 SEM image of a silicalite-1 layer on a porous silicon nitride support.

sumed in the synthesis mixture by growing crystals far away from the substrate, therefore lowering the overall silicon concentration and reducing the transport of silicon to the substrate. So, closing the crystal layer over the pinholes proves to be difficult when applying the monolayer principle.

To investigate the possible bonding of crystals to the support during synthesis, nonporous silicon substrates were coated with a hydrophobic monolayer of organic alkyl groups by boiling for 1 h in tripropylchlorosilane at 180°C or trimethylchlorosilane at 57°C under dry conditions in a nitrogen atmosphere. By applying the surface modification, however, similar results are obtained. The lack of hydroxyl groups on the alkylated surface might prevent crystals from chemical bonding to the substrate but does not prevent gel formation and subsequent crystal layer formation. So, the chemical nature of the surface does not change the synthesis principle.

When consuming the gel film, the crystals grow larger and finally grow together to form the layer. From this point on, diffusion of TPA to the support surface is strongly inhibited because the number of pores as well as the pore sizes decrease between the crystals. Most likely, a small gel film remains present between the crystals and the surface. Due to the lack of TPA, this small gel layer might not be converted into crystalline material, and, therefore, it is expected that only a few or no bonds exist between the as-synthesized layer and the support surface, which will even be more likely in the case of alkylated substrates. It is, therefore, presumed that chemical bonding mostly takes place during calcination.

(a,b)-Oriented silicalite-1 layers

Crystal layers were grown over nonporous silicon nitride windows in a silicon wafer (*Figure 1C*) at 165°C for 19 h using the following molar composition:



The pH and the TPA concentration of this synthesis mixture is slightly lower than in the *b*-oriented concept,

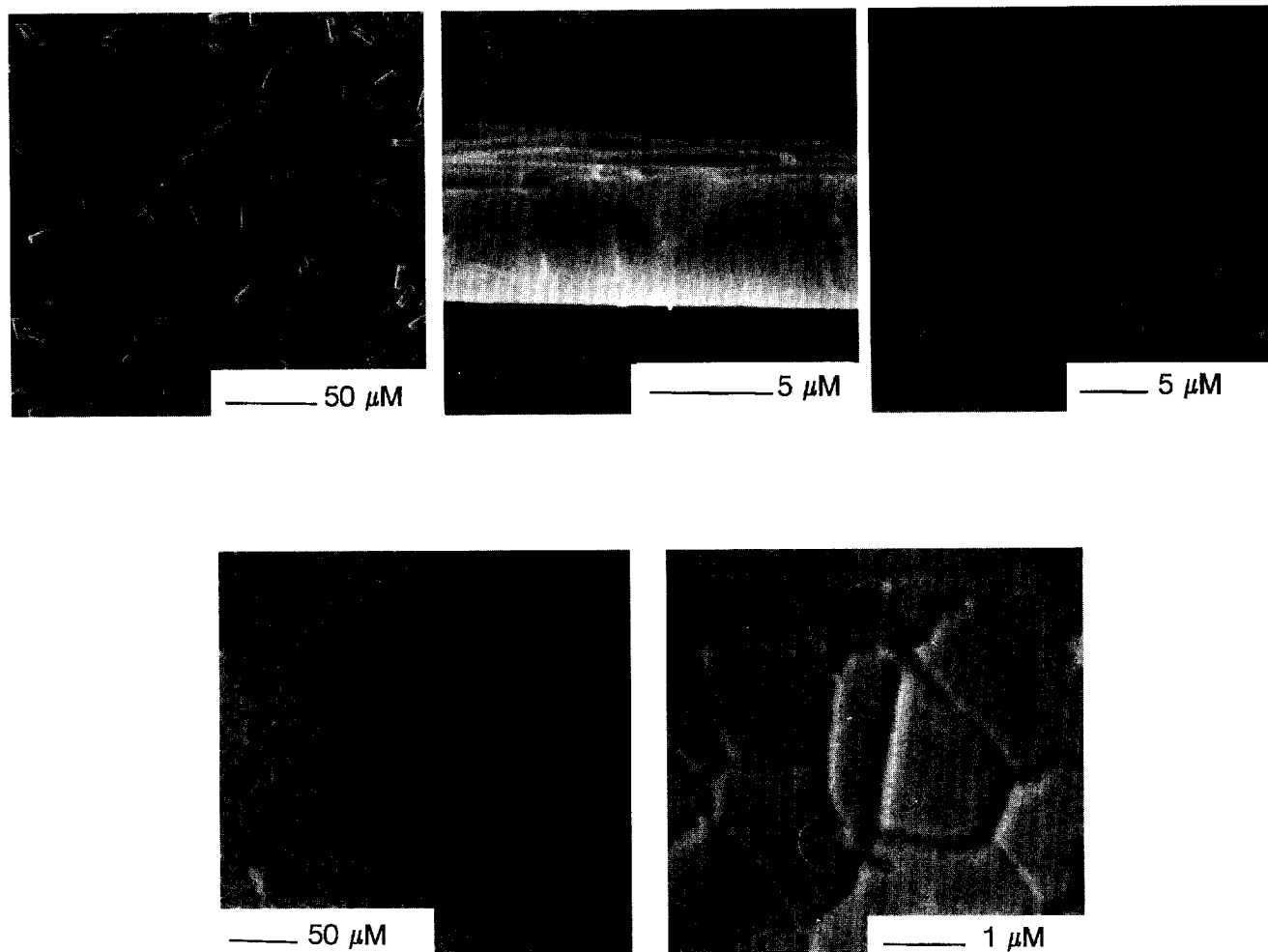


Figure 5 SEM image of an (a,b) -oriented layer on silicon nitride: (A) top view; (B) cross-section after removal of nitride; (C) cross-section under a small angle; (D) overview; and (E) bottom side of the crystal layer after removal of nitride.

described above (initial pH 13.1 and 12.9, respectively) to inhibit nucleation and to grow larger crystals. The pH is still high enough to dissolve the silicon precursor properly, but supersaturation is proceeding slower due to the less pronounced Hofmann degradation. As a result, the synthesis time increases from 2 to 19 h for a layer formation fully covering the support. In *Figure 5*, a top view and a cross-section (after removal of the nitride layer by etching and breaking the layer) are shown of the obtained composite as well as an image of the interface of crystal layer and substrate after removal of the nitride layer.

The XRD spectrum (*Figure 6, a and b*) of such a layer on nonporous silicon reveals $(h00)$ and $(0k0)$ reflections only. Apparently, the crystals show a -oriented as well as b -oriented crystals only. This can be explained by assuming a thin layer of crystalline material on which crystals grow. The obtained image of the interface of nitride and crystals shows a grain-like structure (*Figure 5E*), which was shown not to be due to the nitride substrate on which the layer was grown, because the nitride layer is flat and does not exhibit such details. Moreover, these details are not visible on the silicon surface after removal of the nitride and are therefore

not due to the remainders of the nitride layer. The grain-like structure is comparable to silicalite-1 structures with a thickness of 320 nm on wafers observed elsewhere,¹⁸ and it can be explained as quickly grown silicalite-1, showing no crystal features. The actual crystal layer is then formed from secondary nuclei (a -oriented) growth on the grains and from b -oriented growth of crystals on the precipitating gel phase, both processes occurring at the same time.

Removal of the template versus stress

From crystallographic data²² it can be seen that the unit cell of MFI changes due to the removal of TPA ions from the framework. The values are listed in *Table 1*. A phase transition from the orthorhombic (Pnma) to the monoclinic ($P2_{1/n}$) form occurs, at a temperature depending on the Si/Al ratio as well as on defects of the framework. Due to the removal of TPA^+ , a -oriented crystals expand 1.009% parallel to the substrate surface, whereas b -oriented crystals shrink 0.814%.

If the c -direction of both a - and b -oriented crystals is presumed to be random in the crystal layer, the ratio of both orientations can be calculated as needed for a

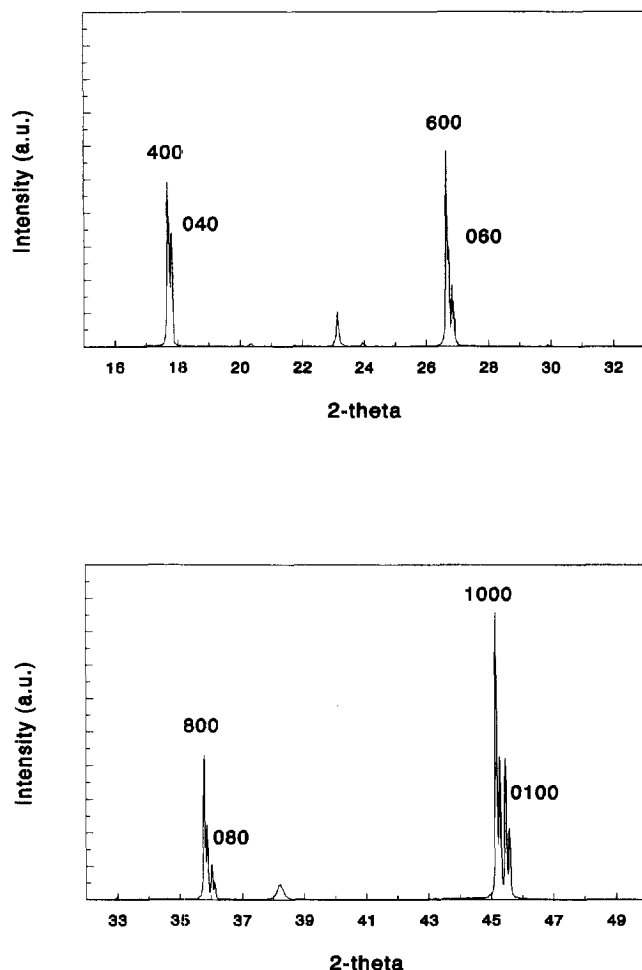


Figure 6 XRD spectrum of an (*a*, *b*)-oriented layer on nonporous silicon or silicon nitride.

netto change of the crystal layer that equals zero, according to the following equation:

$$\frac{X}{100} * 1.0094 + \frac{(100 - X)}{100} * -0.8143 = 0 \quad (1)$$

where *x* is the percentage of *a*-oriented crystals and 100-*x* the percentage of *b*-oriented crystals. So, when a layer is formed of 44.7% of *a*-oriented crystals and of 55.3% of *b*-oriented crystals, the change of the crystal layer equals zero at 25°C after the removal of the template. Considering the fact that the layer is presumed to withstand a compressive stress better than a tensile stress (crack formation), the amount of *a*-oriented crystals may exceed 44.7%. A layer consisting of *a*-oriented crystals only would expand 1.0%, whereas *b*-oriented

Table 1 Crystallographical data (Å) of the unit cell of MFI before and after calcination

	As-synthesized	Calcined	Change
<i>a</i> -axis	20.022	19.879	-0.71
<i>b</i> -axis	19.899	20.107	+1.05
<i>c</i> -axis	13.383	13.369	-0.105

layers would shrink 0.8%. The behavior of the crystal-support composite therefore depends strongly on the orientation.

The thermal expansion coefficient (TEC) of silicon (α) amounts to $2.6 \cdot 10^{-6}/^{\circ}\text{C}$. The change of the substrate surface from 25°C to the calcination temperature applied (400°C) can be derived from:

$$L_t = L_0 * (1 + \alpha t) \quad (2)$$

where L_0 and L_t represent the length of Si at 25°C and a temperature T , respectively.

From Equation (2), an increase of 0.1% of the substrate can be calculated over this temperature interval. However, the expansion of silicon is reversible. If the chemical bonding of the crystals to the silicon or silicon nitride surface takes place at a temperature of 400°C, the crystal layer will experience an extra compressive stress due to the 0.1% decrease of the substrate surface when cooling down to 25°C. The actual stress imposed on the crystal layer therefore depends on (1) the orientation of the crystals, (2) the temperature when chemical bonding to the surface takes place versus the state of the (preceding) removal of the organic template, and (3) the thermal behavior of the support.

From temperature-programmed XRD analysis of silicalite-1/TPA it could be derived that the framework expands in the temperature interval 25–300°C (TEC $\sim 8.5 \times 10^{-6}/^{\circ}\text{C}$). This expansion is approximately three times higher than the expansion of silicon. It is assumed that in the heating up transition of the calcination procedure the zeolite approximately follows the behavior of the support, whereas no stress occurs because of the lack of chemical bonding between crystals and support. Then, the actual stress occurring in the crystal layer depends on the removal of the template only and the temperature when chemical bonding takes place.

The XRD spectrum of the obtained (*a*, *b*)-oriented layer (Figure 6) reveals (h00) and (0k0) reflections only. Therefore, the layer consists of both *a*- and *b*-oriented crystals, respectively. If the lengths of the *a*- and *b*-axes of the crystals are equal (aspect ratio 1) and the intensities of both diffracting (h00) and (0k0) planes in silicalite-1 are presumed to be equal, an estimate can be made of the ratio of both orientations by determination of the intensities (surface area) of the observed reflections. When averaging the intensities of the 400/040, 600/060, 800/080, and 1000/0100 reflections, a ratio of *a*- and *b*-oriented crystals of 2.65 is found. Correction for the observed intensities found in a powder diffraction measurement²² results in a ratio of 2.98. Apparently, some 75% of the crystals show an *a*-oriented growth, and 25% a *b*-oriented growth. Repeated syntheses on both silicon and silicon nitride give highly reproducible results, meaning that no differences are observed in the ratio of *a*- and *b*-oriented crystals.

Due to the removal of the organic template at 400°C, such a crystal layer expands 0.55%. As a result, the crystal layer would experience a severe compressive stress when chemical bonding to the silicon has taken place before the actual calcination of TPA. From Figure

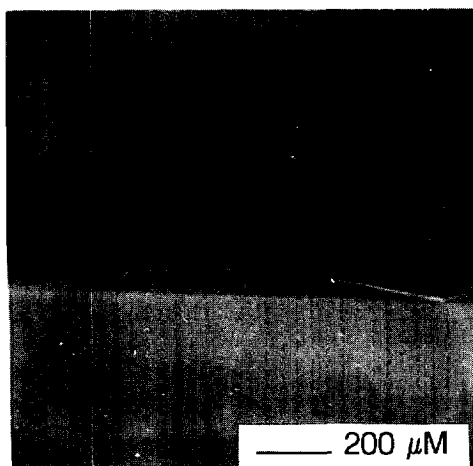


Figure 7 Cross-sectional view of an (a,b) -oriented nonsupported layer in a silicon wafer after stepwise calcination to 400°C.

7, it can be observed that curving of the crystal layer occurs when the nitride is removed by etching before the calcination. Now the layer is unsupported and can reveal its nature upon calcination. Apparently, the layer tends to release pressure. This would be in agreement with the observed crystal orientation, causing the layer to expand. In *Figure 7*, it is clearly shown that the severe pressure imposed on the layer results in crack formation, preferentially along the interface of crystals and silicon rather than through the crystal layer, although the latter occurs too.

On porous supports like stainless steel or ceramics, crystals show a random orientation. Here, a , b , and c -axes of the crystals point out to any direction, including out of the crystal layer. When the orientation is purely random, the overall stress is presumed to be low.

Although a b -oriented layer is presumed to shrink due to the removal of TPA, no cracks are observed in a (0.5- μm thick) monolayer, synthesized on silicon wa-

fers.¹⁸ It is therefore presumed that the structural changes upon calcination might be overruled by the chemical bonding of the zeolite to the support when the zeolite layer is thin. Upon an increase in the layer thickness (for the $[a,b]$ -oriented layer, 7 μm) the behavior of the zeolite will be more pronounced, resulting in stress, especially without support here. The presumed shrinkage of a thin and nonsupported b -oriented layer could not be investigated due to the extreme fragility of such a system.

Calcination versus crack formation

Two types of calcination procedures were used on (a, b) -oriented layers, both performed in air: (1) 4 h at 400°C with a ramping of 0.5°C/min (one step); and (2) a sequential increase in temperature with steps of 50°C. After each step (ramping 0.5°C/min and 4 h at a constant temperature), the composite was cooled down to 25°C and again heated to a temperature, increased with 50°C steps. Both procedures are applied on silicon wafers containing silicon nitride windows that have been removed by etching. The window size was varied to investigate the geometry of crack formation: 4 \times 4 mm² (4 windows per 1-cm² wafer), 1 \times 1 mm² (4 windows per 1-cm² wafer), and 0.5 \times 0.5 mm² (49 windows per 1-cm² wafer). The 4 \times 4 mm² windows seemed to be fragile and could easily be damaged by shocks. They are further disregarded in this study.

When procedure (1) is used, cracks are formed in the corners of the window (*Figure 8*), independent of the size of the window. The compressive stress imposed on the layer results in cracks in the corners rather than in the center of the window. This is not surprising because the center part of the window can release pressure by moving away from the silicon substrate, whereas this is impossible in the corners. The cracks, however, are observed in the crystal layer, whereas the interface of crystals and substrate remains intact. Apparently, the

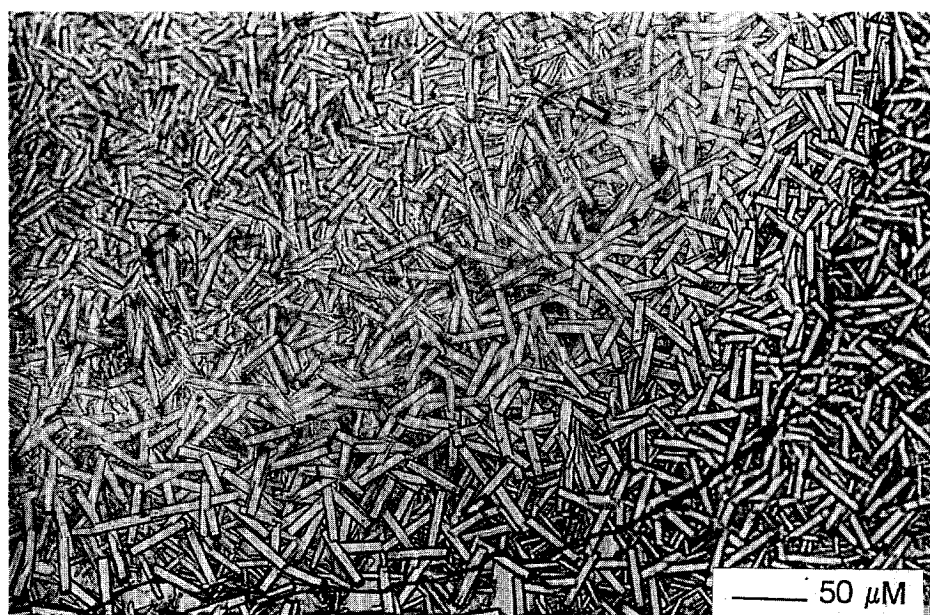


Figure 8 Crack formation of a nonsupported (a,b) -oriented crystal layer after direct calcination at 400°C (0.5°C/min, 4 h).

bonding between silicalite-1 crystals and silicon is of sufficient strength to resist the stress.

When the stepwise calcination procedure (2) is used, crack formation in the corners of the $1 \times 1\text{-mm}^2$ windows does not appear, but cracks do appear in the layer curves (Figure 7) and finally along the interface. The smaller $0.5 \times 0.5\text{-mm}^2$ windows do, however, form cracks in the corners. Although the expansion of the layer (%) is independent of the size of the layer, the occurring stress that is imposed on the corners will be larger because a small crystal layer can less easily bend and release its stress. Moreover, it is expected that, due to a slight deformation of the window corners by the expansion of the silicon substrate (0.1%), extra stress occurs in the corners. As a result, the total stress imposed on the layer is then too large to prevent cracking.

From light microscopy it could be derived that the first visible stress (curving of the crystal layer) in the stepwise calcination of the $1 \times 1\text{-mm}^2$ windows occurs around 300°C , whereas a calcination directly to 300°C ($0.5^\circ\text{C}/\text{min}$) leads to crack formation. The layer remains intact in a direct calcination to 250°C . This observed temperature behavior is in agreement with the removal of TPA from the framework structure. Although no quantitative analysis can be made with FT i.r. spectroscopy, the spectrum remains the same, revealing that up to a temperature of 300°C , even after 48 h, no loss of template occurs. After a calcination of 48 h at 350°C , hardly any C-H vibrations can be observed in the spectrum, revealing the complete removal of TPA.

Damage to the layer, however, remains the same for both calcinations at 350°C and 400°C . This is understandable because the stress is imposed on the layer due to the removal of the template rather than due to the slight extra thermal expansion of the silicon substrate over the interval of 50°C . The amount of stress can probably only be changed when the template can be removed from the framework before chemical bonding to the surface of the substrate. The latter apparently starts below 350°C .

To remove the template at low temperatures before possible chemical bonding of the crystals on the substrate, calcination was performed for 12 h at 600 W and 1.5 mbar in an oxygen plasma. From FT i.r. spectroscopy it could, however, be derived that hardly any template is removed by the plasma. The reason might be found in a negatively charged crystal surface due to electrons from the plasma, lowering the possible penetration depth of oxygen ions and radicals. This is in agreement with the observed removal of TPA in silicalite-1 by means of an oxygen plasma.^{23,24} In this study it was shown that TPA can only be removed at 100°C from the pore system of silicalite-1 up to a depth of 2.5 μm . The thickness of the (*a*, *b*-oriented layer exceeds this value.

In a direct calcination (400°C) of the composite without removal of the nitride support, cracks are still observed through the crystals (Figure 9). In this case, the zeolite layer forms bonds with the support during the calcination and cannot release the stress by moving away (bending). Although the orientation (*c*-direction) of the crystals is assumed to be random over a large

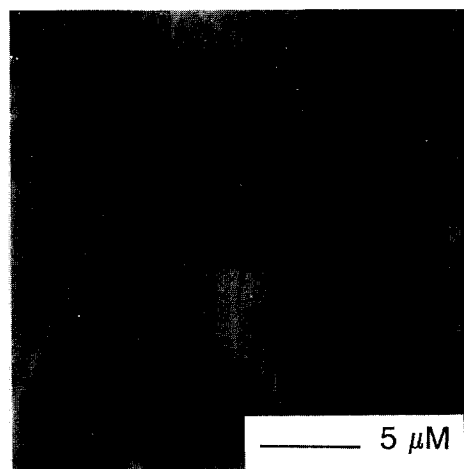


Figure 9 SEM image of a silicon supported (*a,b*)-oriented zeolite layer after calcination at 400°C .

area, local orientation is not. As a result, local spots of stress may occur. As can be seen from the SEM image (Figure 9), cracks are observed in the crystal layer, sometimes breaking crystals parallel to their *c*-plane. Although crack formation can take place in large silicalite-1 single crystals, such cracks run through the crystal parallel to the *a*- or *b*-plane. The observation of cracks parallel to the *c*-plane of the crystal suggests severe stress within the layer.

The possible reduction of stress by oxide layers in between the zeolite layer and the substrate was investigated by precalcination of the substrates at 950°C for 45 min. This procedure results in an oxide layer of 30 nm on the interface of zeolite and silicon (111) and a layer of 15 nm on the interface of zeolite and silicon (100).

The behavior of the zeolite layer in both calcination procedures, however, remains unchanged. The stress, occurring in the zeolite layer, is too large to be absorbed by such layers.

EVALUATION

From the observed behavior of the zeolite-substrate composite during calcination can be derived that the orientation of the crystals and the removal of the template determine the possibility of crack formation. When dealing with zeolite-based membranes, a careful choice should be made in the supports that can be applied. The roughness of the support can play a major role in the orientation of the crystals and in the stress imposed on the composite resulting from the orientation. Defects in random-oriented crystal layers might be caused by two principles: (1) a small gel layer between crystals that forms pores upon calcination due to the removal of water and the shrinkage of the gel occurring due to surface tension; and (2) local stress evolving from the removal of the organic template and/or structural changes of the zeolite applied.

The formation of mesopores between crystals can determine the overall performance of the membrane, because a part of the transport will take place through nonzeolitical pores. The performance of silicon-zeolite

devices for sensing purposes will, however, be influenced less by a small amount of intercrystalline pores because the adsorption of gases in the zeolite crystals, forming a nearly complete coverage, will make up most of the increase in mass of the zeolite-support composite.

We have not been able to create an oriented monolayer on a porous support so far that could resist stress imposed upon the layer. Therefore, the existence of intercrystalline pores in such layers (not due to crack formation) is unknown. When a thermostable device can be prepared, permeation experiments may reveal such pores.

CONCLUSIONS

Oriented thin layers of the zeolite MFI can be produced without support by using selective etching procedures. The method can make the interface of crystal layer and support visible. Investigations of this interface show a dense grain-like structure.

Due to the removal of the organic template (TPA) and due to subsequent expansion and contraction of the crystals, cracks are formed within the layer.

MFI layers on porous supports (RVS, alumina) show random orientation of the crystals. One might wonder whether this is necessary for a membrane to resist stresses or not. It may even turn out that oriented membranes are too fragile, but further research is needed in this respect.

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