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Pure Silica Zeolite Beta Membrane: A Potential Low Dielectric Constant Material For Microprocessor Application

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Abstract: The semiconductor industry needs low dielectric constant (low k-value) materials for more advance microprocessor and chips by reducing the size of the device features. In fabricating these contents, a new material with lower k-value than conventional silica (k = 3.9-4.2) is needed in order to improve the circuit performance. The choice of the inorganic zeolite membrane is an attractive option for low k material and suitable for microprocessor applications. A pure silica zeolite beta membrane was synthesized and coated on non-porous stainless steel support using insitu crystallization in the presence of tetraethylammonium hydroxide, TEA (OH), as structure directing agent, fumed silica, HF and deionized water at pH value of 9. The crystallization was carried out for the duration of 14 days under hydrothermal conditions at 130°C. The membrane was characterized by thermogravimetric analysis (TGA), nitrogen adsorption and Scanning Electron Microscope (SEM). SEM results show a highly crystalline; with a truncated square bipyramidal morphology of pure silica zeolite beta membrane strongly adhered on the non-porous stainless steel support. In the present work, the k-value of the membrane was measured as 2.64 which make it suitable for the microprocessor applications.

Key words: Zeolite beta membrane, low dielectric constant material, semiconductor technology

INTRODUCTION

In the microprocessor manufacturing industry, a material with a low dielectric constants (k-value lower than 3) and optimally lower than 2.2 is needed for the design of very small devices, e.g., 100 nm, features. There has been constant research effort in the search for the materials with low k-value, which might be suitable for advanced microprocessors. The recent International Semiconductor Technology plan envisages that a material with a dielectric constant, k-value of 1.6 will be needed by 2010. These materials can reduce the RC delay (R for resistance and C for Capacitance), crosstalk noise and power dissipation. The main properties for the microprocessor are: low dielectric constant, thermally stable at temperature >450°C, low thermal expansion, high thermal conductivity, low water absorption, high mechanical strength, good adhesion to a variety of surfaces and substrate, good chemical stability, good electrical properties and low reactivity with conductor metals at elevated temperatures (Treichel *et al.*, 1998; Maier *et al.*, 2001; Yan *et al.*, 2003).

Polymers are potentially attractive materials for this application and a large variety of polymers have been proposed for use as materials with low dielectric constants for the applications in microelectronics. For example poly(tetrafluoroethylene) exhibits the lowest dielectric constant with k<2. However, the low thermal conductivity of the polyamide and moisture uptake were identified to be the key problems for further developments. Dielectric constants below 2.5 will probably not be possible for polymers with thermal stabilities of 450°C or even 400°C (Maier *et al.*, 2001). In addition there is concern that these materials may react with metals used as conductors at elevated temperatures (Yan *et al.*, 2003).

Since the beginning of the semiconductor industry, dense (nonporous) pure silica has been the material of choice for dielectrics and the introduction of porosity into silica is an important and promising approach to reduce the k-value. Sol-gel silica, surfactant-templated mesoporous silica and pure silica zeolite are three major classes of porous silica. Sol-gel silica and surfactant-templated mesoporous silica have extremely low k-value (k = 1.1-1.3), however, both of these materials can not be used as a low dielectric constant materials because of its characteristics like low mechanical strength, low thermal conductivity and hydrophilicity

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(Mitra *et al*., 2004; Hrubesh *et al*., 1993; Hrubesh *et al*., 1998; Seraji *et al*., 2000; Zhao *et al*., 1998; Baskaran *et al*., 2000; Davis *et al*., 2002; Yu *et al*., 2002).

Zeolites are inorganic microporous crystalline material (Breck, 1974; Baerlocher *et al*., 2001) with uniform micropore structure, high mechanical strength, high heat conductivity, good thermal stability and resistance to relatively extreme chemical environment (Shan *et al*., 2004). Pure silica zeolite beta is a silica zeolite having only silicon and virtually no aluminium. It possesses a three-dimensional pore structure, consisting of three sets of mutually perpendicular 12-membered ring channels. Pure silica zeolite beta is hydrophobic which could help to reduce the water adsorption (Mitra *et al*., 2004). Although there are more than 130 zeolites and zeolite type materials available currently, only 13 of them have been synthesized in pure silica form (Baerlocher *et al*., 2001) and the reports on the synthesis of zeolite beta membrane are very limited in the literature.

The present work is focused on the synthesis and characterization of Pure-Silica-Zeolite-Beta (BEA) membrane coated on the non- porous stainless steel support, a potential as low dielectric constant material for microprocessor applications.

APPROACH AND METHODS

Support cleaning: A 25 mm diameter non-porous stainless steel disc support was first cleaned with a detergent and soaked for 30 min in 1 M NaOH solution followed by soaking in 1 M HNO_3 solution. The support was washed thoroughly with deionized water in the ultrasonic bath for 10 min and dry in the oven at 100°C overnight.

Synthesis gel preparation: The fumed silica (99.9 wt%, Fluka) is added slowly to an aqueous solution of tetraethylammonium hydroxide TEA(OH) (35wt%) in a polypropylene bottle under stirring at room temperature, 25°C. The stirring was continued for a period of nearly 3 h until a semitransparent mixture was obtained. Aqueous HF (40wt%) was added dropwise under vigorous stirring. A homogenous, high viscous solid like gel was formed. The final gel molar composition obtained was:

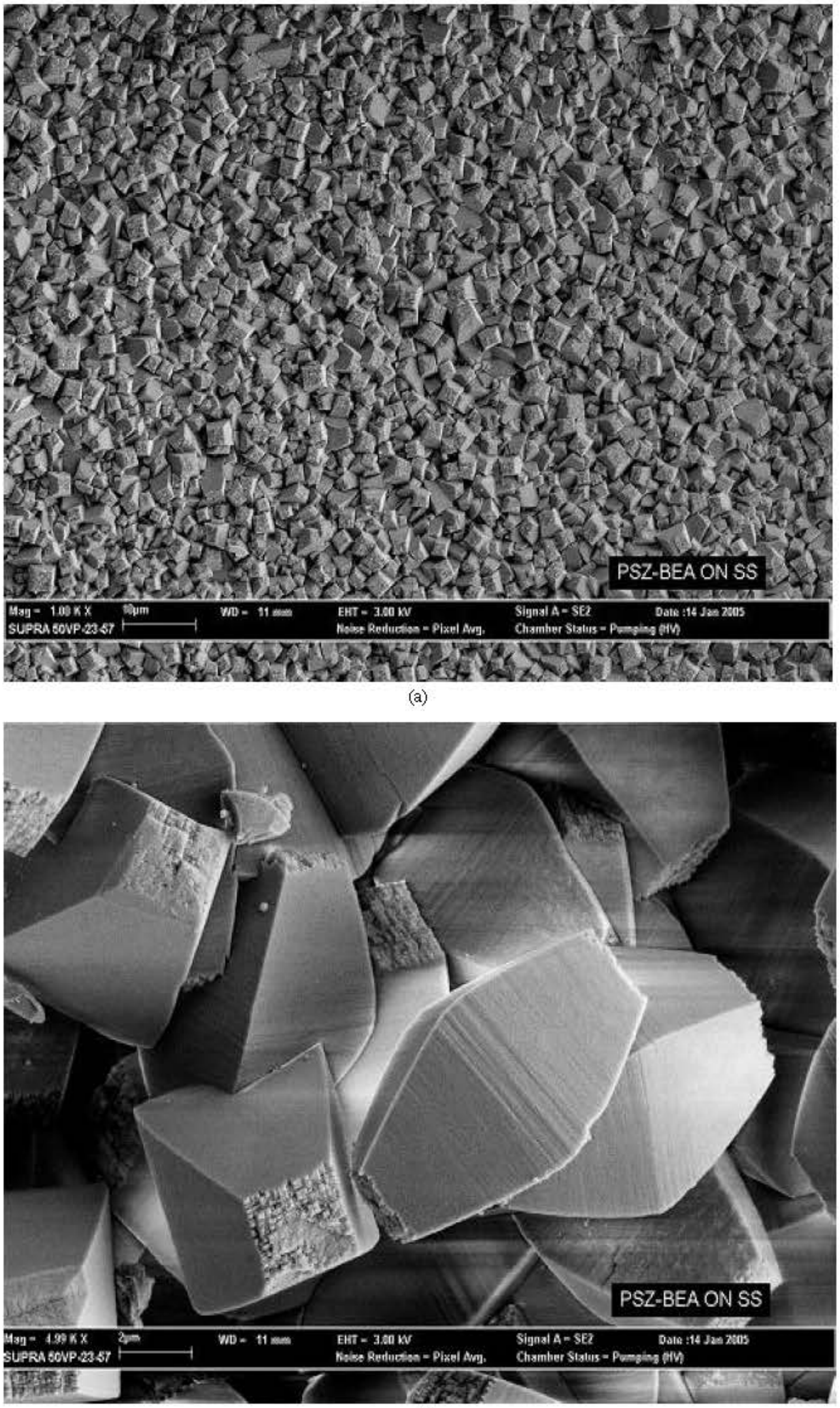
$$SiO_2\text{: 0.6 TEAOH: 0.6 HF: 10.1 }H_2O.$$

***In situ* crystallization:** The high viscous solid like gel was transferred to a Teflon-lined Parr reactor (Model 4842) for crystallization under hydrothermal conditions. The crystallization temperature was kept constant at 130°C and time for crystallization was nearly 14 days. A non-stainless steel support was placed vertically inside the reactor and completely covered by the gel during crystallization. The synthesized membrane and solid product were washed thoroughly with deionized water in the ultrasonic bath. The solid product was then separated from the remaining liquid phase by filtration. After that, the sample was dried for 8 h at 100°C in the oven before calcined in static air at 500°C for 10 h with ramping rate 5°C min^{-1} to remove the TEAOH template from the zeolite framework.

Characterization: The samples were characterized using X-ray diffraction (XRD), (SEM) scanning electron microscope, thermogravimetric analysis (TGA) and nitrogen gas adsorption-desorption isotherm. XRD analysis was done using Siemen diffractometer (Model 1820) with graphite monochromated CuKα (λ = 1.5406Å) source operated at 40 kV and 40 mA. The SEM of the membrane was studied by using SUPRA 50VP-23-57 scanning electron microscope (SEM), operated at 3.00 kV. Nitrogen gas adsorption-desorption measurement was performed at 77 K on a Autosorb I (Quantachrome Automated Gas Sorption System). The samples were first degassed for 3 h under vacuum at 300°C prior to the analysis. TGA of as-synthesized and calcined pure silica zeolite was conducted at 700°C by using Perkin Elmer TGA 7, at a heating of 10°C min^{-1} under a nitrogen flow rate of 30 mL min^{-1}. For dielectric measurement, aluminium dots with a dimension 3×3 mm were deposited on the film by thermal evaporation with pressure 3.2×10^{-5} bar and low temperature (4.5 A, LT) through a contact mask, using vacuum coating unit (Edwards Auto 306). The capacitance of metal-membrane-metal structure was measured at a frequency of 100 kHz on capacitance voltage system with standard Signaton microprobe station and micropositioner. The capacitance of the membrane was measured in a voltage range of -4V to 4V. The k-value of the membrane was calculated using Eq. 1:

$$\varepsilon_r = \frac{Ct}{\varepsilon_o A} \qquad (1)$$

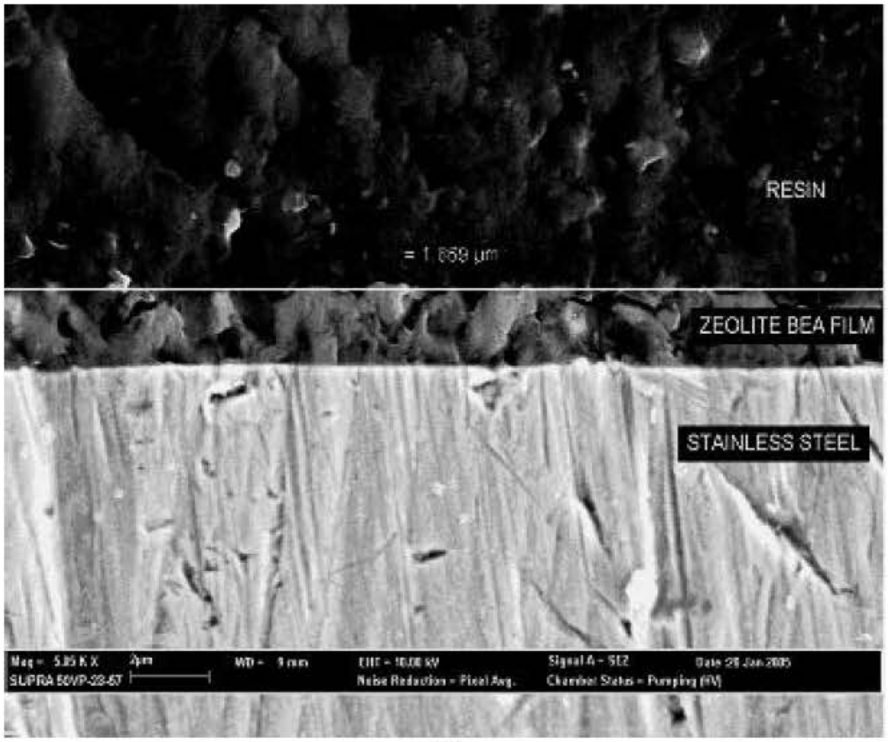
where, ε_r is dielectric constant, k-value of the membrane, C is capacitance of the membrane, Faraday (F), ε_0 is constant, 8.85×10^{-12} Faraday/m, A is cross sectional area aluminium dot, m^2 and t is thickness of the membrane, m. To measure the thickness of the membrane by SEM, the sample was first moulded using epoxy. After that, the sample was polished with sand papers using grit number of 180, 240, 320, 600 and 2000, respectively. This was followed by fine polishing with diamond suspension from 45, 30, 15 to 9 micron using a grinder polisher.



(a)

(b)

Fig. 1: SEM micrographs of pure slica zolite bta membrane coated on non porous stainless steel support after calcinations: (a, b) Top view (without polishing)



(c)

Fig. 1c: Cross sectional view of SEM micrograph for Pure Silica Zeolite Beta membrane coated on non porous stainless steel support after calcinations (after polishing)

RESULTS AND DISCUSSION

SEM micrographs of the pure silica zeolite beta membrane are shown in Fig. 1a-c, respectively. SEM micrographs reveal that a well intergrown, continuous and polycrystalline membrane was grown on the non-porous steel support. Obvious defects such as intercrystal gaps and cracks were not presented in the membrane. Highly crystalline, truncated square bipyramidal morphology of pure silica zeolite beta membrane coated on stainless steel is shown in Fig. 1b. The crystal size is approximately 2.5 µm, fully covered the surface of the support. The membrane thickness of around 2 µm is shown in Fig. 1c. The TGA curve for as-synthesized pure sample is shown in Fig. 2a and the TGA curve for calcined sample is shown in Fig. 2b. TGA provided valuable information on the hydrophilicity/hydrophobicity of the sample and thermal decomposition of the Structure Directing Agent (SDA). The as-synthesized sample (powder form) was dried at 100°C overnight and was used for the study of thermal decomposition of SDA while the calcined sample.

Figure 2a shows that, the weight % loss for as-synthesized pure silica zeolite beta sample was 22.7% due to the loss of the SDA content of the sample. The weight % loss was constant when the temperature reached 500°C. As shown in Figure 2(b),the weight % loss of the calcined sample is 1.15% which exhibited very low moisture content. The weight % loss was constant for temperature above 200°C and the moisture could be readily removed at a temperature 200°C. This shows that the pure-silica-zeolite beta is a hydrophobic membrane with a high thermal strength. The moisture content has significant influence on the k value of the membrane, thus the lower moisture content of the sample can result in a lower k value.

The BET surface area and average pore diameter for the samples were measured by nitrogen adsorption-desorption isotherm and presented in Table 1. Pure silica zeolite beta was a microporous solid exhibiting a high proportion of microporosity (90%). The t-method micro pore volume for the sample was 0.21 $cm^3\ g^{-1}$, closed to value 0.23 $cm^3\ g^{-1}$ as reported in literature. The total pore volume of the sample obtained in this experiment was 0.29 $cm^3\ g^{-1}$, which was also closed to the value 0.26 $cm^3\ g^{-1}$ reported in the literature for pure silica zeolite beta (David *et al*., 2001).

The Nitrogen adsorption-desorption isotherm for the samples was obtained and presented in Fig. 3. A smooth

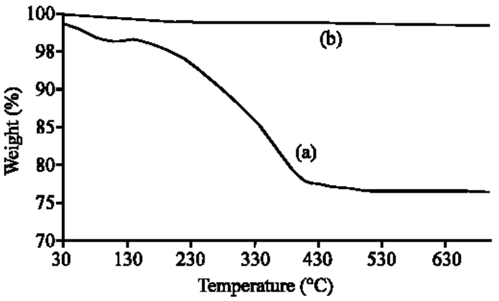


Fig. 2: Thermogravimetric Analysis (TGA) Curves for (a) As-Synthesized; (b) Calcined, Pure Silica Zeolite Beta

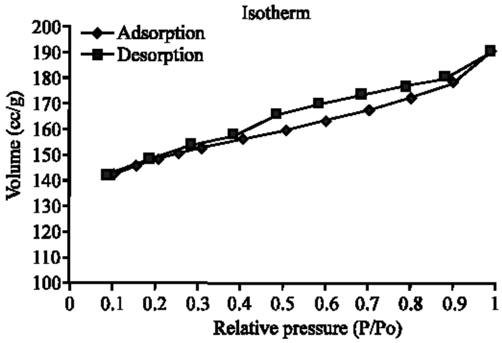


Fig. 3: Nitrogen adsorption-desorption isotherms for the samples

Table 1: Surface area and average pore size for the calcined sample

Data	Pure Silica Zeolite Beta obtained in the present work
BET Surface Area ($m^2\ g^{-1}$)	435
Total Pore Volume ($cm^3\ g^{-1}$)	0.29
Average pore diameter (Å)	6.7

curve without any sharp increase was obtained and the volume adsorbed was varied from 142 to 190 $cm^3\ g^{-1}$ for P/Po reading from 0.1 to 1.0. These results were the same with the isotherm curves reported in the literature for pure silica zeolite beta (David *et al*., 2001). Thus, the pure silica zeolite beta synthesized in the present study was highly crystalline. The high crystallinity of the sample is also confirmed from the XRD pattern.

The thickness of the membrane is required for the calculation of k-value and the thickness measurement is shown in Fig. 1c, pure silica zeolite beta membrane has outstanding mechanical strength and adhesion with the support. This is because the membrane is still strongly adhered to the substrate and did not cause cracking even after polishing.

The capacitance of the membrane was measured and used to calculate the dielectric constant, k-value of the membrane by applying equation (1). The capacitance

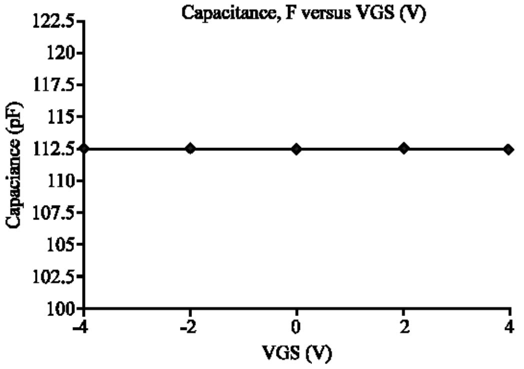


Fig. 4: Capacitance of calcined pure silica zeolite beta membrane on non-porous stainless steel support

value, as a function of voltage was constant in the range of -4 V to 4 V as 112.5×10^{-12} F, as shown in Fig. 4. The dielectric constant, k-value obtained in the present work was 2.64, which was lower than k-value as 3. Therefore, pure silica zeolite membrane is a promising low-k material and suitable for microprocessor application.

CONCLUSIONS

Pure silica zeolite beta membrane coated on the non-porous stainless steel support was synthesized under hydrothermal crystallization at 130°C within a period of 14 days. The SEM results revealed that a well intergrown, continuous and polycrystalline membrane was coated on the support with the absence of the structural defects like intercrystal gaps and cracks. The thermogravimetric analysis results show that pure silica zeolite beta is highly hydrophobic membrane with very low moisture content. The membrane has outstanding mechanical strength and strongly adhered to the support even after polishing. The dielectric constant k-value for the membrane was 2.64 which makes it suitable for microprocessor applications.

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