

Fabrication of sub-100nm thick Nanoporous silica thin films

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Abstract

Low refractive index thin films have generated substantial interest for use in optical devices particularly in Light Emitting Diodes (LEDs). Applications include photonic cavities, mirrors, etc. Such films are required to have precise control over both thickness and refractive index. Here, we investigate fabrication of Omni Directional Reflectors (ODRs) using nanoporous silica films. Sub-100 nm thick nanoporous silica films of low refractive index (high porosity) are fabricated by spin coating on III-V compound semiconductor substrates. Thicker nanoporous silica films (~1 μm) on silicon substrates have been fabricated and characterized in past (Jain et al, 2001). We have modified the process to fabricate excellent quality sub-100nm thick nanoporous silica films, which were used in successful fabrication of more efficient ODRs. Interfacial forces between the substrate and nanoporous silica solution are believed to affect the adhesion of the film on the substrate and to play an important role in developing the final film properties like the thickness and the refractive index. In particular, the role of interfacial slip during films spinning to explain above-mentioned results is investigated in this paper. Both theoretical and experimental studies support the assertion that interfacial slip occurs due to an alteration in intermolecular forces that exist between the substrate and the film.

Introduction

Nanoporous silica is emerging strongly as novel material for low-refractive index films in optical devices. A good control in tailoring the porosity of nanoporous silica films has been achieved for its use as a dielectric material (Jain et al, 2001; Nitta et al, 1999). Hence, desired refractive index from 1.1 to 1.45 can be achieved making our low refractive index films suitable for optical devices. NPS films also find their applications in fabrication of reflectors. ODRs are double layered structures, which have alternate low and high refractive index films (Figure 1).

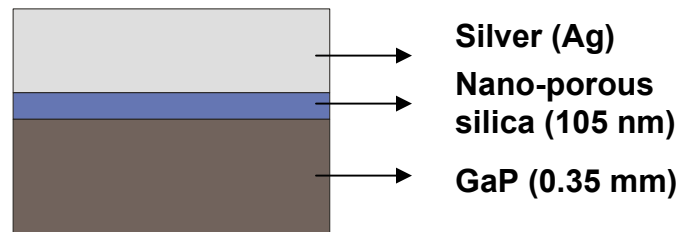


Figure 1: schematic of ODR

Our films serve as low refractive index films for this structure (Xi et al, 2004). These were fabricated by spin coating and a good control on film thickness and refractive index is required to achieve optimum efficiency in ODRs. Thickness is believed to depend not only on spin speed, viscosity and time for spin coating but also on intermolecular adhesion, which produces slip at liquid-solid interface. Our results support this theory.

Experiment

Ultra thin Nanoporous silica films were required for fabrication of above-mentioned ODRs. Our fabrication process to fabricate thicker low-dielectric constant films was modified to suit the requirements for ODRs. For optimum results thickness and refractive index were calculated as $n_{low} = 1.23$ at 632.8 nm and $h_{low} = 105$ nm.

Thin film fabrication

Thin Nano-porous silica films were prepared by TEOS based sol-gel process that is driven by acid base catalysis. HCl and NH_4OH were used acid and base catalysts. We use double solvent process involving Ethanol and Glycol to tailor porosity of the films. Glycol increases viscosity of the solution resulting in thicker films. Hence, the solution was diluted by Ethanol to reduce the viscosity. Addition of Glycol leads to higher porosities and addition of Ethanol results in fabrication of thin films required for our ODRs. Gel time (T_{gel}) for the films increased to 45 min by Ethanol dilution.

Compound semiconductors (like GaAs, GaSb, and GaP etc) do not form a native oxide layer like silicon and hence are hydrophobic in nature. Any aqueous drop results in a very high contact angle. Our spin coating solution is mostly comprised of Ethanol and thus substrate should be wetting for good adhesion. Spin coating on bare GaP lead to cracked films due to improper adhesion between liquid and solid substrate. To improve solid-liquid adhesion these substrates were treated in Oxygen plasma for 60 sec. Other plasma conditions were fixed at $P = 100$ mtorr, Power = 250 W. Native GaAs has no dangling bonds to improve adhesion with our sol, on plasma exposure the oxide layer forms dangling bonds, which increases the surface wettability for Ethanol and results in formation of cracks free Nanoporous films.

Our Sol-gel solution was Spin coated on the plasma treated GaP. Spin speed and spin time were 6000 rpm and 60 sec respectively. It was observed that after surface modification by Tri-Methyl-Chloro-Silane (TMCS), cracks appeared on the films. Highly reactive Chlorine in TMCS reacts with underlying GaAs (Park et al, 2002). Hence, surface modification was then performed using Hexamethyl disilazane (HMDS), which does not affect the adhesion of Nano-porous SiO_2 film to the substrate. A heating step to $250^\circ C$ was carried to reduce OH bonds in the porous matrix.

Resulting films were absolutely crack-free. Films were characterized using Ellipsometer and SEM. Film thickness and refractive index were found to be 105 nm and 1.24 measured at 630 nm respectively. Xi et al, 2004, are publishing results on efficiency of ODRs that were fabricated using these thin nanoporous films. A minimum thickness value of ~ 100 nm

was also successfully fabricated by above-mentioned recipe. Refractive index could be tailored to as low as 1.18, which is equivalent to 60% porosity. Maximum refractive index corresponds to 1.45, which is 0% porosity case. Roughness values on these films were found out to be around 5%. A discussion on control of thickness follows in next section. SEM pictures also show (Figure 2) that these are good quality films.



a) Cross section view

b) Top view

Figure 2: SEM picture of thin Nanoporous silica films

Adhesion and thickness control

Same procedure of spin coating when applied to Silicon substrate leads to significantly thicker Nanoporous silica films (Figure 2). Experiments and modeling was carried out to determine possible cause of thickness variation with choice of substrate.

a) Model

Role of liquid slip at the boundary is in existence since a long time now (Yanagisawa et al, 1987). We have adopted a model from Yanagisawa et al, 1987. Dilution of spin coating solution by Ethanol leads to very high T_{gel} (45 min) and our solution can be safely assumed as Newtonian fluid.

Different thermal conductivities of substrates can result in varying heat transfer from substrate to the film and result in different thickness (Birnie et al, 1995). Surfaces of silicon wafer with native oxide and a silicon wafer with a thick (~1 μ m) PECVD oxide are chemically similar. Contact angle of sol with both the surfaces was similar (~0 degrees). Thermal conductivity value for silicon is 1.412 W/cm-K whereas for silicon oxide it is 0.01 W/cm-K. For a 1.3 μ m thick PECVD oxide film effective thermal conductivity is calculated to be 0.90 W/cm-K. Spin coated films on PECVD oxide do not show difference in thickness when compared to films coated on silicon wafer (Table 1). Therefore role of thermal conductivity on final thickness can be neglected. We do not consider effect of evaporation on thickness variation in our model. Here, the purpose is to study role of interfacial forces in final

thickness of our films and added complexity due to evaporation effects will not be dealt with.

Table 1: Thermal conductivity of substrates and corresponding thickness

Substrate	Thermal conductivity	Thickness (nm)
	Effective (W/cm-K)	
Silicon	1.412	2662
Si/SiO ₂ (1.3 um)	0.9	2630
GaAs	0.55	1904
GaSb	0.32	1750

Model for our system was adopted from Yanagisawa et al, 1987. The model results in following equation for thickness evolution with time,

$$\partial h / \partial t = - 2\rho\omega^2 h^2 (h + 3\lambda) / \eta; \tag{1}$$

Where, λ is η / ϵ and ϵ is external friction coefficient, η is viscosity, ρ is density, ω is rotation speed, h is film thickness. Here, λ is the fitting parameter termed as slip coefficient; model results are fitted on experimental results to obtain λ . Equation (1) is solved with slip boundary condition at the solid liquid interface.

Model results clearly indicate that incorporation of slip at boundary reduces the final thickness and leads to agreement in results (Figure 3). External friction coefficient value where model results match experimental results was found to be 8200. Thickness reduces with increasing slip coefficient.

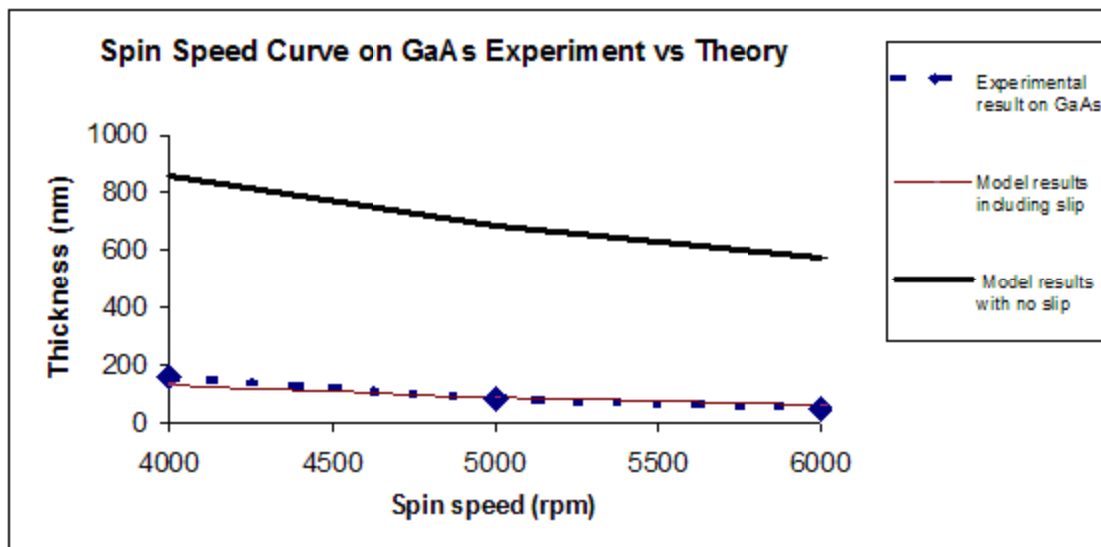


Figure 3: Comparison of numerical results for slip for GaAs with no slip values.

b) Experiments

To measure effect of adhesion on Nano-porous film thickness, a measurement should be done just after spin coating without involving further steps. Hence, thickness measurements reported in table 2 below were taken just after films were spin coated on the substrates and baked for 60 seconds.

Table 2: Thickness and contact Angle data.

	Thickness (Å) t=0	Contact angle (Degrees)	Spreading Coefficient (mJ/m ²)
Silicon	2662	~0	0
GaAs	1904	3.7	-0.051
GaSb	1750	6.4	-0.153

Contact angle indicates the degree of adhesion between liquid and solid at the interface. We have measured surface tension for the liquid using Tensiometer. Spreading coefficient values were determined using surface tension and contact angle data using $S = \gamma(1 - \cos\theta)$, where γ is the surface tension and θ is the contact angle. Spreading coefficient by definition is negative free energy associated with the process of spreading of a liquid over a solid surface. Spreading coefficient gives an estimate of liquid–solid adhesion. A direct measurement of interfacial forces is not possible therefore in our study we will use value of spreading coefficient as an indication of order of intermolecular forces. Measurement of contact angle of solution on three substrates, namely Silicon, GaAs and GaSb was done. Interferometry technique was used to measure contact angle. These results were then confirmed using goniometer. Results are reported in Table 2. Surface tension for our spin coating solution was found to be 24.6 mJ/m²

Obtained spreading coefficient values are reported in the Table 2. Decrease in spreading coefficient below 0 results in decreasing adhesion between solid and liquid. Spreading coefficient is found to decrease in Si > GaAs > GaSb order. Thus intermolecular forces decrease in the same order. We calculate slip coefficient from our model for three substrates. Slip coefficient from our model also results in the same order. Both slip coefficient and spreading coefficient are dependent on interfacial adhesion of liquid with solid and a relation between the two is shown in Figure 4.

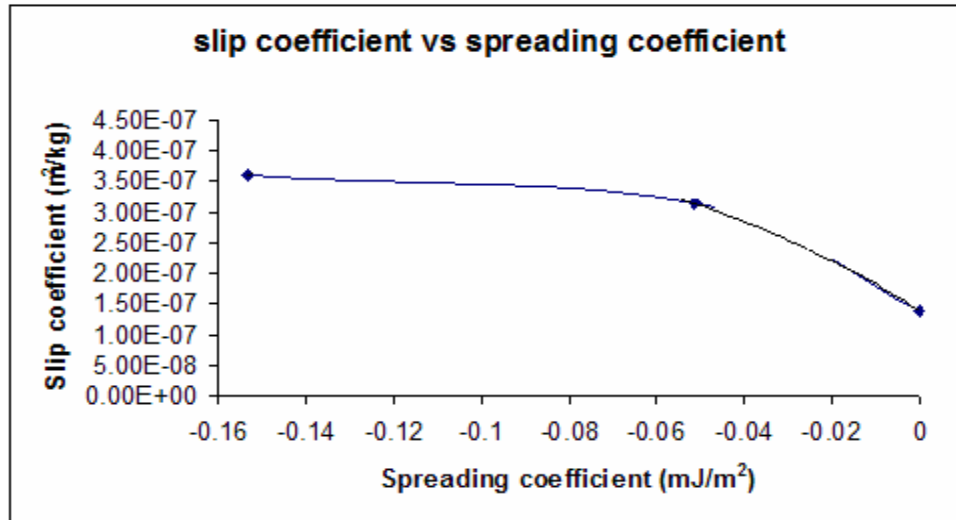


Figure 4: Spreading coefficient vs. Slip coefficient for different substrates.

Conclusion

Successful fabrication of 100 nm thick films was achieved. Integration of these films for ODRs was also carried out successfully. Result of intermolecular forces during spin coating is seen as variation in thickness of the Nano-porous silica films. Interfacial forces determine adhesion between spin coating solution and the substrate, which varies with the choice of substrate. These intermolecular forces between substrate and solution determine the final film thickness. Further work is required to quantitatively determine these forces.

It can be seen that as contact angle increases slip coefficient also increases. Thus slip increases as the contact angle increases. For sub 100 nm thin films substrate properties affect the film thickness to a great extent. A study on adhesion between film and substrate is very important for process control on these films. Results obtained so far are indicative of presence of strong intermolecular forces while spin coating.

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