

Mechanical properties of low k SiO₂ thin films templated by PVA

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Abstract

Porous silica films as low- k interlayer dielectric were prepared via a sol–gel method. Tetraethoxysilane (TEOS) was used as raw material and polyvinyl alcohol (PVA) with different degrees of polymerization as molecular template. The precursor was deposited on to coated platinum silicon substrates and annealed at different temperatures. The films were modified with trimethylchlorosilane (TMCS) for hydrophobicity, which can make the porous films present a stable characteristic of low k . The effects of annealing temperature and polymerization degree of PVA on mechanical properties were investigated. Significant improvement occurred for the sample annealed at 700 °C, the hardness and the Young modulus of the silica film templated by HPVA are 0.91 GPa and 15.37 GPa, respectively. These values are comparable with that of MOCVD low k silica sample.

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1. Introduction

With the miniaturization of the integrated circuits (IC), interconnect resistance–capacitance (RC) delay, crosstalk and power consumption have been the bottleneck for the development of the industry [1]. Low k dielectrics with dielectric constant of less than 2.6 are being researched for low capacitance. Since the introduction of air ($k=1$) can greatly reduce the dielectric constant of materials, porous silica films have attracted attention because of its integrated compatibility with silicon wafers and related materials used in existing IC technology [2]. However, it can be estimated that the mechanical properties of porous materials are weaker than bulk because of the voids. And that the porous silica films prepared by the wet chemical methods do not show low k character, because there are many –OH groups on the surface of the films which have 80 of dielectric constants. So they have to undergo hydrophobic treatment to wipe off the –OH groups. It is very important that the pores in porous silica films do not collapse after modification process and thus, able to endure the stress and not be fractured or stripped during the integrated manufacturing process. That is, the

mechanical properties of porous silica films are very important for practical use.

Polyvinyl alcohol (PVA) is a nonionic polymer surfactant; the hydroxyls in the molecular chain enable it to have good water-solubility and film-forming ability. Our research has demonstrated that PVA itself can form worm-like porous microstructure with about 50% porosity at proper concentration and possess template effect guiding nucleation and growth of porous silica films. In other words, the porous silica films have the same microstructure with the PVA template after excluding PVA organic parts [3]. In our previous works [3,4], we focused on the preparation and hydrophobic treatment of porous silica films, and also discussed the effect of the treatment processing on microstructure according to AFM patterns. In this paper, we will report the mechanical properties of the silica porous films after hydrophobic treatment.

2. Experiments

2.1. Synthesis of PVA/SiO₂ sol

Tetraethoxysilane (TEOS) was used as raw material to produce SiO₂ molecules by hydrolyzing. Ammonia was used

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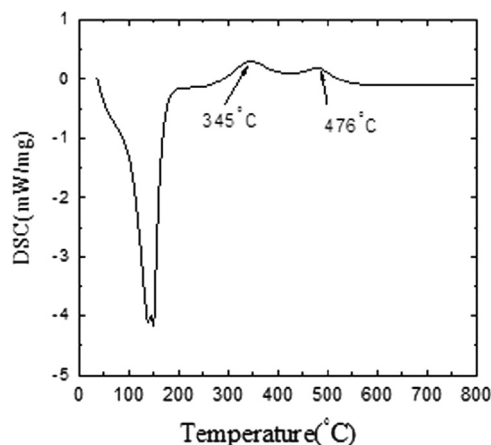


Fig. 1. DSC/DTA curve of PVA/SiO₂ sol.

as catalyst to promote the condensation polymerization of the SiO₂ molecules. PVA with different degrees of polymerization (1750 and 500) was used as the templates to prepare porous silica films. PVA of 1750 and 500 polymerization degrees is abbreviated as HPVA and LPVA, respectively.

First, SiO₂ sol was prepared by mixing H₂O, TEOS and ammonia. The volume ratio of H₂O:TEOS:NH₄OH is 100:15:4, and the pH value of the solution is 10. The TEOS mixture solution was stirred for more than 24 h to make TEOS hydrolyze completely. Second, both template solutions contained 3% HPVA and 8% LPVA in weight ratio were prepared separately by water bath heating for more than 4 h for the dissolution of PVA. Third, SiO₂ sol and HPVA solution or LPVA solution were mixed together, the mass ratio of PVA to SiO₂ was 1.2:1. The mixture was heated at 75 °C for several hours in order to promote the reaction of SiO₂ with PVA and evaporate the water for concentration of the PVA/SiO₂ precursor sol. The details of preparation can be found in the previous works [3,4].

2.2. Preparation of porous SiO₂ films

First of all, differential thermal analysis (DTA) of the PVA/SiO₂ sol using a Q1000DSC thermal analysis system was used to establish calcination regulations. It can be seen in Fig. 1 that there are three significant peaks. The endothermic peak of 70–160 °C represented the evaporation of water. The exothermic peaks of 345 °C and 476 °C should be the thermal decomposition of organic groups.

The PVA/SiO₂ sol was deposited on silicon substrates coated platinum at the speed of 3000 r/min for 40 s and prebaked for 2 min at 200 °C, then the PVA/SiO₂ films were pyrolyzed at 400 °C for 3 min and annealed at different temperatures (450 °C, 500 °C, 600 °C and 700 °C) for 5 min by the rapid thermal process. The films were made several layers for thicker thickness.

2.3. Surface hydrophobic treatment of porous SiO₂ films

It was proven that some organic solvents with hydrophobic groups such as methyltrimethoxysilane (MTMS) and

trimethylchlorosilane (TMCS) can substitute the –OH groups and reduce water absorption [5,6]. Singh et al. used multiple organosilanes to modify the porous silica film and received good result [7].

The surface hydrophobic treatment of porous SiO₂ films was done according to the optimal conditions in our previous study [4]. Trimethylchlorosilane (TMCS) and hexane were used as the modification reagents. The concentration of TMCS and modification time were 60% and 2 h. Before the experiment, the films were kept at 150 °C in an electric oven for an hour to exclude physisorption water. Then the dried films were immersed into the 60% TMCS solution for 2 h, and the treated films were put into pure hexane for 30 min to get rid of the byproduct HCl molecules which would decrease the effect of the modification. Finally, the samples were heated at 150 °C for an hour to evaporate the residual solvent in the films.

2.4. Property measurement of low *k* SiO₂ films

Thickness of the porous SiO₂ films templated by HPVA is 2.9 μm and which templated by LPVA is 3.6 μm (measured by Dektak-6M profiler). Round Au top electrodes with diameter of 1 mm were deposited by DC sputtering. Capacitance was mea-

Table 1
Properties of low *k* SiO₂ films prepared by the PVA and MOCVD method.

Methods	Sample no.	Annealing temp. (°C)	<i>k</i>	Roughness (nm)	Hardness (G Pa)	Young modulus (G Pa)
Templated by HPVA	1	450	2.60	1.452	0.3019	5.157
	2	500	2.66	1.655	0.3295	6.2525
	3	600	2.82	1.587	0.6643	12.4859
	4	700	2.65	1.501	0.9096	15.3741
Templated by LPVA	5	450	2.45	1.759	0.3549	5.1234
	6	500	2.48	1.734	0.4961	5.7909
	7	600	2.42	1.269	0.5410	6.5516
	8	700	2.60	1.354	0.5902	6.7507
MOCVD	9	–	2.40	0.293	0.6524	6.0598
	10	–	2.50	0.382	0.8799	10.9314

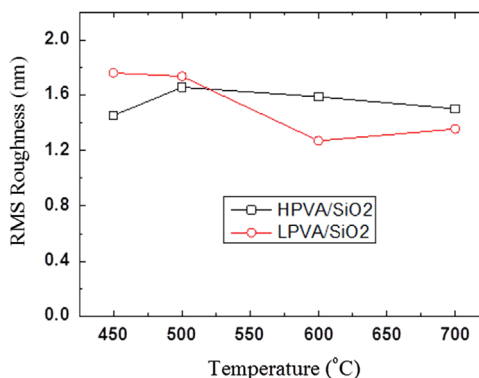


Fig. 2. Roughness of porous SiO₂ films by the sol–gel method.

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