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Microstructure developments of F-doped SiO_2 thin films prepared by liquid phase deposition

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ABSTRACT

This study presents a systematic investigation of the microstructure dependence of liquid phase deposition (LPD) of SiO_2 films on solution parameters and deposition temperature. The corresponding deposition rate and film roughness were also evaluated under various deposition conditions. Smooth and sufficiently dense SiO_2 films, which are the prerequisite for reliable low-k dielectric applications, were deposited on both silicon and fluorine-doped tin oxide coated glass substrates from supersaturated hydrofluorosilicic acid (H_2SiF_6) solution with the addition of boric acid (H_3BO_3). It is shown that H_2SiF_6 acid controls the surface morphology and grain structure through surface reaction while H_3BO_3 acid prompts bulk precipitation in solution. For the 208-nm thick SiO_2 film, the breakdown field exceeded 1.9 MV/cm and the leakage current density was on the order of 10^{-9} A/cm^2 at 4 V, indicating excellent insulating properties of LPD SiO_2 films. The strong presence of Si–O–Si and some Si–F with little Si–OH bond as shown in FT-IR spectra indicate that the LPD SiO_2 films have mostly a silica network with some fluorine (F) content. F-doping was self-incorporated into the silica films from the H_2SiF_6 solution during deposition process.

1. Introduction

As the ultra-large-scale integrated circuit structure becomes more complicated and the device geometry of integrated circuits becomes smaller, the main challenge of the interlayer technique is to reduce the signal delay time or time constant which is expressed as the product of wire resistance and capacitance between wires and substrate. An interlevel dielectric with a low dielectric constant (low-k) is essential to reduce the parasitic capacitance [1–5]. Several approaches have been investigated to lower the dielectric constant of silicon dioxide (SiO_2) films, and conventionally, the dielectric constant of SiO_2 films can be reduced through the introduction of porosity with controllable pore size and distribution [6–9]. Increased porosity may, however, degrade mechanical strength. The dielectric constant of SiO_2 films can also be decreased by doping of fluorine ions into SiO_2 films to reduce the electronic polarization. Plasma-enhanced chemical vapor deposition introduced F into the silica film with a low dielectric constant (2.4) using TEOS/C_4F_8/Ar mixtures [10].

Recently, liquid phase deposition (LPD) of SiO_2 films has been reported to possess a lower leakage current, a higher dielectric breakdown strength and a lower dielectric constant than conventional SiO_2 films prepared by sputtering or chemical vapor deposition, and is being considered as one of the most promising interlayer dielectric [11–16]. In our previous work, the as-deposited LPD SiO_2 films were reported to exhibit Young's modulus in the range of 17 to 29 GPa and a dielectric constant below 2.7, much lower than that of conventional SiO_2 ($k = 4.0$), depending on the microstructure and fluorine content of the film [17].

During the LPD process, the addition of boric acid is the most common way to increase the degree of supersaturation of the precursor solution and to prompt the precipitation of SiO_2. But a large variation was noticed when attempted to compare the results obtained from different research groups for the SiO_2 deposition rate as a function of boric acid addition [18]. And there was no report on the dependence of the microstructure of the LPD SiO_2 films on processing conditions such as chemical composition and temperature of the precursor solution. In this study, a systematic investigation of the microstructure developments of LPD SiO_2 films at various solution parameters and deposition temperatures was explored. In addition, the corresponding deposition rate and surface roughness were evaluated under various deposition conditions.

One goal of this study is to identify an underlying mechanism that can explain the SiO_2 film formation involving nucleation, growth, and agglomeration/coarsening of the SiO_2 nanoparticles in supersaturated solution. The other goal is to find a suitable processing condition for

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deposition of smooth and sufficiently dense SiO_2 films, required for a reliable dielectric layer, at very low solution temperatures. Low-temperature processing capability will also allow these films to be deposited on polymer substrates that can be used in flexible electronics.

2. Experiment details

2.1. Liquid-phase deposition of SiO_2

The liquid phase deposition system includes a Teflon beaker and a temperature-controlled water bath. The preparation procedures of the precursor solution for LPD silica films in this study are (i) dissolution of excess silicic acid powder ($SiO_2 \cdot xH_2O$) in 35 wt.% hydrofluorosilicic acid (H_2SiF_6) aqueous solution, (ii) stirring for 12 h at 25 °C to ensure that hydrofluorosilicic acid solution is saturated with silica, (iii) removal of undissolved silica powder by filtration and centrifuge, and (iv) diluting the saturated H_2SiF_6 solution with deionized (DI) water and boric acid aqueous solution to a desired H_2SiF_6 concentration (0.5 M,1.0 M, 1.5 M or 2.0 M) for deposition. The concentration of boric acid was also adjusted from 0 to 10 mM in the precursor solution. For example, a 100 ml deposition solution with 2.0 M hydrofluorosilicic acid and 5 mM boric acid can be prepared by mixing 62 ml saturated hydrofluorosilicic acid solution with 33 ml DI water followed by slowly adding 5 ml of 0.1 M boric acid solution. The deposition temperature was set at 40 °C, 50 °C or 60 °C. The deposition was conducted in a stepwise fashion, that is, the precursor solution was drained and fresh precursor solution was filled after every step of deposition. After desired deposition steps were finished, the substrates were taken out from the solution, thoroughly rinsed with DI water, and dried under a stream of nitrogen at room temperature. Table 1 summarizes the processing conditions for the SiO_2 film depositions used in this study.

2.2. Treatment of the substrates

The substrates used in this study were n-type silicon wafers (Silicon Quest International, Santa Clara, CA, USA) and F-doped tin oxide (FTO)-coated glass (Hartford Glass Co. Inc., IN, USA). The substrates were first sonicated in acetone for 10 minutes, and then cleaned with freshly prepared piranha solution (98% H_2SO_4 / 30% $H_2O_2 = 7/3$ (v/v)) at 85 °C for 40 minutes to obtain a highly hydrophilic surface. To avoid the settlement of precipitated particles and corresponding aggregates from the precursor solution, the substrates were held vertically in a Teflon holder during the film deposition.

Table 1
Summary of the processing conditions for the LPD SiO_2 films used in this study.

Sample ID[a]	[H_2SiF_6] (M)	[H_3BO_3] (mM)	Deposition temperature (°C)	Number of steps	Total deposition time (h)	Film thickness (nm)
F1	0.5	5	50	6	6	318.5 ± 29.7
F2	1.0	5	50	6	6	941.8 ± 19.9
F3	1.5	5	50	6	6	1000.8 ± 24.7
F4	2.0	5	50	6	6	984.8 ± 17
B1	1.0	0	50	5	5	305.1 ± 22.4
B2	1.0	2.5	50	5	5	601.9 ± 11
B3	1.0	5	50	5	5	984.8 ± 16.9
B4	1.0	10	50	5	5	740.5 ± 15.5
T1	1.0	5	40	3	6	373 ± 25.1
T2	1.0	5	50	5	5	976.5 ± 13.4
T3	1.0	5	60	5	5	1094.7 ± 18.3
S1	2.0	2.5	60	6	3	208 ± 3.4

[a] For sample T1, 2 h/step was used; for sample S1, 30 min/step was used; for all other samples, 1 h/step was used.

2.3. Characterization of the films

The morphology of the film was observed through field emission scanning electron microscope (FESEM, Zeiss Supra 55, Carl Zeiss SMT Inc., Germany) with a carbon coating. All the SEM images were taken at an accelerating voltage of 2 kV and with a working distance of around 5 mm. Fractured samples were positioned vertically to take cross-sectional SEM images. Elemental compositions of as-deposited films were analyzed by energy dispersive X-ray spectrometry (EDS) equipped in SEM, for which a 10 kV accelerating voltage and an 8 mm working distance were used.

The thickness of the films was measured through a step height from the undeposited area to the film surface by a stylus profiler (Dektac 8 Advanced Development Profiler, Veeco Instruments, NY, USA). For this, an average of 5 measurements at different locations was used. To measure the roughness of the films, 20 μm × 20 μm atomic force microscope images were taken at three different locations of the film by the nanoindenter with a Berkovich tip (TriboIndenter, Hysitron Inc., MN, USA). The chemical bonding and structure of the as-deposited silica films were investigated using an FT-IR spectroscopy (Shimadzu, JAPAN) in the transmission mode with the undeposited silicon area as a reference for baseline subtraction. To measure the leakage current and the breakdown voltage (Agilent 4156A precision semiconductor parameter analyzer), the LPD SiO_2 films were deposited on FTO-coated glass, and silver dots with an area of 1–2 mm^2 were patterned on the top surface of the film (Ag/LPD silica/FTO).

3. Results and discussion

The liquid phase deposition of silicon dioxide is the result of the reaction between hydrofluorosilicic acid (H_2SiF_6) and water, as represented by reaction (1). In most of our depositions, boric acid was added to the precursor solution to react with HF (reaction (2)) at an elevated temperature prior to immersing the substrate for deposition, making it more supersaturated with SiO_2, and to form nanoparticles through homogeneous nucleation.

$$H_2SiF_6 + 2H_2O \leftrightarrow 6HF + SiO_2 \tag{1}$$

$$H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O \tag{2}$$

As will be shown in the following sections, there exists significant microstructure variation of the LPD SiO_2 films deposited under different processing conditions.

3.1. Effect of boric acid concentration

Boric acid plays a critical role in producing a SiO_2 film in the LPD process by adjusting the level of supersaturation. The dependence of the deposition rate and surface roughness of LPD SiO_2 films on the added boric acid quantity is shown in Fig. 1. Depositions were conducted in 1.0 M hydrofluorosilicic acid at 50 °C with the addition of 0 mM, 2.5 mM, 5 mM and 10 mM boric acid in a stepwise mode, i.e., 1 hour per step. The deposition rate was calculated from the thickness of the deposited films after 5 steps of deposition.

It was found that SiO_2 films can be grown at a rate of around 60 nm/h in 1.0 M supersaturated hydrofluorosilicic acid solution without the addition of boric acid, resulting in a dense and smooth film morphology with a few growing particles embedded in the film, as well as smaller particles from bulk precipitation adsorbed onto the growing film (Fig. 2(a)). The particles seem to involve coarsening by displaying a 'neck' formation between them.

From the reaction (2), boric acid reacts with excess HF in the solution, driving the equilibrium toward the right-hand side of reaction (1) and generating more SiO_2. Therefore, at higher boric acid concentration, a higher degree of supersaturation of the