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Synthesis and characterization of low-*k* films for large area imaging applications

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An organic liquid polymer based on methyltriethoxysilane has been synthesized. The material;when spin-coated onto wafers and thermally treated;lead to dielectric films of low permittivity;which can be used in hydrogenated amorphous silicon (a-Si:H) thin film transistor (TFT) based large area imaging arrays as an inter-level dielectric between the TFT and pixel levels. Fourier Transform Infrared Spectroscopy (FTIR) shows prominent peaks of Si–CH_3 stretch and Si–O stretch modes. The dielectric constant (*k*) of the film was found to decrease with increasing curing temperature (T_{cure}). However;*k* values were < 3 for $T_{cure} < 260$ °C;which is the upper limit for our a-Si:H process. Thermogravimetric analysis showed that major weight loss takes place for up to 200 °C;and the film stabilizes thereafter. The stress in the films was found to be compressive;and increased from 50 to 220 MPa when T_{cure} was increased from 250 to 450 °C. The low stress for low T_{cure} is a desirable property for film integration.

1. Introduction

Low dielectric constant (low-*k*) materials are very attractive as inter-level dielectrics in integrated circuit processing. A low-*k* material is very essential for improved performance, notably for reduced RC delay in ICs [1]. Several organic and inorganic low-*k* materials have been studied for this purpose [2]. The principal techniques used to deposit such materials are chemical vapour deposition and spin-coating [3]. In addition to the application in ICs, low-*k* materials can also be used as inter-level dielectrics in pixelated a-Si:H TFT arrays for imaging and display applications [4–6]. For this purpose, we synthesized an organic liquid polymer using methyltriethoxysilane [7] as the base material. An experimental set-up was built for synthesis steps such as refluxing, hydrolysis, agitation, and polymerization. The final product is a high flowing brownish liquid, which is spin-coatable and yields a film after coating and thermal curing. The cured films as well as the initial liquid material were found to be very stable. In the present work, we report on the synthesis and characterization of methyltriethoxysilane-based polymeric dielectric films. The films have been characterized by FTIR, high-frequency (1 MHz) capacitance, film thickness, film stress, and thermogravimetry.

2. Experimental

2.1. Experimental set-up for the synthesis of the polymeric solution

The synthesis of the polymeric solution was performed using the reflux technique. Fig. 1 shows the experimental set-up used in the synthesis. A 500-ml, three-necked, round-bottomed flask with a stirrer and thermometer was used as the reaction vessel. The liquid reagents were introduced into the flask by means of a pipette. A stirrer/agitator (Caframo BDC 3030) with a digitally controlled brushless DC motor was used for agitation control. The stirrer was connected to the complete assembly with a glass shaft and a ground bearing through an adaptor. A Teflon made stirrer blade with a long-groove keyhole provided easy insertion into flask neck and proper positioning for the stirring action. The agitation speed was kept sufficiently high to ensure thorough mixing. A water jacketed condenser was used to prevent the vapour from escaping. The condenser consists of two concentric tubes with the outer cooling tube sealed onto the inner tube. The water that is circulated through the outer tube removes the heat from vapours arising within the inner tube and condenses them. The cooling water enters into the condenser from the top and exits through the bottom. The inner tube of the condenser has a ground joint at its bottom. A trace of silicon grease was used as lubricant in all the joints. The overall glassware assembly was immersed in a water bath, where the temperature was controlled by a Brinkmann heater.

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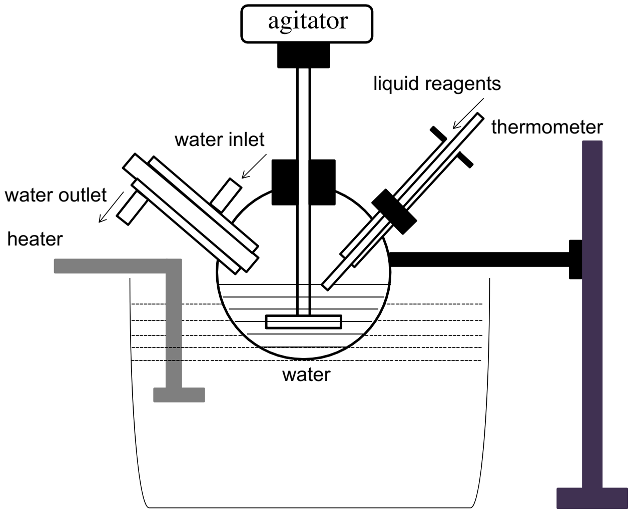

Fig. 1. Schematic diagram of the experimental setup used for polymeric film synthesis.

2.2. The synthesis process

The polymeric solution was synthesized based on two silane coupling agents: (3-3-3-trifluoropropyl) trimethoxysilane and methyltriethoxysilane [7]. The procedure starts by the hydrolysis of 3-3-3-trifluoropropyl trimethoxysilane mixed with ultra pure water and ethanol in the molar ratio of 1:2:1. Under the right experimental conditions, the 3-3-3-trifluoropropyl trimethoxysilane hydrolyzes stepwise in water to give the corresponding silanols, and then condenses resulting in siloxanes that have high molecular weight.

Step 1:

$$CF_3CH_2CH_2Si(OCH)_3 + H_2O \rightarrow CF_3CH_2CH_2Si(OH)_3$$

Step 2:

$$CF_3CH_2CH_2Si(OH)_3 \rightarrow (CF_3CH_2CH_2)(OH)Si(OH)[(O)(OH)Si(CF_3CH_2CH_2)]_n(O) \times (OH)Si(CF_3CH_2CH_2)$$

The reflux technique was used during hydrolysis. The temperature of the water bath was adjusted to a level in such a way that the liquid being heated under reflux travelled only part way up the condenser tube before condensing. Hence the liquid ran back to the flux below the condensation point. While the hydrolysis was relatively fast, the condensation process was rather slow. Therefore the overall process lasted about 2 h. Then in the hydrolyzed solution, (3-3-3-trifluoropropyl) trimethoxysilane was mixed with methyltriethoxysilane, titanium(di-I-propoxide)bis (acetylacetonate), ethyl alcohol, water and ethyl acetoacetate in the molar ratio of 1:4:0.1:0.2:15:20. This reaction was conducted for about 1 h. The final solution, which is brownish and high flowing, is used for spin-coating. The solution was stable and can be stored at room temperature.

2.3. Film preparation and characterization

The synthesized solution was used to form thin dielectric films on either glass or p-type Si (8–12 Ω cm;<100>) wafers by spin coating. The wafers were placed in the spin coater and 4–6 ml of synthesized solution was placed on the wafer;which was then spun at high speed to produce a thin and uniform coating. The spin speeds ranged between 3000 and 5000 rpm and the spin-time was 30 s. After the coating the films were thermally cured to outgas the volatiles from the film and to enhance the adhesion with the wafer. The films were cured for 30 min at different T_{cure} ranging between 150 and 450 °C. The thickness of the films was determined using a profilometer by scanning across a groove formed on the film. FTIR measurements on the films deposited on Si wafers were performed using an infrared spectrophotometer. The absorbance of the bare Si wafer was first measured (base spectrum) and then the absorbance of the polymer/Si was measured. The net absorbance of the films was obtained by subtracting it from the base spectrum. In order to determine the dielectric constant of the films;high frequency capacitance–voltage (*C*–*V*) measurements were carried out at 1 MHz on metal–polymer–silicon (MPS) capacitor test structures. To fabricate the test capacitors;an Al film of thickness ~120 nm was first sputtered on the unpolished side of p-type Si wafers;the dielectric film was then spin-coated on the other side of the wafer and cured. *C*–*V* measurements were performed on Hg/polymer/Si/Al (MPS capacitor) structure using a mercury probe as front contact. The dielectric constant was determined from the accumulation capacitance. Thermo gravimetric analysis was performed by a Thermal Analyst 2100 system. The experiment was performed by heating the polymer solution at the rate of 15 °C/min from room temperature to 450 °C in a helium gas flow stream. Platinum cups (for reference and sample) were used in this study. The synthesized polymer solution was poured onto the sample cup and the weight of the sample cup was compared with the reference cup. The starting solution volume was 2.3 ml. The weight versus temperature curves were recorded for both heating and cooling. The weight-loss rate was also obtained for the same temperature range. Film stress measurements were carried out using a stress gauge on glass wafers that were pre-deposited with sputtered Al of 120 nm thickness on one side (for optical reflection) and the dielectric film on the other. The system optically measures the stress-induced deflection in the wafer. The bow at the centre of the wafer was measured before and after the low-*k* film formation;and the film stress was calculated from the net deflection at the centre of the wafer.

3. Results and discussion

3.1. Film thickness

The thickness of the films depends on the spin speed and on curing temperature. As shown in Fig. 2, for spin speeds between 3000 and 5000 rpm, the film thickness is in the range of 0.5–0.3 μm for a T_{cure} of 200 °C for 30 min. Variation in thickness is due to uncertainties with the thickness profilometer. For spin speed < 3000 rpm, the solution precipitates and the film uniformity

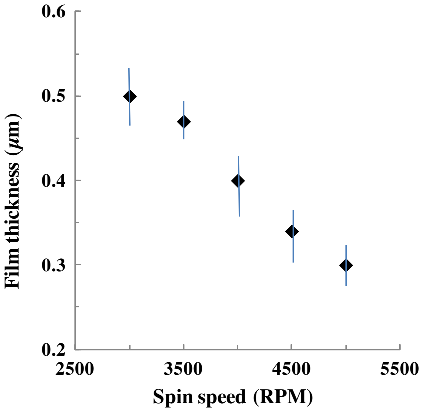

Fig. 2. Film thickness as a function of spin speed for the samples cured at 200 °C, 30 min.