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Deposition characterization of low-*k* hybrid thin films using methyl methacrylate for ULSI applications

Bhavana N. Joshi, Ashok M. Mahajan*

Department of Electronics, North Maharashtra University, Jalgaon 425001, Maharashtra, India

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ABSTRACT

Hybrid low dielectric constant (low-*k*) materials have been emerged immensely as interlayer dielectrics (ILD). Hence, in this paper we have presented the annealing temperature effect on dielectric constant of the spin coated hybrid thin films prepared by incorporating methylmethacrylate (MMA) as organic material. The process parameters have been optimized for obtaining lower dielectric constant of hybrid thin films so as to achieve better interconnect layer characteristics in ULSI applications. The structural and electrical properties of thin films have been carried out by using, Fourier transform infrared (FTIR) spectroscopy, Ellipsometer, Energy Dispersive Spectroscopy (EDAX), Scanning Electron Microscopy (SEM) and Capacitance–Voltage (CV) analyzer. The FTIR and EDAX characterization confirms formation of hybrid thin films. The lower values of strain of the deposited films, calculated from Si–O–Si stretching peak makes them suitable for ILD application in ULSI circuits that controls extrusion of metal. The data obtained from ellipsometer and FTIR characterizations have been used to deduce the values of dielectric constant of the deposited thin films by means of novel formulation reported by Takuya Fukuda et al. The values obtained through this formulation shows that, the dielectric constant of the hybrid thin films is successfully reduced. The dielectric constants have been found to be decreased from 2.656 to 2.637 with the increase in annealing temperature from 200 to 400 °C and the dielectric constant of 2.67 determined through CV analyzer for annealing temperature of 200 °C is almost matches.

1. Introduction

With the rapid decrease in physical dimension of today's devices, the complexity of interconnect structure increases as a requirement of high performance and high functionality ultra large scale integrated (ULSI) circuits [1]. Thus, interlayer dielectric materials with low dielectric constant (i.e. $k < 4.1$) are required for next generation of ULSI circuits as an isolation in multilevel interconnects. This low-*k* ILD in back end of line (BEOL) reduces the resistance capacitance (RC) delay and power consumption of circuit [2–4]. Recently various materials including organic polymers, porous silica, F doped SiO_2 and organic–inorganic hybrid materials are being extensively investigated for ILD as an alternative to SiO_2 [5–8]. Among these, hybrid materials are prominent in ULSI application. These films have better adhesion, transparency, flexibility, reduced surface roughness and good mechanical strength [9–10]. The hybrid films form the less polarizable bonds in dielectric material due to addition of organic material. The important task in synthesis of such hybrid materials is to control the phase separation between organic moieties and it depends on interaction between organic segment and inorganic network [11]. The formation of hydrogen bonding in hybrid materials prevents phase separation [12] hence it is important part to be studied. The literature survey shows that, the incorporation of polymer in SiO_2 reduces the dielectric constant and enhances mechanical strength. Huang et al. studied thermal properties of SiO_2-polymerized methyl methacrylate (PMMA) hybrid films synthesized by using trimethoxysilyl propyl methacrylate (MSMA). However they reported that, in absence of MSMA the silica and polymer remains separate in sol [13]. Almaral-Sanchez et al. also used MSMA additive and benzoyl peroxide (BPO) as initiator for polymerization of MMA and deposited the films by sol–gel [12]. The MMA in copolymerized form was also used by Fu et al. [14] for deposition of nanoporous low-*k* polymide films by Reversible Addition Fragmentation chain Transfer (RAFT)-grafted polymerization where PMMA decomposes at 265 °C in air.

In present work, the incorporation of monomer methylmethacrylate (MMA) in SiO_2 matrix has been carried out. The deposited films are having good adhesion with the Si substrate and found to be suitable for interlayer dielectric applications in ULSI because of their low dielectric constant obtained through FTIR. The presence of small peak in FTIR spectra of deposited films at 1632 cm^{-1} is related to C=C group [15] that confirms incorporation

* Corresponding author. Tel.: +91 257 2257476; fax: +91 257 2258403/406.
E-mail addresses: jbhavana@rediffmail.com (B.N. Joshi), ammahajan@nmu.ac.in (A.M. Mahajan).

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Table 1
Wavenumber of different bonds present in films M1–M5.

Sample no.	Annealing temperature (°C)	Si–O–Si rocking (cm^{-1})	Si–O–Si bending (cm^{-1})	Si–OH stretching (cm^{-1})	Si–O–Si stretching (cm^{-1})	C=C stretching (cm^{-1})
M1	200	458.78	800.03	961.05	1072.64	1643.86
M2	250	448.74	798.81	962.21	1077.64	1632.25
M3	300	455.01	804.04	962.62	1078.21	1633.69
M4	350	447.72	804.0	962.33	1078.97	1639.48
M5	400	447.33	811.70	964.98	1079	1632.53

of MMA in SiO_2 matrix. Thus, we have successfully incorporated the MMA monomer by eliminating the step of polymerization to lower the dielectric constant of deposited thin film. A series of hybrid films of MMA-SiO_2 have been prepared by sol–gel process combined with spin coating technique is explained in Section 2 of this paper. These deposited films have been annealed at different higher temperatures for 1 h and characterized further by techniques like ellipsometer, FTIR, SEM/EDAX, CV and current–voltage (I–V) analyzer are discussed in Section 3. Section 4 concludes the paper.

2. Experimental

2.1. Materials

Methylmethacrylate (MMA of s.d. fine make), tetraethylorthosilicate (TEOS of Lancaster make), ethanol 99% pure AR grade were used for experimental work in as received form.

2.2. Preparation of hybrid thin films

TEOS was used as source of silicon dissolved in parent alcohol ethanol. The molar ratio of TEOS:ethanol kept to be 1:3.8 and distilled water then further added to this sol with TEOS:water ratio 1:2. Hydrofluoric (HF) acid was used as a catalyst to accelerate the hydrolysis and condensation reaction rate. The electronegativity of the Fluorine (F) in HF is advantageous to reduce the Si–OH formation in order to achieve lower dielectric constant. To this sol MMA monomer was added with constant stirring for 15 min and the optimized TEOS:MMA molar ratio was kept to be 1:0.5. This hybrid sol with optimized precursor ratio was further deposited on pre-cleaned 1 cm × 1 cm p-type silicon substrate (resistivity 10 Ω cm). These films were further dried for 10 min in an oven at 200 °C temperature. Annealing of deposited films after drying was carried out at different elevated temperatures from 200 to 400 °C to study the effect of annealing on dielectric property of MMA doped thin films. These films were characterized further by ellipsometer (Philips SD-1000) for refractive index and thickness measurements, FTIR (Nicolet 380) for chemical bonding analysis, SEM/EDAX for surface morphology and elemental analysis. The CV (Keithely 590) measurements were also carried out for capacitance estimation and dielectric constant measurement by forming the metal–insulator–semiconductor (MIS) structure. The MIS were formed by depositing the aluminum metal as a back and upper electrode with upper metal contact area of 1.9×10^{-3} cm^2.

3. Results and discussion

The FTIR characterization has been carried out using FTIR spectrometer with 4 cm^{-1} resolution and 128 scan rates in 400–4000 cm^{-1} range. The absorbance FTIR spectrum with different peaks is shown in Fig. 1. The presence of intense peaks at 458.78, 800.03, 961.05, 1072.64, 1643.86 cm^{-1} and a broad band between 3100 and 3600 cm^{-1} are associated with the absorption due to Si–O–Si rocking, Si–O–Si bending, Si–OH stretching, Si–O–Si stretching, C=C stretching and –OH stretching modes respectively. The Si–O–Si stretching peak in the range 1072–1078 cm^{-1} shows the formation of Si–O–Si network in all the hybrid films. The literature survey shows that the organic–inorganic interfacial interactions gives hydrogen bonding, such hydrogen bond formation is observed in all hybrid films by presence of Si–OH and –OH bonds in FTIR spectra. Thus, FTIR confirms the deposition of hybrid thin films. The inset of Fig. 1 is deconvolution of peak at 960 cm^{-1} that contains two peaks one of Si–F at 932 cm^{-1} and other is of Si–OH at 960 cm^{-1}. The presence of Si–F lowers the polarizability of Si–O bonds. The wavenumber of various peaks present in M1–M5 thin films annealed at different temperatures are presented in Table 1. It has been observed that there is nonlinear change in the C=C stretching wavenumber whereas, the presence of C=C bonding carbon remains in film at 400 °C annealing temperature also. The presence of carbon in film reduces the dielectric constant due to its lower atomic weight and the use of HF catalyst also reduces the Si–OH formation by introducing the Si–F bond that makes Si–O network less polarizable due to higher electronegativity of F. These significant changes with HF as catalyst and MMA incorporation ultimately contribute in lowering the dielectric constant of thin films.

The effect of annealing temperature on Si–O–Si stretching wavenumber and peak intensity presented in Fig. 2 shows the stretching wavenumber increases slightly after 300 °C temperature. The change in absorbance intensity of Si–O–Si peak shows that, the removal of organic species begins from 300 °C, hence intensity is observed to be reduced after 300 °C. The films annealed above 300 °C temperature lose their luster may be due to removal of carbon from film. The microscopic strain on film is determined from the Si–O–Si stretching wavenumber by the formula reported by Fen Chen et al. [16] and the strain values are found to be very low i.e. <0.0054 which is advantageous for extrusion control of metal.

The ellipsometer with wavelength 632.8 nm has been used for refractive index and thickness measurements. All the films have the refractive index <1.31 and thickness in the range 200–205 nm. The ellipsometeric and FTIR characterizations are used to study the effect of polarizations on dielectric constant of films. The dielectric constant ($\varepsilon(\omega)$) of film depends on electronic ($\varepsilon_{ele}(\omega)$), ionic

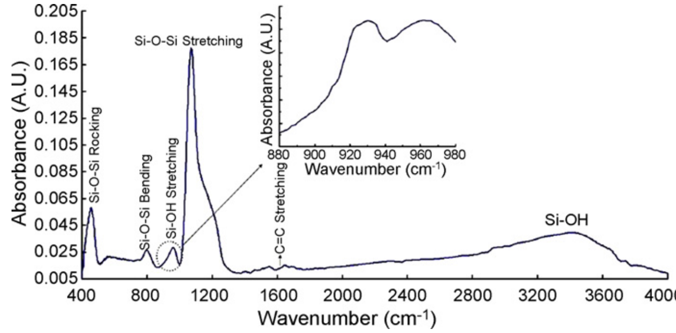

Fig. 1. Absorbance spectra of sample M1 inset figure shows the deconvolution of Si–F and Si–OH overlapped peak at 961 cm.