Growth and characterization of MMA/SiO₂ hybrid low-*k* thin films for interlayer dielectric applications

BHAVANA N JOSHI, M A MORE[†] and A M MAHAJAN*

Department of Electronics, North Maharashtra University, Jalgaon 425 001, India

[†]Department of Physics, University of Pune, Pune 411 008, India

MS received 9 November 2008; revised 27 April 2010

Abstract. The methylmethacrylate (MMA) incorporated SiO₂ thin films having low dielectric constant ($k = 2.97$) were deposited successfully to realize new interlayer material for the enhancement of electrical performance of on-chip wiring in very large scale integrated (VLSI) circuits. We have successfully incorporated MMA monomer and eliminated the polymerization step to lower the dielectric constant of deposited thin film. The presence of peak of C=C bond in Fourier transform infrared (FTIR) spectra and carbon peak in energy dispersive (EDAX) spectra confirms the incorporation of carbon in the film due to MMA. The concentration of MMA has great impact on the peak area and full width at half maxima (FWHM) of the Si–O–Si bond, which decreases the density by low atomic weight elements and consequently decreases the dielectric constant. The surface morphology analysed by scanning electron microscopic (SEM) image shows excellent uniformity of the film. The refractive index of 1.31 was measured by ellipsometer for 0.5 ml MMA concentration film. These deposited thin films having low refractive index and dielectric constant are widely applicable for the optical interconnects and interlayer applications in integrated optical circuits and VLSI circuits.

Keywords. MMA incorporation; low refractive index; low dielectric constant; optical interconnects; inter-layer applications.

1. Introduction

The performance of microelectronic and current nano-electronic circuits is significantly influenced by the on chip interconnects structures and miniaturizations. The high packing density lowers the wiring pitch and requires increase in wiring levels. This complexity in the VLSI circuit gives rise to RC delay, which is a great hindrance in the speed performance of the devices. Intensive research is going on to reduce delay by realizing lower dielectric constant material ($k \sim 2\text{--}3.5$) (Kal *et al* 1995; Ma *et al* 1998; Morgen *et al* 2000; Maex *et al* 2003; Baranov *et al* 2006; Wang *et al* 2006; Joshi and Mahajan 2008) for interlayer dielectric instead of conventional SiO₂ used in microelectronics (Vexler *et al* 2006). According to the International Technology Roadmap for Semiconductors (ITRS) (www.itrs.net 2007), it is required to integrate dielectric materials with effective k values between 2.3 and 2.6, so the problem of cross-talk and power dissipation can be minimized to a large extent. The low- k materials can be prepared by lowering the density of material by introducing the porosity and by forming the less polarizable bonds in the material (Nagai

et al 2003; Joshi and Mahajan 2007). The porous low dielectric materials are in demand because of their low dielectric constant but there are many problems in integration of such porous materials. The pores in film remain open and internally interconnected, due to this, during different processes like etching, resist removal, chemical mechanical polishing (CMP) etc. various gases and chemicals easily penetrate in porous structure and change the properties of that material (Jousseume *et al* 2006). Another approach for decreasing polarizability is, the use of organic polymers that contain non-polar C–C bonds having a k value of 2.6–2.8, however, it has poor thermal stability (Link 1972). Thus, it is essential to concentrate on maintaining the mechanical, physical and chemical properties of the deposited low- k films for their wide and imperative applicability for intra- and interlayer dielectrics. In this regard, the hybrid materials are of significant importance as they have composite properties of inorganic and organic materials (Almaral-Sanchez *et al* 2006). Polymer materials are widely used as dielectric for packaging. The researchers suggested that the incorporation of polymer in inorganic material such as SiO₂ reduces the dielectric constant and enhances mechanical strength. Huang and Qiu (1995) studied thermal properties of SiO₂-polymerized methyl methacrylate (PMMA) hybrid films. In their work, they formed the polymerized

*Author for correspondence (ammahajan@nmu.ac.in)

MMA film by using trimethoxysilyl propyl methacrylate (MSMA). Their work suggests that without MSMA sol gives silica and polymer separately (Huang and Qiu 1995). Fu *et al* (2004) deposited nanoporous low- k polyimide films by reversible addition fragmentation chain transfer (RAFT)-grafted copolymerized MMA side chains having $k=2.1$ where PMMA decomposes at 265°C in air. These materials are made up of inorganic metal alkoxides in which organic groups are incorporated. Almaral-Sanchez *et al* (2006) also used MSMA additive and benzoyl peroxide (BPO) as initiator for polymerization of MMA and deposited film by sol gel. To the best of our knowledge, very few reports are available on monomer MMA incorporation out of which a paper by Nocun *et al* (2003) who used monomer MMA motivated us to study the effect of monomer MMA incorporation in SiO₂ thin films in order to lower the dielectric constant by eliminating the step of polymerization.

In the present work, the incorporation of monomer methylmethacrylate (MMA) in SiO₂ matrix has been carried out. The presence of small peak in FTIR spectra of deposited film at 1632 cm⁻¹ related to C=C group (Burkey and Gleason 2003) that confirms incorporation of MMA in SiO₂ matrix. The deposited films have good adhesion with the Si substrate and are found to be suitable for interlayer dielectric (ILD) applications in VLSI because of its low dielectric constant obtained through FTIR. Here, we have successfully incorporated the MMA monomer by eliminating the step of polymerization to lower the dielectric constant of deposited thin film. The PMMA/SiO₂ thin films have also been deposited and C=O incorporation is observed through FTIR by a peak at 1731 cm⁻¹ (Heise *et al* 2000; Rajendran and Uma 2000). The deposited material has importance in integrated optics as cladding material due to its low refractive index.

2. Experimental

The p -type (100) Si wafers, with resistivity ~10–20 ohm-cm, were cleaned using trichloroethylene and acetone and methanol were used as substrates. The TEOS (tetraethyl-orthosilicate, Lancaster make) was used as a source of Si due to its non-toxicity and ease of handling (Mahajan *et al* 2004). With TEOS, ethanol of ER grade with 99.9% purity was used as solvent to which deionized water was added for hydrolysis. In this solution, MMA (S.d. Fine make) was added as it is for incorporation of carbon and the solution was stirred vigorously for 15 min. Further, in this solution HF was added as catalyst to accelerate the reaction rate. The optimized molar ratio of TEOS : ethanol : water : MMA : acid kept was at 1 : 3.8 : 2 : 0.5 : 0.3. The films were deposited on precleaned Si substrates by a spin coating technique with optimized viscosity. These deposited films were dried at a temperature of 200°C for 10 min in an oven. The concentration of MMA was varied

from 0.5 to 2 ml. It was observed that as MMA concentration increased the gelation time increased and above 2 ml the adhesion property of the film got degraded. Further, the deposited films were characterized by standard characterization techniques like FTIR, ellipsometer, capacitance–voltage (C – V) analyser and SEM/EDAX to study the chemical composition, refractive index and thickness, dielectric constant and surface morphology with elemental analysis, respectively. The effect of variation of concentration of MMA on the properties of deposited films by spin coating technique has been discussed in the next section.

3. Results and discussion

The deposited films were characterized by the Nicolet 380 FTIR spectrometer to obtain information about chemical bondings in the films. Figure 1 shows the absorbance spectra of the deposited thin films with variations in MMA from 0.5–2.0 ml. The spectra were recorded with 4 cm⁻¹ resolution and 128 scans for both sample and background (reference). The Si–O–Si stretching peak present at 1074.34 cm⁻¹ indicates formation of Si–O–Si network by sol–gel process. It is revealed from figure 1 that, as MMA concentration increases, the peak of C=C bond at 1641.92 cm⁻¹ increases. The peak of C=C bond validates the incorporation of MMA (CH₂=C(H)COOCH₃) in film because no such C=C is present in TEOS (Si(–OC₂H₅)₄). According to the recently reported literature, the formation of hydrogen bonds shows the interfacial interaction of organic–inorganic compounds (Huang and Qiu 1997; Almaral-Sanchez *et al* 2006). Similarly, the residual silanol groups present in the film forms hydrogen bond and it reveals from the presence of absorption peak in the range of 960–970 cm⁻¹. Hence, FTIR spectra validate the formation of homogenous matrix of organic MMA and SiO₂ hybrid film. The keen observation of spectra clearly shows the increase in broadness of Si–O–Si stretching peak, that is because of formation of Si–O–C bonds (Srivatsa *et al* 2008) overlapped in 1000–1200 cm⁻¹. Table 1 explains different bonds present in film at specific wavenumbers with variations of MMA. The intensity and FWHM of peak due to

Table 1. Chemical bonds present in deposited film with variation in MMA.

Sr. no.	Mode of vibrations	Wavenumbers (cm ⁻¹)			
		M0.5	M1	M1.5	M2
1	Si–O–Si rocking	454.87	451.56	456.10	456.79
2	Si–O–Si bending	796.63	801.71	801.98	802.56
3	Si–OH bending	959.52	963.1	965.2	964.02
4	Si–O–H stretching	1074.34	1076.28	1078.65	1078.64
5	C=C stretching	1641.92	1634.88	1637.17	1632.50

Figure 1. (a)–(d) Absorbance spectra of deposited film with increase in MMA concentration from 0.5–2.0 ml.

Figure 2. Effect of MMA concentration variation on Si–O–Si stretching frequency.

Figure 3. Influence of MMA concentration variation on peak area and FWHM of Si–O–Si stretching peak.

C=C bond increases up to 1.5 ml MMA concentration and then decreases as presented in table 2. Figure 2 clearly shows that, as the MMA concentration increases, the Si–O–Si stretching frequency increases up to 1.5 ml and thereafter it remains constant. The constant nature of Si–O–Si stretching peak frequency and decrease in C=C intensity show the inhomogeneity of MMA in SiO₂ sol with its higher concentration.

The significant observation of FWHM and peak area of Si–O–Si stretching peak from FTIR study is revealed in figure 3. The increase in the peak area and FWHM with increase in MMA concentration is due to the formation of Si–O–C bonds in film that makes the Si–O–Si stretching peak broad.

Table 2. Intensity and FWHM values of absorbance peak of C=C bond.

Sr. no.	Sample no.	Intensity	FWHM (cm ⁻¹)
1	M0.5	0.026	49.65
2	M1.0	0.037	50.26
3	M1.5	0.052	63.02
4	M2.0	0.044	47.66

The refractive index (RI) and thickness of the film have been measured by the ellipsometer (Philips SD-1000). It has been observed that, the refractive index of

the MMA incorporated SiO_2 film (sample no. M0-5) decreases to 1.31 as compared to that of conventional SiO_2 (RI = 1.46) and thickness of the film is 295 Å. The lowering of the refractive index is due to formation of porosity and the Si–O–C bond i.e. the assimilation of carbon in the deposited film. As concentration of MMA

Figure 4. SEM image of M0-5 film (MMA concentration, 0.5 ml).

Figure 5. EDAX of sample M0-5 (MMA concentration, 0.5 ml).

Table 3. Characteristic properties of deposited thin film.

Sr. no.	Characteristics of MMA/ SiO_2 hybrid thin film	Measured values of sample M0-5
1	Refractive index	1.31
2	Dielectric constant	2.97
3	Thickness (Å)	295

increases, the strain on film increases hence it is difficult to measure RI of other films. The decrease in RI is due to presence of carbon in film. The refractive index, thickness and calculated value of dielectric constant of film are presented in table 3. The dielectric constant was determined by $C-V$ analyser (Keithley 590) at 1 MHz frequency by forming metal–insulator–semiconductor (MIS) structure with aluminum metal electrode of area, 0.185 mm².

The MMA/ SiO_2 films were also characterized by scanning electron microscope (SEM, JSM-6360) for morphological study of the film. SEM micrograph of 295 Å thick MMA/ SiO_2 hybrid film surface with very high resolution of 0.1 µm is shown in figure 4. The MMA concentration in SEM characterized film was 0.5 ml. The film has amorphous nature. After optimization of the hybrid thin films deposition on various substrates it has been observed that the films show good adherence to the Si substrate and gives smooth and crack free uniform films. Energy dispersive spectroscopy (EDAX) measurements of deposited MMA/ SiO_2 hybrid film were taken for elemental analysis as shown in figure 5. The presence of carbon, oxygen, and silicon is confirmed by the peaks appearing at 0.27, 0.525, 1.739 keV, respectively. The presence of carbon peak in EDAX spectra validates the incorporation of carbon SiO_2 thin film. From EDAX and FTIR spectral analyses, it is clear that the carbon incorporated in the film is due to MMA. Such appearance of carbon in EDAX is not observed in SiO_2 films deposited from TEOS without MMA (Joshi and Mahajan 2010).

4. Conclusions

MMA incorporated SiO_2 hybrid films with good mechanical strength and low dielectric constant have been successfully deposited using the spin coating technique. It reveals from the study that, the carbon incorporation is also possible without polymerization of MMA. The presence of peak of C=C bond in FTIR spectrum confirms the presence of carbon in film due to MMA. The EDAX result shows the presence of carbon in the deposited film. The refractive index and dielectric constant of MMA/ SiO_2 film were measured to be 1.31 and 2.97, respectively. The SEM image shows excellent surface morphological visualization of deposited film that reveals thickness uniformity in the film. Overall, these MMA/ SiO_2 hybrid films are suitable for the optical interconnects and interlayer application in today's demanding devices like integrated optics and VLSI circuits.

Acknowledgement

Authors would like to acknowledge the University Grants Commission, New Delhi, for providing financial assistance for this work (vide F. No. 30-27/2004 (SR)).

References

- Almaral-Sanchez J L, Lopez-Gomez M, Ramirez-Bon R and Munoz-Saldana J 2006 *J. Mater.* **2** 1
- Baranov I L, Tabulina L V, Stanovaya L S and Rusalskaya T G 2006 *Semiconductors* **40** 915
- Burkey Daniel D and Gleason Karen K 2003 *J. Appl. Phys.* **93** 5143
- Fu G D, Zong B Y, Kang E T, Neoh K G, Lin C C and Liaw D J 2004 *Ind. Eng. Chem. Res.* **43** 6723
- Heise Andreas, Ngyuen Cattien, Malek Raouf, Hedrick James L, Frank Curtis W and Miller Robert D 2000 *Macromolecules* **33** 2346
- Huang Zhi Hua and Qiu Kun Yaun 1995 *Polym. Bull.* **35** 607
- Huang Z H and Qiu K Y 1997 *Polymer* **38** 521
- Joshi B N and Mahajan A M 2007 *Optoelectron. & Adv. Mater. Rapid Commun.* **1** 659
- Joshi B N and Mahajan A M 2008 *J. Optoelectron. Adv. Mater.* **10** 422
- Joshi B N and Mahajan A M 2010 *Mater. Sci. Semicond. Process.* **13** 41
- Jousseume V, Favennec L, Zenasni A and Passemard G 2006 *Appl. Phys. Letts* **88** 182908
- Kal S, Kasko I and Rysseu H 1995 *Bull. Mater. Sci.* **18** 531
- Link G L 1972 *Polymer science* (ed.) A D Jenkins (London: North Holland) **2** p. 1283
- Maex K, Baklanov M R, Shamiryan D, Iacopi F, Brongersma S H and Yanovitskaya Z S 2003 *J. Appl. Phys.* **93** 8793
- Mahajan A M, Patil L S and Gautam D K 2004 *Surf. Coat. & Technol.* **188–189** 314
- Ma Yanjun, Yang Hongning, Guo J, Sathe C, Agui A and Nordgren J 1998 *Appl. Phys. Letts* **72** 3353
- Morgen Michael, Todd Ryan E, Zhao Jie-Hua, Hu Chuan, Cho Taiheui and Ho Paul S 2000 *Ann. Rev. Mater. Sci.* **30** 645
- Nagai Hisao, Hori Masaru, Goto Toshio, Fuji Toshiaki and Hiramatsu Mineo 2003 *Jpn J. Appl. Phys.* **42** 2775
- Nocun M, Leja E and Bugajski W 2003 *Mater. Sci.* **21** 471
- Rajendran S and Uma T 2000 *Bull. Mater. Sci.* **23** 27
- Srivatsa K M K, Bera M, Basu A and Bhattacharya T K 2008 *Bull. Mater. Sci.* **31** 673
- Vexler M I, Tyaginov S E and Shulekin A F 2006 *Semiconductors* **40** 491
- Wang C L, Weber M H and Lynn K G 2006 *J. Appl. Phys.* **99** 113514
- www.itrs.net (2007 chapter: interconnect)