Enhancement in mechanical properties of silica low-*k* thin films using wet chemical technique

Yogesh S Mhaisagar, Anil S Gaikwad, Anil G Khairnar & Ashok M Mahajan*

Materials and Devices Laboratory for Nanoelectronics, Department of Electronics, North Maharashtra University, Jalgaon 425 001, India

Received 9 November 2013; revised 26 December 2013; accepted 5 February 2014

Silica low-*k* films have been deposited on silicon wafer using sol-gel spin-on method. The tetraethyl orthosilicate (TEOS) has been used as a precursor solution. In order to improve the properties, the deposited films have been surface treated by wet chemical treatment at different trimethylcholosilane (TMCS) volumetric concentrations in hexane. The presence of hydrophobic (CH₃) groups observed around 2900 cm⁻¹ confirms the surface modification of films. Further, the water contact angle of as-deposited and surface treated film at 20% TMCS concentration in hexane have been found to be 83° to 104°, respectively. This significant change in water contact angle after surface modification confirmed the change in surface of film from hydrophilic to hydrophobic. The mechanical properties of films have been determined by using nano-indentation techniques. The depth of penetration of indent in film surface has been observed to be decrease from 75 nm to 45 nm after surface modification at 20% TMCS concentration in hexane. This shows the improvement in mechanical properties of film after surface modification. The Young's modulus and hardness of surface modified films at 20% TMCS have been observed to be 78 GPa and 3.45 GPa, respectively.

Keywords: Porous low-k, ULSI, TMCS, Contact angle, Nano-indentation

1 Introduction

The porous thin films with ultra-low dielectric constant are in great demand as interlayer dielectric film to reduce interconnects RC delay and power dissipation in ULSI circuits¹. However, during integration the porous low-k film goes through different processes that effect on reliability and other properties of film². The active oxygen radicals produced during fabrication process form a silanol groups (Si-OH) which make the film surface hydrophilic. This hydrophilic surface of film adsorbs the moisture from environment and increases the k value³. Further porous low-k materials have very low mechanical strength compared to the traditional dielectric films. Due to this, the film leads to delamination and cracking during chemical mechanical polishing (CMP)⁴. Therefore, to overcome the previously mentioned issues it is necessary to enhance the properties of low-k film for successful integration in current fabrication technology. From literature survey, it is observed that by altering the composition and structure of bonding network using surface modification technique results in the improvement of low-k thin film properties⁵. Further in

order to prevent moisture adsorption, the hydrophobic surface of the film can be obtained by replacing the hydrogen of the –OH radical of silica matrix with some organic non-hydrolyzable Si–C bond⁶.

Taking in to consideration aforesaid issues the present work focused on improvement of silica low-k thin film properties like mechanical strength and film surface hydrophobicity. The silica low-k films were deposited by using sol-gel method. Further, in order to enhance the properties, the deposited films were surface treated with wet chemical method using TMCS as a surface modifying agent.

2 Experimental Procedure

The silica thin films were prepared by sol-gel spin coating method on *p*-type silicon (Si) wafer using tetraethyl orthosilicate (TEOS) as a precursor and ethanol as a solvent. The molar ratio of TEOS: ethanol kept to 1:4 and de-ionized (DI) water added to this sol with TEOS: DI molar ratio of 1:2. The hydrofluoric (HF) acid was used as an acid catalyst with molar concentration of 0.01 to accelerate the hydrolysis reaction rate. The mixture solution then stirred at room temperature for 1 h at constant speed. The prepared sol was then spun on silicon substrate at 3500 rpm for 30 s using spin coater (model 2000s

^{*}Corresponding author (E-mail: ammahajan@nmu.ac.in)

spinner, Milman Thin Films Pvt Ltd). The spin coated thin films were then baked at 100 °C for 30 min. Finally, the deposited films were annealed in closed furnace at 300 °C for an hour. Further, in order to improve the properties of films, the surface treatment was given to the deposited thin films by wet chemical technique. For surface treatment, TMCS ((CH)₃SiCl) is used as a surface modifying agent with 10% and 20% volumetric concentration in hexane solution. After surface treatment, the surface modified films were annealed at 80 °C for an hour.

The films before and after the surface modification were characterized by using Ellipsometer (Philips SD 1000) having He-Ne laser at wavelength 632.8 nm for thickness measurement. The surface bonding characteristics and evidence of surface modification were carried out by using Fourier Transform Infrared Spectroscopy (FTIR-Nicolet 380). The hydrophobic nature of the surface modified films was confirmed by using water contact angle meter (GBX make) by measuring the water contact angle with films surface. The mechanical properties, viz., hardness and elastic modulus of the as-deposited and surface modified low-k thin films were measured by using TI-900 HysitronInc Minneapolis (USA make) Nano-indenter with a diamond tip.

Results and Discussion

3.1 FTIR spectroscopy

The average thickness of silica low-*k* films is measured to be about 120 nm. The changes in chemical structure of film after surface treatment have been observed through the FTIR spectrometer with 4 cm⁻¹ resolution and 128 scan rates in 400-4000 cm⁻¹ range. Figure 1 (a-c) shows the FTIR spectra of as deposited, film surface treated with 10 % and 20% of TMCS/hexane solution, respectively. The most intense peak observed around 1076 cm⁻¹ is associated



Fig. 1—FTIR absorption spectra of (a) as-deposited film, film surface-modified at (b) 10% and (c) 20% TMCS concentration

with the Si-O-Si asymmetric stretching mode and which confirms the formation of Si-O-Si network in films⁷. The broad band of Si-OH and H₂O around 3300-3500 cm⁻¹ is observed due to the –OH stretching vibration. This presence of –OH groups illustrated the hydrophilic nature of the film surface⁸.

As shown in FTIR spectra (Fig. 1 (b,c)) the appearance of methyl group (CH₃) peaks around 2800-2900 cm⁻¹ after TMCS surface treatment confirms the surface modification of the films. This presence of CH₃ groups reveals the hydrophobic surface of film. The hydrophobicity of the film was determined by water contact angle method. Further, from FTIR spectra (Fig. 1 (a)) weak cage type broad Si-O absorption bond near 1140 cm⁻¹ is observed. The FTIR spectra (Fig. 1 (b)) of film treated with 20% TMCS concentration shows that the cage type Si-O absorption band observed to be diminishing and from a stable Si-O-Si network⁹. Thus, it can be concluded that the surface modification process rearranges the chemical structure and results in improvement in film properties.

3.2 Nano-indentation characterization

The mechanical properties such as hardness and elastic modulus of thin films were determined from nano-indentation technique. Figure 2 shows the load versus indentation displacement in film surface, obtained during cycle of loading and unloading. To avoid surface and substrate effects, the average hardness and Young's modulus are calculated by using the load-displacement data with penetration depths between one tenth and one fifth of the film thickness.

The film modified at 20% of TMCS in hexane solution shows the penetration depth of 44nm while



Fig. 2—Load vs depth of penetration at different TMCS concentration

the films without surface modification had higher penetration depth of 75 nm. The reduction more than 40% of penetration depth shows the improvement in the hardness of film as shown in Fig. 3. The hardness of the as-deposited and surface modified films at 10% and 20% of the TMCS concentration was found to be 1.56, 2.87 and 3.45 GPa, respectively.

Further, from the achieved nano-indentaion data, the Young's modulus of films skeleton has been determined by Eq. (1) using reduced modulus¹⁰:





Fig. 3—Young's modulus and hardness at different TMCS concentration



Fig. 4-Water contact at different TMCS concentration



Fig. 5—Water contact angle on surface of silica thin films surface treated with 20% TMCS concentration in hexane

Where, E_r is the reduced moduli, which is due to the effect of elastic deformation of indenter. E_s , v_s , V_s and v_i are the elastic moduli and Poisson's ratio of the specimen and indenter, respectively. The v and E for indenter is 0.07 and 1140, respectively. The effect of TMCS concentration on Young's modulus is shown in Fig. 3. The as-deposited film shows a lower modulus of 51 GPa while after surface treatment the modulus of the film observed to be increased. The film surface treated with 20% TMCS concentration shows a higher modulus of 78 GPa. The achieved young's modulus of surface modified low-k films found to be better than the value, i.e., 35 Gpa as reported by Xiao et al.¹¹. This significant improvement in the Young's modulus of silica low-k thin films after the surface treatment is due to the rearrangement of chemical structure and enhancement in stable Si-O-Si networkas depicted in FTIR spectra $(Fig. 1)^{5,12}$.

3.3 Water contact angle measurement

The hydrophobicity of the film after the TMCS surface treatment has been determined by measuring the contact angles (θ) of the water droplet placed on the surface of the film. The contact angle of as-deposited film is obtained to be 83° ($\theta < 90^{\circ}$) that shows the hydrophilic nature of surface which is due to the presence of silanol (Si-OH) group as observed in FTIR spectrum. From Fig. 4, it is observed that, the water contact of the film increases with increase in TMCS concentration in hexane solution. The water contact angles of the film modified at 10% and 20% are found to be 93° and 104°, respectively. Such significant change in water contact angle confirms the modification of the hydrophilic surface of the film to the hydrophobic after the surface modification, as the contact angle¹³ $\theta > 90^{\circ}$. Figure 5 shows the water contact angle of the film surface modified at 20% TMCS concentration.

Conclusions

In order to enhance the properties of films, the solgel deposited silica thin films were surface modified by using wet chemical treatment method. The presence of CH_3 peaks observed in FTIR spectra after surface treatment confirms the surface modification of the films. The decrease in depth of penetration in films surface from 75 nm to 45 nm after surface treatment shows the improvement in hardness of the film. The hardness of the film is found to be increased from 1.56 to 3.45 GPa after surface treatment. The films surface treated with 20% TMCS concentration shows a higher Young's modulus of 78 GPa. The hydrophobicity of the film was confirmed by water contact angle method. The significant change in water contact angle from 83° to 104° confirms the change in surface from hydrophilic to hydrophobic after surface treatment of the silica film. Such surface modified silica thin films with improved properties and hydrophobic surface can be used as interlayer dielectric applications in ULSI circuits.

Acknowledgement

Authors thank to the SERB, DST, New Delhi for providing financial assistance to carry out this work (vide letter No.SR/S3/EECE/0131/2011). Authors are also grateful to the Metallurgical Engineering & Materials Science Department, IIT Bombay for Nano-indentation providing facility for characterization. The Centre of Excellence in Nanoelectronics (CEN), IITB (under IIT INUP at IITB, which have been sponsored by DIT, MCIT, and Government of India) is also being acknowledged for providing the water contact angle measurement facility during this work.

References

- Sinha H, Ren H, Nichols M T, Lauer J L, Tomoyasu M, Russell N M, Jiang G, Antonelli G A, Fuller N C, Engelmann S U, Lin Q, Ryan V, Nishi Y & Shohet J L, *J Appl Phys*, 112 (2012) 111101.
- 2 Baklanov M R, Jean-Francois de M, Shamiryan D, Urbanowicz A M & Shi H, *J Appl Phys*, 113 (2013) 041101.
- 3 Shoeb J & Kushner M J, J Vac Sci Technol A, 30 (2012) 041304.
- 4 Vella J B, Adhihetty I S, Junkerand K & Volinsky A A, Int J Fract, 119/120 (2003) 487.
- 5 Wada A, Sasaki T, Yasuhara S & Samukawa S, *Jpn J Appl Phys*, 51 (2012) 05EC01-1- 05EC01-4.
- 6 Mhaisagar Y S, Joshi B N & Mahajan A M, Bull Mater Sci, 35 (2012) 151.
- 7 Joshi B N & Mahajan A M, Mater Sci Eng B, 168 (2010) 182.
- 8 Bao J, Shi H, Liu J, Huang H, Ho P S, Goodner M D, Moinpour M & Kloster G M, *J Vac Sci Technol B*, 26 (2008) 219.
- 9 Oka Y, Uedono A, Goto K, Hirose Y, Matsuura M, Fujisawa M & Asai K, *Jpn J Appl Phys*, 50 (2011) 05EB06-1-05EB06-5.
- 10 Panich N, Yong S, KMITL Sci J, 5 (2005) 483.
- 11 Xiao X, Shan X M, Kayaba Y, Kohmura K, Tanaka H & Kikkawa T, *Microelec Eng*, 88 (2011) 666.
- 12 Yoshino T, Ohnuki N, Hata N & Seino Y, *Jpn J Appl Phys*, 48 (2009) 050210.
- 13 Park Y B, Rhee S W, Imaizumi Y & Urisu T, J Appl Phys, 80 (1996) 1236.