Thin Solid Films 520 (2012) 5018–5020

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Study of dilution of Spin-On Glass by Fourier transform infrared spectroscopy

Miguel Dominguez [a,*], Pedro Rosales [a], Alfonso Torres [a], Mario Moreno [a], Abdu Orduña [b]

[a] National Institute for Astrophysics, Optics and Electronics (INAOE), Electronics Department, Luis Enrique Erro No. 1, Puebla 72840, Mexico
[b] CIBA-Tlaxcala, Instituto Politécnico Nacional, Tepetitla, Tlax. 90700, Mexico

ARTICLE INFO

Article history:
Received 29 September 2011
Received in revised form 25 February 2012
Accepted 7 March 2012
Available online 14 March 2012

Keywords:
Fourier-transform infrared spectroscopy
Spin-on glass
Insulator
Low-temperature

ABSTRACT

In this work, we study the dilution of Spin-On Glass (SOG) in order to obtain high quality SiO_2 films at 200 °C, with optical and electrical characteristics similar to those of the thermally grown SiO_2. For the production of SiO_2 films we used 2-propanol and deionized water (DI) as diluents for the SOG and we compared the electrical and optical film properties with those of the films obtained from undiluted SOG. From Fourier transform infrared spectroscopy we observed a considerable reduction of Si–OH (920 cm^{-1}), O–H (3490 cm^{-1}) and C–H, C–O bonds (1139 cm^{-1}) in the films produced from SOG diluted with DI. Besides the above, the insulator breakdown field was approximately 21 MV/cm, the refractive index and the dielectric constant were close to those of the thermally grown SiO_2. Our results suggest that the film produced from SOG diluted with DI and cured at 200 °C is an excellent candidate to be used as insulator on flexible and large-area electronics.

1. Introduction

At present time, insulator materials obtained at low temperatures have received much attention for their use on flexible and large-area electronics as gate insulators on Thin-Film Transistors [1–3]. However, insulators obtained at temperatures below 300 °C present lower performance characteristics when are compared with those obtained at high temperatures (>800 °C) in Complementary Metal-Oxide-Semiconductor technology [4]. Therefore, alternative techniques that allow the deposition of high quality insulator materials at low temperatures (<300 °C) are an issue.

In this aspect, silicon oxide films (SiO_2) deposited by Spin-On Glass (SOG) at low temperatures have very attractive results. The advantages of SOG include a low defect density in the films deposited, low process cost, its excellent for planarization applications, filling gaps and smoothing the surface with multiple coatings.

SOG is an interlevel insulator that is supplied in liquid form. The SOG solution form an arrangement of silicate polymers with a Si–O structure, these polymers are in an alcohol solvent system. The datasheet of SOG suggests a curing in the range of 400–900 °C to obtain a SiO_2 thin film. However, for flexible substrate applications it is necessary to use much lower temperatures for curing.

In this work, we study the deposition of SiO_2 films using SOG cured at 200 °C. Two solvents (2-propanol and deionized water — DI) were used as diluents for the SOG in order to observe its effect on the electrical, optical and compositional characteristics of the SiO_2 films produced.

2. Experiment

Three solutions were used in order to produce SiO_2 films from SOG solution (semiconductor grade 700B from Filmtronics, Inc.): A) SOG diluted 3:1 with deionized water (DI), B) SOG diluted 3:1 with 2-propanol, and C) undiluted SOG. Silicon wafers were used as substrates and before the SOG deposition they were chemically cleaned. First, the wafers were cleaned in trichloroethylene for 10 min, followed with acetone also for 10 min in ultrasonic bath. Later, the samples were cleaned with the RCA1 solution ($NH_4OH:H_2O_2:H_2O = 1:1:5$ at 75 °C for 15 min), followed with the RCA2 solution ($HCL:H_2O_2:H_2O = 1:1:6$ at 75 °C for 15 min). Finally, after rinsing the wafers with deionized water, buffered HF was used for 10 s to remove the thin native oxide on the silicon surface. After that, the SOG was deposited on the silicon wafers with the following procedure:

- For measurements of the refractive index: liquid application of SOG (using a dropper) at room temperature on the silicon wafers at 3000, 4000 and 5000 spinning revolutions per minute (RPM) for 30 s.
- For Fourier transform infrared (FTIR) spectroscopy: liquid application of SOG at room temperature and at 3000 RPM for 30 s.
- Annealing at 100 °C for 15 min to reduce humidity and evaporate most of the solvents.
- Curing for 6.5 h at 200 °C in N_2 ambient.

* Corresponding author. Tel.: +52 222 266 3100; fax: +52 222 247 0517.
E-mail address: mdominguez@inaoep.mx (M. Dominguez).

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2012.03.013

The IR absorption spectra of the films were measured with a "BRUCKER" FTIR spectrometer, Model Vector-22. The IR spectrum was observed for wave numbers between 4000 and 400 cm^{-1}. The absorbance spectrum is converted to absorption coefficient (α) using Eq. (1), where A is the absorbance and t the thickness of the sample (260 ± 10 nm for undiluted SOG, 61 ± 4 nm for SOG diluted with 2-propanol and 43 ± 4 nm for SOG diluted with DI).

$$\alpha = -\ln(1-A)/t \quad (1)$$

To measure refractive index a Gaertner ellipsometer L117 equipment was used. For the determination of dielectric constant k, MIM (Metal-Insulator-Metal) structures were fabricated. Then, the capacitance was measured with a PM 6303 automatic RLC meter (from Philips) and using Eq. (2), k was calculated.

$$C = k\varepsilon A/d \quad (2)$$

In Eq. (2), ε is permittivity, A is the area of the capacitor, d is the insulator thickness and k is dielectric constant. The MIM structures have an area of 0.015006 cm^2 and also were used to calculate the insulator breakdown field, which is an important parameter that supply information related to the quality of the SiO_2 films produced.

3. Results and discussion

The effect of the spinner speed (RPM) for the SOG deposition on the refractive index of the SiO_2 films was studied. Fig. 1 shows the refractive index as a function of the spinner speed for the SOG deposition, for three different solutions: A) undiluted SOG, B) SOG diluted with DI and C) SOG diluted with 2-propanol. The refractive index of undiluted SOG films shows a strong dependence with the spinner speed. At low spinner speed refractive index is low, close to 1.25 (for 3000 RPM), while increasing the spinner speed it increases as well, to about 1.6 (for 5000 RPM).

On the other hand, the films produced from diluted SOG do not show a significant change on refractive index. A possible reason is that the solvents used as diluents for SOG provide an easier way for the evaporation of the organic materials contained in the SOG solution. The refractive index value of the films produced from diluted SOG is close to that of thermally grown stoichiometric SiO_2.

Fig. 2 shows the absorption coefficient of the films prepared from SOG. It was identified as the Si–O bond (at 1072 cm^{-1}), which is also found on thermally grown SiO_2 [5]. The Si–OH (at 920 cm^{-1}), O–H (at 3490 cm^{-1}), C–H and C–O (at 1139 cm^{-1}) bonds are probably related to the organic solvent material present on the SOG [5]. We observed a considerable reduction of Si–OH (920 cm^{-1}) and O–H bonds (3490 cm^{-1}) in the films produced from diluted SOG, which is an indication of a good quality film.

The deconvolution of the peaks in the region from 1250 cm^{-1} to 1000 cm^{-1} for the films produced from diluted SOG is shown in Fig. 3a) SOG diluted with 2-propanol and Fig. 3b) SOG diluted with DI.

We found a shift in the position of the Si–O stretch peaks for samples produced from diluted SOG. For the films obtained from SOG diluted with 2-propanol the position was 1070 cm^{-1} and for that obtained from SOG diluted with DI the position was 1074 cm^{-1}. We believe that this is because the properties of the films produced from SOG diluted with DI approach a thermal oxide state. In accordance with this, M. P. Woo et al. found that the Si–O peak shifts to higher wave numbers when the organic solvents are completely removed from the film, converting the siloxane into a silicate structure [6]. This occurs when the Si–O peak position approaches to 1080 cm^{-1} during the annealing. Also, they found that as the SOG transforms into a silicon dioxide state, the area ratio of asymmetric Si–O stretch (1070 cm^{-1}): Si–O–Si stretch (1200 cm^{-1}) approaches 5.7:1. In the films produced from SOG diluted with 2-propanol the area ratio is 3.1:1, while in the films produced from SOG diluted with DI the area ratio is much higher than 5.7:1, which is possibly related to the fact that the Si–O–Si stretch apparently is imperceptible. From the above mentioned, we believe that the films produced from SOG diluted with DI have a similar structure to that of the thermally grown SiO_2.

On the other hand, the deconvolution shows a reduction of the C–H, C–O peaks (1139 cm^{-1}) in the films produced from diluted SOG samples. That supports our supposition that the solvents (2-propanol and DI) make easier the evaporation of the organic material presented in the SOG.

Table 1 shows the content of the areas of the Si–O stretch bonds and the C–H, C–O bonds. The ratio of the areas is shown also. In the films produced from undiluted SOG the area ratio is 0.86 due to the higher content of C–H and C–O bonds, while in the films produced from SOG diluted with 2-propanol is 2.92 and for the films produced from SOG diluted with DI is 16 due to the much lower content of C–H, C–O bonds. These results are in agreement with those obtained above.

In the MIM structures we measured the current–voltage characteristics in order to obtain the insulator breakdown field. Fig. 4 shows the breakdown field for the MIM structures containing a film produced from SOG diluted with 2-propanol and SOG diluted with DI.

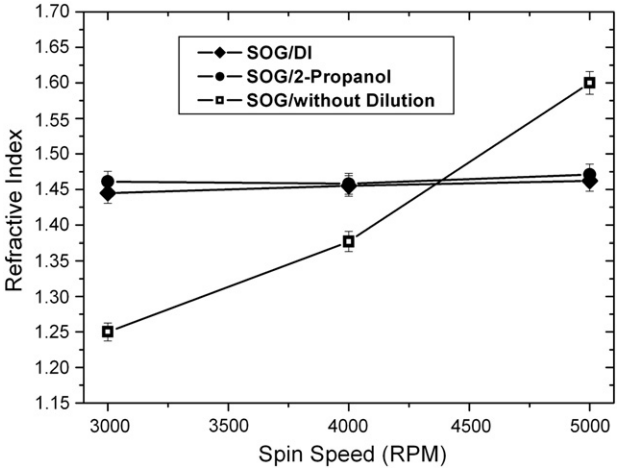

Fig. 1. Refractive index of SOG vs spin speed.

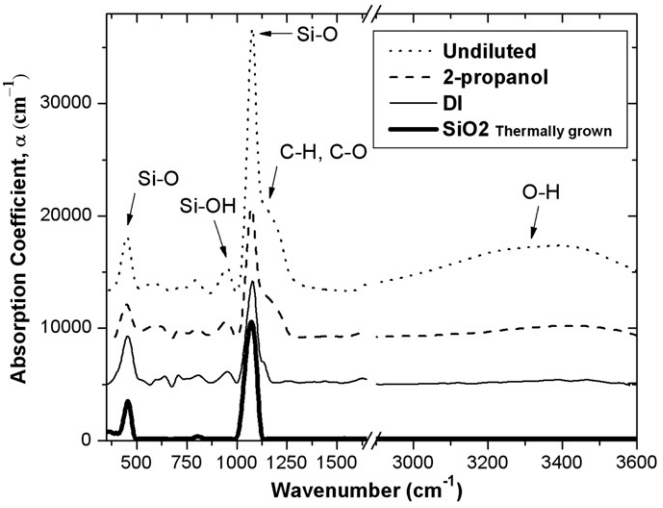

Fig. 2. Absorption coefficient versus wavenumber for diluted and undiluted SOG samples.

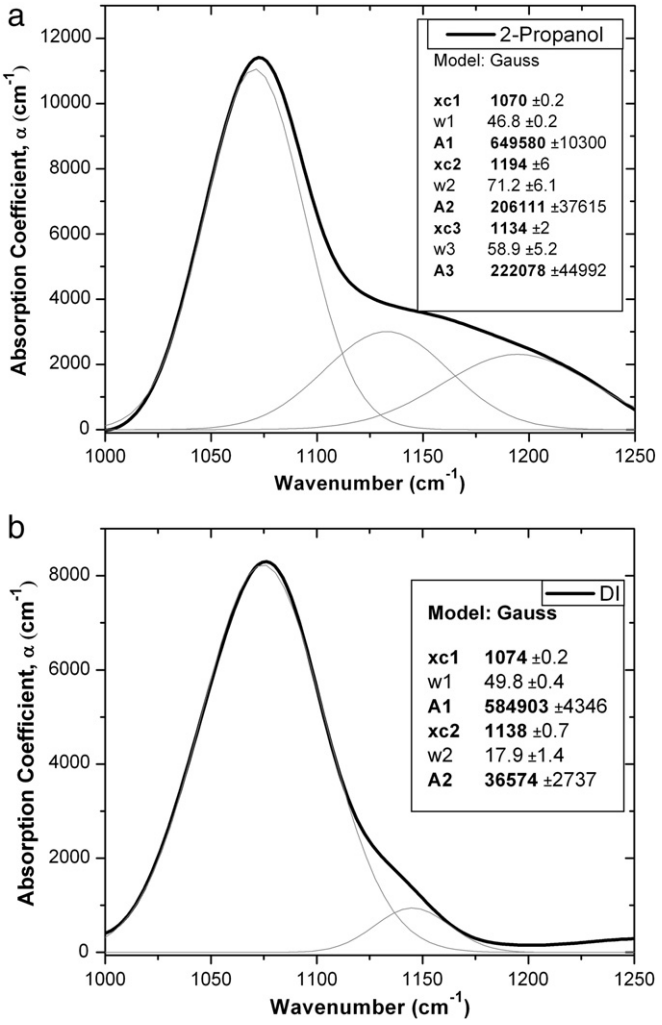

Fig. 3. Deconvolutions of the FTIR peaks located at 1000–1250 cm^{-1} of the SiO_2 films produced from a) SOG diluted with 2-propanol and b) SOG diluted with DI.

Table 1
Area content of Si – O and C – H, C – O bonds and the area ratio of them.

	Content Si – O stretch (area cm^{-2})	Content C – H, C – O (area cm^{-2})	Area ratio Si – O: C – H, C – O
Undiluted SOG	1.0×10^{6}	1.2×10^{6}	0.86
SOG/DI	$584.9\pm4.3\times10^{3}$	$36.6\pm2.7\times10^{3}$	16
SOG/2-propanol	$650\pm10\times10^{3}$	$222\pm45\times10^{3}$	2.92

The maximum voltage applied to the samples was 100 V. The insulator breakdown field for the MIM structure containing a film produced from SOG diluted with 2-propanol was approximately 4.5 MV/cm, while for the MIM structure containing a film produced from SOG diluted with DI was approximately 21 MV/cm. The dielectric constant k of the SiO_2 films prepared from diluted SOG is approximately 4.1. These results are even better than those obtained from methylsiloxane SOG deposited at 425 °C, from SiO_2 deposited by Low-temperature chemical vapor deposition (CVD) and by plasma enhanced CVD, and from SiNx films deposited at low temperatures [7–10]. Our results suggest that the SiO_2 film produced from the SOG diluted with DI is an excellent candidate to be used as insulator on semiconductor devices fabricated on flexible and large-area substrates.

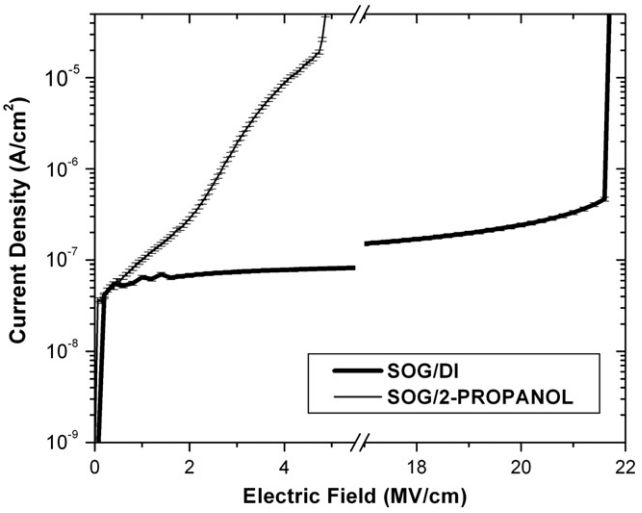

Fig. 4. Breakdown field for the MIM structures containing a SiO_2 film produced from SOG diluted with 2-propanol and diluted with DI.

4. Conclusions

The study of SiO_2 films produced from SOG diluted with 2-propanol, and DI is presented. We demonstrated that dilution of SOG is necessary to obtain good quality films cured at 200 °C. From FTIR spectroscopy we observed a considerable reduction of Si – OH bonds (920 cm^{-1}) and O – H bonds (3490 cm^{-1}) in diluted samples. Besides, the deconvolutions of the peaks located at 1250–1000 cm^{-1} show a notable reduction of the C – H, C – O peaks in the films produced from SOG diluted with DI. This confirms our supposition that the solvents used together with the SOG make easier the evaporation of the organic material presented in the SOG solution.

The results are in accordance with those obtained from the optical and electrical characterization. The films produced from diluted SOG showed a refractive index and dielectric constant very close to those of the thermally grown SiO_2. The insulator breakdown field for the MIM structures with SiO_2 films produced from SOG diluted with DI was approximately 21 MV/cm. All these results suggest that SOG diluted with DI is an excellent candidate to be used as insulator on flexible and large-area electronics.

Acknowledgments

The authors acknowledge the microelectronics laboratory staff of INAOE and M. Dominguez acknowledges CONACYT for the scholarship No. 160547.

References

[1] H. Gleskova, S. Wagner, V. Gasparik, P. Kovac, J. Electrochem. 148 (2001) G370.
[2] J.J. Huang, C.J. Liu, H.C. Lin, C.J. Tsai, Y.P. Chen, G.R. Hu, C.C. Lee, J. Phys. D Appl. Phys. 41 (2008) 245502.
[3] J. Jang, K. Cho, S. Lee, S. Kim, Nanotechnology 19 (2008) 015204.
[4] P.C. Joshi, A.T. Voutsas, J.W. Hartzell, ECS Trans. 19 (9) (2009) 35.
[5] A.L. Smith, Applied Infrared Spectroscopy, Wiley-Interscience, New York, 1979, p. 287.
[6] M.P. Woo, J.L. Cain, C. Lee, J. Electrochem. 137 (1990) 196.
[7] J.H. Cheon, J.H. Bae, W.G. Lee, J. Jang, Electrochem. Solid State Lett. 11 (2008) H77.
[8] L. Teng, W. Anderson, Mater. Res. Soc. Symp. Proc. 483 (1998) 147.
[9] H. Chatham, M. Mogaard, Y. Okuyama, H. Treichel, Mater. Res. Soc. Symp. Proc. 913 (2006) D0308.
[10] K. Park, G. Parsons, J. Vac. Sci. Technol., A 22 (2004) 2256.