Available online at www.sciencedirect.com
SCIENCE DIRECT®

Applied Surface Science 228 (2004) 48–52

applied surface science

www.elsevier.com/locate/apsusc

Thermal annealing in FHD Ge-doped SiO_2 film for applications in optical waveguides

Letian Zhang[a,*], Wenfa Xie[a], Jian Wang[b], Aiwu Li[a], Hua Xing[a], Wei Zheng[a], Yushu Zhang[a]

[a]*National Integrated Optoelectronics Laboratory, Jilin University, Changchun 130023, PR China*
[b]*College of Physics, Jilin University, Changchun 130023, PR China*

Received 20 October 2003; received in revised form 20 October 2003; accepted 17 December 2003

Abstract

Thermal annealing effects on the microstructures and optical properties of Ge-doped SiO_2 films fabricated by flame hydrolysis deposition were investigated. Microstructure modifications from rough to smooth were measured by atomic force microscope at different annealing temperatures. The refractive index (n) and extinction coefficient (k) were obtained by variable angle spectroscopic ellipsometry. It is concluded that k decreased and n increased with increasing annealing temperature. The results suggest the improvement of the film quality can be achieved by thermal annealing.

Keywords: Ge-doped SiO_2; Flame hydrolysis deposition; Thermal annealing

1. Introduction

Planar lightwave circuits (PLCs) based on silica waveguides offer an attractive and low-cost technology for both passive and active devices [1–3]. Because of the high optical transparency and its photosensitivity to ultraviolet light which enables direct writing of planar waveguide, combined with low propagation and low waveguide to fiber coupling losses, Ge-doped SiO_2 glass have found a wide range of application for PLCs [4,5]. A planar waveguide is composed of under-cladding, core and overcladding layer. The Ge-doped SiO_2 film is used as core layer, and its refractive index can be tuned by adjusting the Ge doping level. Many techniques such as chemical vapor deposition [6,7], sol–gel [8], magnetron rf-sputtering [9] and flame hydrolysis deposition [10–13] have been employed to deposit Ge-doped SiO_2 films. FHD process allows low-loss waveguides to be defined with well-controlled thickness and refractive index over large areas, which appears to be one of the promising methods.

In this paper, we have fabricated Ge-doped SiO_2 films on Si substrates by FHD. The annealing process is then carried out for consolidation in air. The aim of the present work is to investigate the effect of thermal annealing on the microstructure and optical properties of Ge-doped SiO_2 films.

2. Experimental

Samples used are Ge-doped silica films prepared on (1 0 0)Si substrates by flame hydrolysis deposition

* Corresponding author. Tel.: +86-4318499017; fax: +86-4318981524.
E-mail address: letianzhang@hotmail.com (L. Zhang).

0169-4332/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2003.12.022

(FHD). The same experimental setup as described in our previous letter was used in the present experiment [13]. In this study, $SiCl_4$ and $GeCl_4$ mixtures carried by He gas were used as source gas, and introduced into the oxy/hydrogen torch through mass flow controllers, respectively, where they are subsequently hydrolyzed on Si substrate placed on the turntable. The temperature of the substrates was kept constant during deposition by water-cooling the substrate holder. As a consequence, SiO_2–GeO_2 glass particles were formed on Si substrate placed on the turntable. During deposition process, we adjusted the $GeCl_4$ flow rate to control the GeO_2 concentration, while the values of H_2/O_2 and $SiCl_4$ flow rate keeping constant. After that, the Si wafers with the porous particles were put into electric furnace heating up to different temperatures of 1000, 1050, 1100 and 1150 °C for 2 h for consolidation in air.

The chemical compositions of the films were analyzed by X-ray photoelectron spectrometer (XPS) on VG ESCALAB MK II in vacuum at a base pressure of 1×10^{-7} Pa with the resolution of 0.2 eV using a Mg Kα source. The film was also studied using Digital Nanoscope IIIa AFM equipped with an integrated silicon tip in tapping mode to present analytic details of the surface roughness and surface microstructure. The refractive indices of the samples were determined using M-2000 variable angle incidence spectroscopic ellipsometer (VASE) made by J.A. Woollam Co. Ltd., and the VASE data were acquired at four angles of incidence (55°, 60°, 65°, 70°) over the spectral range of 250–1700 nm.

3. Results and discussion

The purity and composition of 1150 °C annealed sample were performed by XPS. The peak cores of the sample at 32.7, 102.7 and 531.7 eV correspond to the binding energies of Ge 3d, Si 2p and O 1s, respectively. And the quantification of peaks of Ge 3d and Si 2p for the 1150 °C annealed film gives the ratio of Ge:Si as 10:90.

Fig. 1 shows the comparison of refractive indices of $10GeO_2$–$90SiO_2$ films annealed at different temperatures (1000, 1050, 1100 and 1150 °C) in air for 2 h on wavelength by VASE. As the wavelength increases, the refractive index of the film decreases. And when the annealing temperature increases, the refractive index rises. It is well known that densification occurs when the silica film is annealed at different temperatures, and higher annealing temperature result in higher densities and refractive indices [14,15]. It can be observed that the refractive index is almost identical at lower temperatures and marked distinct at higher temperatures. This is due to the higher thermal annealing temperature. The more interfusion with GeO_2 and SiO_2, the higher the refractive index will be obtained.

In order to further investigate this, AFM was used to examine the surface morphologies of the films deposited on (1 0 0)Si substrates. For comparison, Fig. 2 shows the AFM images of the films annealed at different temperatures for 2 h, with the scanning area of 1 μm × 1 μm. It can be seen that appearance of the surface depends strongly on the thermal treatment.

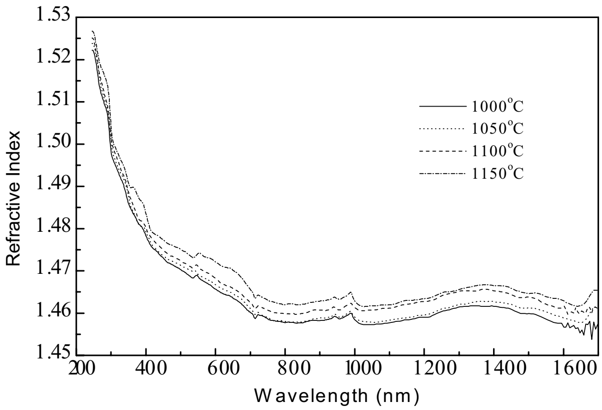

Fig. 1. Comparison of the refractive indices of the films annealed at 1000, 1050, 1100 and 1150 °C for 2 h, respectively.

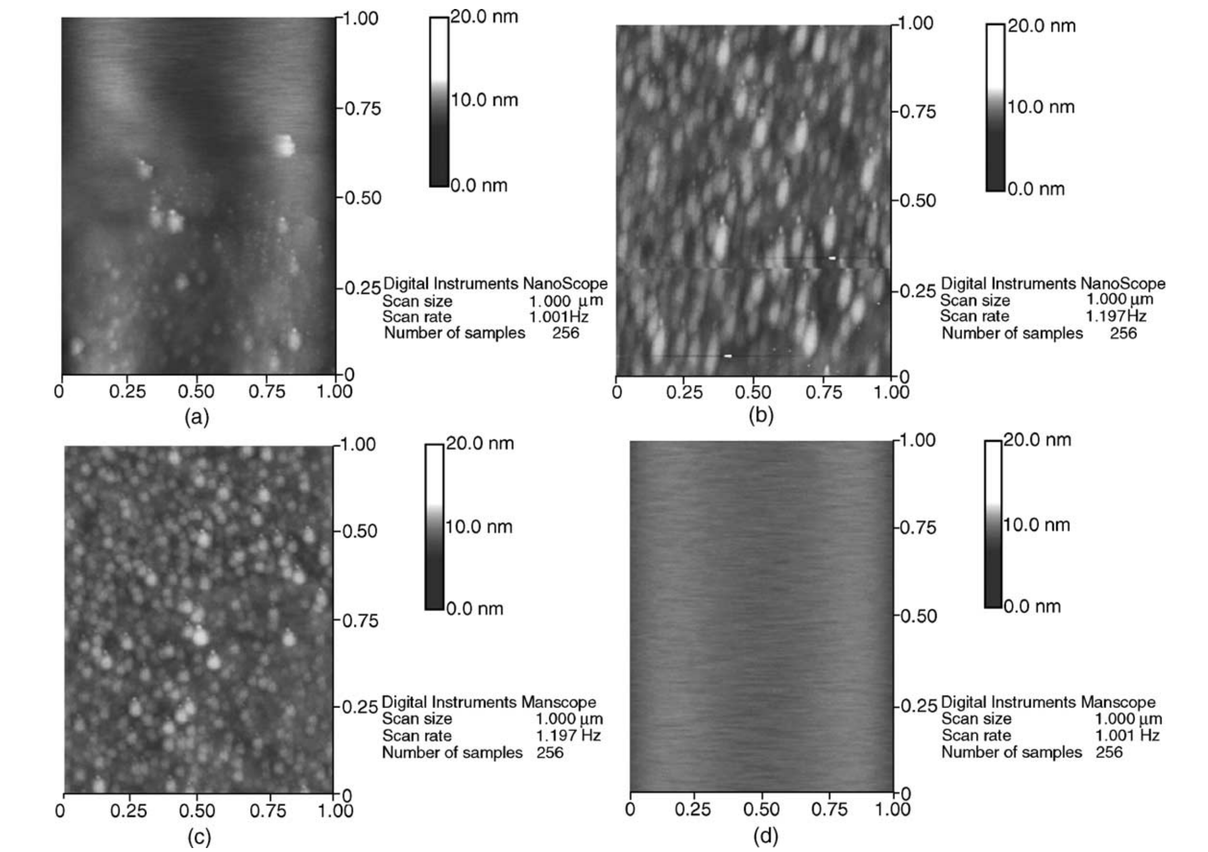

Fig. 2. AFM images (1 µm × 1 µm) of the films annealed at different temperature: (a) 1000, (b) 1050, (c) 1100 and (d) 1150 °C for 2 h.

When it was annealed at 1000 °C, no continuous grains were observed throughout the surface of the films. When the annealing temperature reaches 1050 °C, the surface becomes rough, and the particles observed in Fig. 2(b) are 30–70 nm in diameter. For 1100 °C annealing temperature in Fig. 2(c), the film become more and more organized and the surface is made up of small crystals, which is smaller than that observed in (b). As the temperature is higher enough to 1150 °C, there is a distinct change of the surface structure and it becomes smooth uniformly without any defects. The parameter commonly used for describing the roughness characteristics of a surface is the root-mean-square (rms) roughness R_{rms}. The R_{rms} of the films in Fig. 2(a)–(d) are 0.484, 0.339, 0.327 and 0.217 nm, respectively. As the temperature becomes higher, the fusion of the film can be occurred much easier than that annealed at lower temperature, which leads to the smallest value of R_{rms}. It can be concluded that all the films are in good quality due to such low roughness. The decreases with the roughness are attributed to the changes in the densification by thermal annealing.

The influence of annealing temperature on the refractive index at 1550 nm with different GeO_2 concentration measured by VASE is shown in Fig. 3. It is observed that the refractive indices become higher as the annealing temperature rises for all the films with different ratios of Ge and Si (measured by XPS). The refractive indices at the wavelength of 1550 nm vary from 1.4555 to 1.4605 for $7GeO_2$–$93SiO_2$, from 1.4586 to 1.4639 for $10GeO_2$–$90SiO_2$ and from 1.4615 to 1.4678 for $14GeO_2$–$86SiO_2$ film. Compared with the lower ratio of Ge and Si at the same annealing temperature, the refractive index of the higher ratio is larger, because the refractive index of GeO_2 is higher

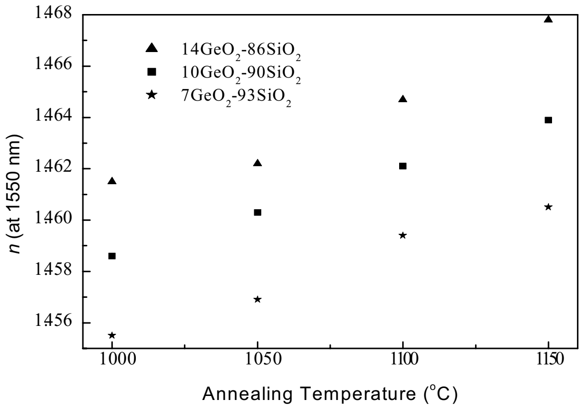

Fig. 3. The influence of annealing temperature on the refractive index (n) at 1550 nm of $7GeO_2$–$93SiO_2$ film (stars), $10GeO_2$–$90SiO_2$ film (squares) and $14GeO_2$–$86SiO_2$ film (triangles).

than that of SiO_2. The variation of the refractive index is approximately linear on the annealing temperature. It is also considered that the film would be more condensed when it is annealed at a higher temperature.

For silica waveguide, the extinction coefficient of the core layer is also important. Fig. 4 shows the extinction coefficients of the as-deposited film and the film annealed at 1150 °C for 2 h. The values are small as a whole, and seem to be zero (less than the order of 10^{-6}) longer than 1100 nm for each film. As apparent from the figure (b), the extinction coefficient decreases after annealing. Their change is obvious in the ultraviolet area, and weak in the visible and infrared ranges by thermal annealing, which is expected for silica waveguide operating at long wavelength.

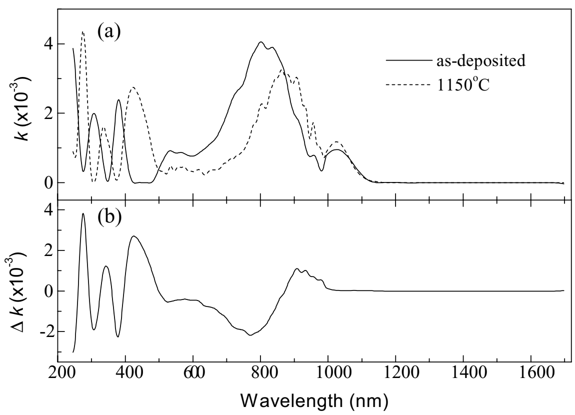

Fig. 4. (a) Extinction coefficients (k) of the as-deposited film (solid line) and the film annealed at 1150 °C for 2 h (dash line). (b) Extinction coefficients change (Δk) induced by the thermal annealing at 1150 °C for 2 h.

As is known that the germanium oxygen deficiency centers (GODCs) exist mainly in Ge-rich areas, therefore, high UV photosensitivity to the defect formation cannot be obtained in a sample that has homogeneous Ge distribution [16,17]. In this work, the Ge-doped SiO_2 film is uniformly distributed with Si–O–Ge and has no inhomogeneous Ge distribution areas from the analyses above. Thermal annealing improves the quality on the structure and optical properties of Ge-doped SiO_2 film, but not leads to the photosensitivity to UV light that enables direct writing of gratings or planar waveguide devices. To solve this problem, Lemaire et al. [18] have reported a simple technique named "hydrogen loading". The proposed model for the reaction in Ge-doped SiO_2 glass is that H_2 molecules react at normal Si–O–Ge sites at high pressure, resulting in the formation of oxygen deficient Ge defects, which contribute to the distinct index change. Using this hydrogen technique, the refractive index change of $14GeO_2$–$86SiO_2$ film described above can reach 0.34% after exposure to KrF excimer laser.

4. Conclusion

Thermal annealing effects on Ge-doped SiO_2 films grown by FHD were studied through surface observations with AFM and optical measurements with VASE. It can be concluded that the films become denser and denser uniformly with the higher annealing temperature, resulting in the higher refractive index with low extinction coefficient. These analyses show that the annealing temperature has a strong influence on the properties of the films and the film annealed at high temperature is in good quality. But this could not lead to high UV photosensitivity related to the oxygen-deficient defect centers associated with Ge, which could be improved through H_2-loading process.

Acknowledgements

This work was supported by the Major State Basic Research Program under Grant No. G2000036602.

References

[1] N.F. Borrelli, D.W. Hall, H.J. Holland, D.W. Smith, J. Appl. Phys. 61 (1987) 5399.
[2] M. Kawachi, Opt. Quantum Electron. 22 (1990) 391.
[3] S. Valette, J. Modern Optics 35 (1988) 993.
[4] F. Bilodeau, B. Malo, J. Albert, D.C. Johnson, K.O. Hill, Opt. Lett. 18 (1993) 953.
[5] S.G. Blanco, A. Glidle, J.H. Davies, J.S. Aitchison, J.M. Cooper, Appl. Phys. Lett. 79 (2001) 2889.
[6] G.. Grand, J.P. Jadot, H. Danis, S. Valette, A. Fournier, A.M. Grouillet, Electron. Lett. 26 (1990) 2135.
[7] M. Svalgaard, C.V. Poulsen, A. Bjarklev, O. Poulsen, Electron. Lett. 30 (1994) 1401.
[8] K.D. Simmons, G.I. Stegeman, B.G. Potter, J.H. Simmons, Opt. Lett. 18 (1993) 25.
[9] A.G. Rolo, O. Conde, M.J.M. Gomes, M.P. Santos, J. Mater. Proc. Thechnol. 92–93 (1999) 269.
[10] M. Kawachi, M. Yasu, T. Edahiro, Electron. Lett. 19 (1983) 583.
[11] N. Takato, M. Yasu, M. Kawachi, Electron. Lett. 22 (1986) 321.
[12] Y. Hibino, T. Kitagawa, M. Shimizu, F.H. Anawa, A. Sugita, IEEE Photon Technol. Lett. 1 (1989) 349.
[13] L.T. Zhang, W.F. Xie, Y.D. Wu, H. Xing, A.W. Li, W. Zheng, Y.S. Zhang, Opt. Mat. 22 (2003) 283.
[14] A.E. Geissberger, F.L. Galeener, Phys. Rev. B. 28 (1983) 3266.
[15] R. Bruckner, J. Non-Cryst. Solids 5 (1970) 123.
[16] H. Hosono, K. Kawamura, H. Kawazoe, J. Nishii, J. Appl. Phys. 80 (1996) 3115.
[17] M. Fujimaki, S. Shimoto, N. Miyazaki, Y. Ohki, K.S. Seol, K. Imamura, J. Appl. Phys. 86 (1999) 5270.
[18] P.J. Lemaire, R.M. Atkins, V. Mizrahi, W.A. Reed, Electron. Lett. 29 (1993) 1191.