Absorption Spectra of Silicon Rich Oxide Films with Different Annealing Time to be Used in Optical Sensor

J. A. Luna-López *, M. Aceves-Mijares, O. Malik
Department of electronic, INAOE, Apdo. 51, Puebla, Pue., México 72000
* Phone: + 52 (222) 2 47-20-11, jluna@inaoep.mx, maceves@ieee.org

Abstract

Silicon Rich Oxide (SRO) has optical properties that can be used in silicon optoelectronic sensors. The study of the SRO optical characteristics and its relation with the absorption would provide information on the mechanism of radiation. In this paper, transmittance spectra, refractive index and I-V characteristics of silicon rich oxide films have been obtained. Absorption spectra were studied and the optical band gap was determined. The optical band gap and refractive index changes conform the relation of flow Ro (Ro = $[N_2O]/[SiH_4]$) and thermal treatments time increased, where excess of silicon constitutes a combined effect of electron-hole pairs in the silicon substrate and photo excited electrons in the SRO films. We constructed photodetectors with different SRO, which show a good photocurrent at different wavelengths depending on silicon excess.

Keywords: Silicon Rich Oxide, Refractive Index, Optical Band Gap, Photodetectors.

Introduction

Silicon (Si) is a material of indirect band which makes a poor light emitter. In the last decade, an intense research activity has been accomplished towards the study of different approaches to solve the physical inability of Si to act as a light emitter. Since the observation of strong photoluminescence (PL) of porous silicon by Canham [1], a lot of works has been done to study Si-based material. Silicon rich oxide, SRO, is one of such materials that have been studied due to its interesting optical and electrical characteristics, which varied with the silicon excess in the films [2, 3]. These characteristics have led towards a variety of applications such as waveguide, no volatile memories, voltage peaks suppressers, detectors and emitting light devices [4, 5, 6]. The last two are interesting optoelectronics applications compatible with the Si technology. SRO films can be obtained by different techniques, such as Chemical Vapour Deposition (CVD), PECVD and LPCVD (PE and LP are for Plasma Enhancement and Low Pressure), ionic implantation of silicon into thermal silicon oxide, sputtering, sol-gel, etc [7, 8, 9, 10]. The optical characteristics such as refractive index of SRO films can be varied from 1.44 to 2. The absorption spectra can also be varied with the silicon excess in the films, which is attractive to fabricate diverse devices.

In the present work, the characteristics of transmittance and refractive index of the SRO films obtained by LPCVD have been studied as a function of the flow ratio Ro, and thermal treatment time (TTt). The differences in the mentioned characteristics show that varying Ro and the annealing time, it is possible to change the optical and electrical properties of the SRO films. Moreover, the absorption spectrum shows that the optical band gap changes with the content of silicon. The refractive index shows similar behavior, increasing with the amount of excess silicon and with thermal treatment time. Therefore, it is possible to obtain photodetectors at different wavelengths. Also, this work presents I-V characteristics that show changes in the photocurrent, which dependent on silicon excess of the SRO films. These characteristics are relevant to the fabrication of sensors devices.

Experiment

SRO films were deposited on sapphire and N type silicon with resistivity 2-5 Ω-cm. The deposition system is a horizontal hot-wall LPCVD reactor using SiH_4 (Silane) and N_2O (nitrous oxide) as reactive gases at 700 ºC. The flow ratio of SiH_4 and N_2O (Ro = $[N_2O]/[SiH_4]$) was used to control the amount of silicon, the pressure varied from 1.64-1.94 Torr. The annealing temperature was 1100 ºC in N atmosphere and thermal treatment time (TTt) was 30, 60 and 180 minutes. The samples used to obtain the I-V characteristics have an Al/SRO/Si MOS-like structure. Al was also evaporated for back contact. Finally, the samples were sintered at 450 °C in forming gas.

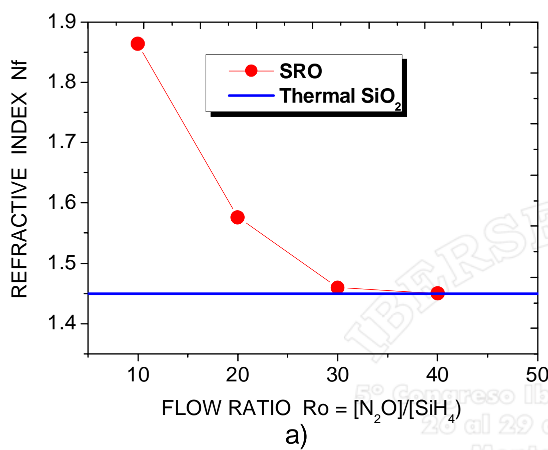
Optical transmittance measurements were made in the range of the U-V to NIR near infrared at room temperature, using spectrophotometer Perkin-Elmer LMBD 3B UV/VIS.

The refractive index and the oxide thickness were measured with an Ellipsometer null Gaertner L117 with a laser of He-Ne (632.8 nm).

I-V characteristics were measured using a computer controlled system. Current was measured using a Keithley electrometer 6517 A, with voltage steps of 1 volt every 2 seconds.

Experimental Results

The refractive index as a function of Ro is shown in Fig. 1 a). Also, Fig. 1 b) shows the behavior of the refractive index at different TTt. With different TTt, the refractive index for Ro = 10 varies without any pattern. The refractive indexes for Ro = 20 and 30 have a slight variation with TTt, and apparently an increase tendency is observed. 660, 450, 460 nm were the SRO thickness of samples with Ro = 10, 20 and 30 respectively.



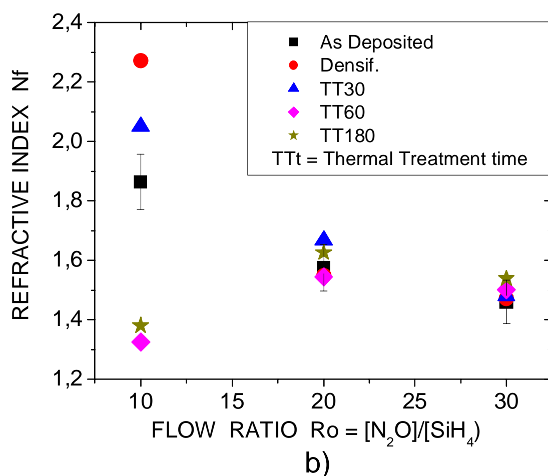


Figure 1. Refractive index of SRO films, a) Refractive index as a function of Ro for as-deposited films, and b) Refractive index as a function of Ro for different annealing times.

The transmittance spectra for SRO films with Ro = 10, 20 and 30 deposited on sapphire are shown in Fig. 2. As can be observed in this Figure, the transmittance of these films deposited on sapphire is high (> 80 %) in the large wavelength range and they reduce as the wavelength moves towards the short wavelengths range. The cutoff wavelength varies with the excess silicon, and a large variation is observed between samples with Ro = 10 and 30.

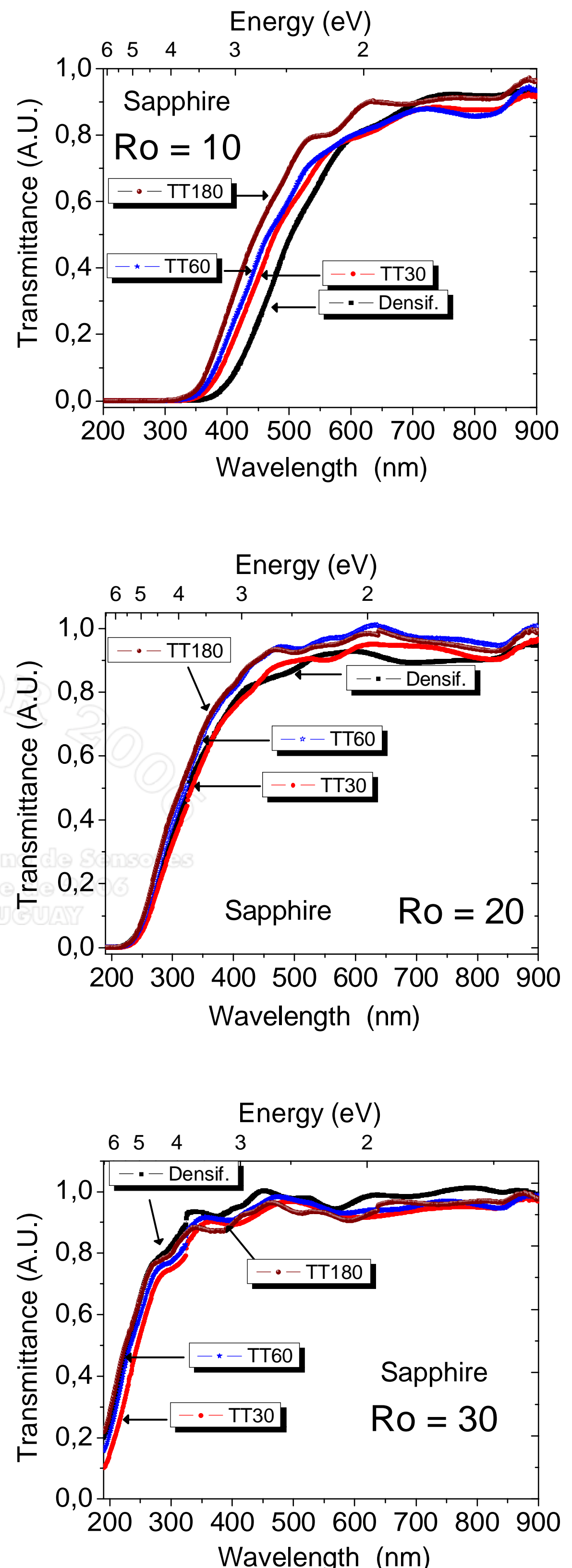


Figure 2. Spectral transmittances are shows in the range of the U-V to NIR for SRO films at different Ro and different thermal treatments time (TT).

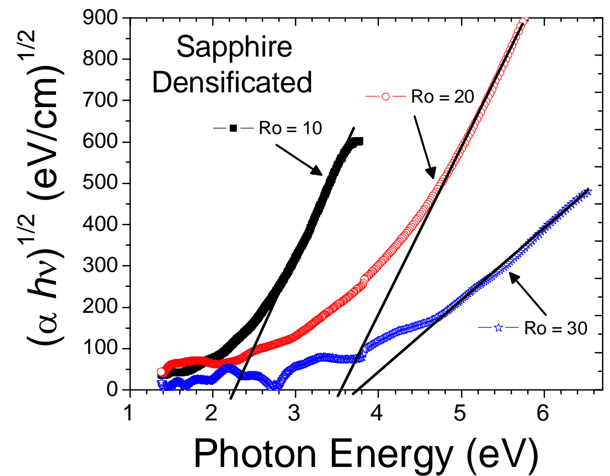
Discussion

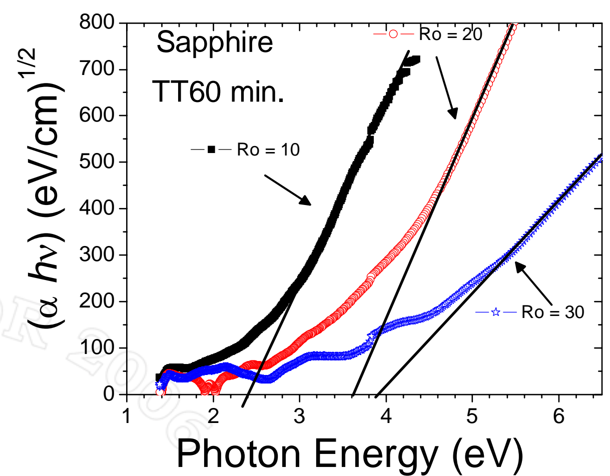
The refractive index of SRO films depends on the excess silicon. As R_0 increases, the refractive index tends towards the SiO_2 value. On the other way, index moves towards the value for the Si. Thus, the inclusion of Si in these films is evident.

Transmittance spectra are used to determine the optical absorption coefficient and optical band gap. The fundamental absorption edge in most semiconductors follows an exponential law. Where, absorption coefficient α is correlates with the transmittance T and the reflectance R of a sample with thickness d through the relation: $T \approx (1-R)^2 e^{-\alpha d}$. Therefore, the absorption coefficient α is obtained from Transmittance (Fig. 2) and with the relation $\alpha(h\nu) = \frac{-\ln(T(h\nu))}{d}$.

The optical band gap was obtained by the Tauc law, which assumes that $(\alpha\hbar\nu)^{1/2} \propto (\hbar\nu - E_g)$ [11]. The graphs of $(\alpha h\nu)^{1/2}$ versus hν are shown in Fig. 3, and as can be observed the position of the absorption edge moves towards higher energy when the Ro increased. The intersection of the Tauc´s slope with the photon energy axis gives the optical band gap. The obtained optical band gaps are listed in Table 2. The optical band gap of SRO films increases as R_0 increases. As R_0 moves towards low values, the optical band gap moves towards that of the crystalline silicon similar to refractive index. In this case, it is suggested that the absorption process is mainly governed by the excess silicon (nc-Si) in the SRO_{10} films, and as known in this samples the excess silicon produces Si nanocrystals. Then, the absorption process is dominated by the Si nanocrystals, and the absorption behaviour of the nanocrystals is similar to that of the bulk silicon. Like bulk silicon, photons have a big interaction with photons below 550 nm, and short wavelengths are probably absorbed in the silicon nc-Si.

After annealing, in SRO_{30} (SRO with Ro = 30) the silicon excess produces non crystalline nanodots and Si-O defects mainly [12] instead nc-Si. Then, the absorption behaviour resembles more to that of SiO_2. However, the defects interact with the short wavelength radiation that causes absorption in the UV region. The interaction with the UV photons allows using this property to sense UV light. Then, the SRO layer could add a component to the photocurrent, and the SRO act as an active electrode.





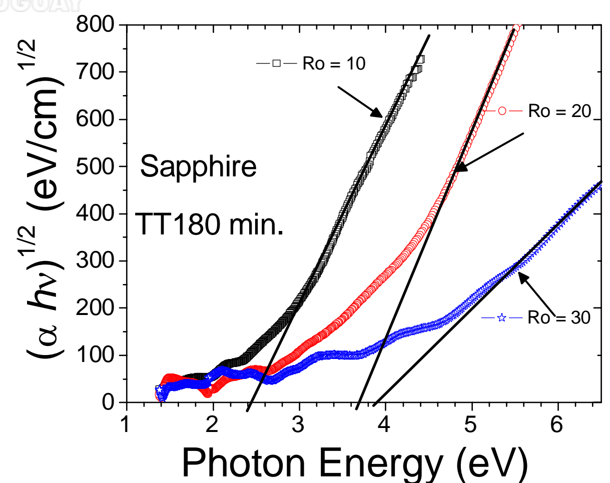


Figure 3. Square root of absorption coefficient α by photon energy $(\alpha h\nu)^{1/2}$ vs. photon energy (hν) for SRO films with different Ro and TT.

Table 2. Optical bang gap in eV for SRO films with different Ro and different TTt.

Ro	Densifícated	TT30 min.	TT60 min.	TT180 min.
	Eg (eV)	Eg (eV)	Eg (eV)	Eg (eV)
10	2.28±0.04	2.4±0.04	2.4±0.02	2.43±0.04
20	3.52±0.03	3.57±0.03	3.6 ±0.06	3.69 ±0.03
30	3.76 ±0.07	3.73 ±0.06	3.86±0.04	3.89±0.04

The behaviour of the optical band gap at different Ro and TTt are compared with c-Si and thermal SiO_2 in Fig. 4. It shows that optical band gap increases in agreement with the increase of the Ro. This confirms our asseverations in previous paragraphs.

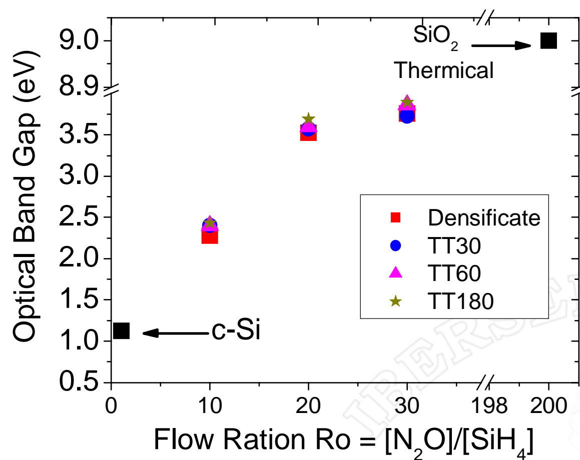


Figure 4. Comparison of optical band gap of c-Si and SiO_2 with SRO at different Ro and thermal treatments time (TT).

Recently works shows that red photoemission in SRO is a result of the deactivation of surface trap, rather of carrier in quantized states [2, 14, 15], in agreement with our propositions.

Understanding these optical properties make possible to propose sensor for different wavelengths. For example in reference [13], in an Al/SRO/Si structure which has opaque aluminium on the active area, it is observed that the photocurrent depends on the Ro of the films. SRO_{10} is much more sensitive to 660 nm wavelength light that SRO_{30}, as shown in Figure 5.

The same kind of device, Al/SRO/Si, but with SRO_{30}, has a high responsivity when illuminated with a lamp rich of 300 nm wavelength, as shown in Figure 6. The responsivity could be due to the characteristic photoemission of SRO in the 650 to 850 nm [16]. If the responsivity is due to the SRO photoemission, then it is necessary to have a PN junction, which could be obtained at reverse voltage due to surface inversion. The Fact that in both cases a response to the photons is obtained confirms that SRO acts as an active layer.

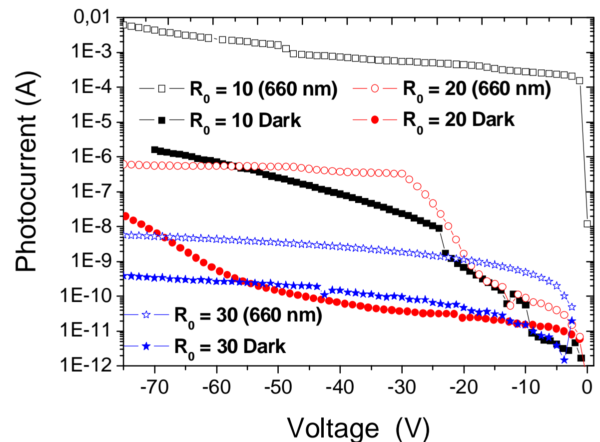


Figure 5. Dark current and photocurrent under 660nm of wavelength for Al/SRO/Si with R_0 = 10, 20, and 30.

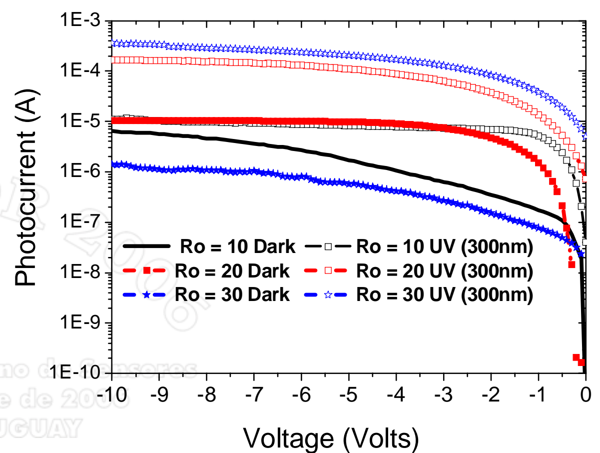


Figure 6. Dark current and photocurrent under approximately 300nm of wavelength for Al/SRO/Si with R_0 = 10, 20, and 30.

Conclusions

Analysis of the Absorption spectra, refractive index and I-V characteristics of silicon rich oxide films were presented. The optical band gap was determined for each one of the SRO films. Al/SRO/Si MOS-like structures were used to obtain photocurrent at different wavelengths (red and UV), where the nc-Si, non crystalline Si nanodots and defects plays an important role in the process of detection of visible and UV light, respectively. It was found that we could significantly enhance the photocurrent by means of SRO films. We demonstrated UV-Visible photodetectors based on thin films (SRO) offer an opportunity for integration of optoelectronics devices on Si and it provides high sensitivity under low voltage.

IBERSENSOR 2006
5º Congreso Iberoamericano de Sensores
26 al 29 de setiembre de 2006
Montevideo - URUGUAY

ISBN: 9974-0-0337-7

Acknowledgements

We would like to thank CONACYT, CONCYTEP-FOMIX for providing support to this work. The authors also thank Pablo Alarcón, Mauro Landa, Carlos Zúñiga, Ignacio Juárez and Netzhualcoyotl Carlos for helping in the preparation of the samples.

References

[1] L. T. Canham; *Silicon Quantum Wire Fabrication by Electrochemical and Chemical Dissolution of Wafers*, Appl. Phys. Letters, 57, 1046 (1990).

[2] Di Maria, J. R. Kirtley, J. Pakulis, D. W. Dong, D. Kuan , F. L. Pesavento, T. N. Theis, N. Cutro, S. D. Brorson; *Electroluminescence studies in silicon dioxide films containing tiny silicon islands*, J. Appl. Phys. Vol. 56, No 2, 401-416, (1984).

[3] M. Aceves, C. Falcony, A. Reynoso, W. Calleja, A. Torres, *The conduction properties of the silicon /off – Stoichiometric SiO_2 diode,* Solid-State Electronics 39, 637 (1996).

[4] M. Aceves, C. Falcony, A. Reynoso, W. Calleja, A. Torres; *The conduction properties of the silicon /off – Stoichiometric SiO_2 diode*, Solid-State Electronics 39, 637 (1996).

[5] D. J. DiMaria, D. W. Dong, F. L. Pesavento; *Enhanced conduction and minimized charge trapping in electrically alterable read-only memories using off-stoichiometric silicon dioxide films*, J. Appl. Phys. 1984; 55 (8): 3000-3019.

[6] M. Aceves, A. Malik, and R. Murphy; *The FTO/SRO/Si structure as a radiation sensor*, In: Sensors and Chemometrics, editors: Maria Teresa Ramirez-Silva *et al*, Research Signpost, ISBN: 81-7736-067-1, 2001, p1-25.

[7] O. Hanaizumi, K. Ono, and Y. Ogawa, Appl. Phys. Lett., (2003), vol.82, pp.538-540.

[8] Y. C. Fang, W. Q. Li, L. J. Qi, L. Y. Li, Y. Y. Zhao, Z. J. Zhang, and M. Lu, Nanotechnology, (2004), vol.15. pp.495-500.

[9] D.Dong et al, J.Electrochem. Soc., (1978), vol.125, pp.819-823.

[10] P. G. Pai, S. S. Chao, and Y. Takagi, J. Vac. Sci. Technol., (1986), vol.A4, p.689.

[11] J.I. Pankove, *Optical Processes in Semiconductors*, Dover New York, 1975.

[12] Herbert R. Philipp, *Optical and Bonding Model Non-crystalline $SiO_x$and SiO_xN_y*, Journal of Non-crystalline solids, (1972), vol. 8-10, pp. 627-632.

[13] A. Luna-López, M. Aceves-Mijares, O. Malik, *Optical and electrical properties of the SRO for Optical Sensors*, published in the Proceedings EUROSENSOR XIX, Vol. I (M, T), No. MP49, 2 Pag. September 11-14, 2005.

[14] Zhixun Ma, Xianbo Liao, and Gonglin Kong et al; *Absorption spectra of nanocrystalline silicon embedded in SiO_2 matrix*, Applied Physics Letters, Volume 75, number 13,1999.

[15] V.I Klimov, Ch. J. Schwars, D. W. McBranch and C. W. White; *Initial carrier relaxation dynamics in ion-implanted Si nanocrystals: femtosecond transient absorption study,* Appl, Phys. Lett., 73, 2603 (1998).

[16] D. Berman, M. Aceves, L. Beriel et al, *Silicon-rich silicon oxide films boost UV sensitivity*, Laser Focus world, pp. 103-104, 2005.