

Some Scientific and Technological Results of the Research on the off Stoichiometry Silicon Oxide

Resultados Científicos y Tecnológicos de la Investigación del Óxido de Silicio Fuera de Estequiometría

Mariano Aceves Mijares¹, J. Pedraza, A. Malik¹, J. Carranza¹, Francisco Flores Gracia¹,
Joel Méndez Morado¹, Jesús Carrillo López², Carlos Domínguez³ and C. Falcony⁴

¹INAOEP, Apartado Postal 51, Puebla, Pue. México

²CIDS, BUAP, Apartado Postal 1651, Puebla, Pue. México

³IMB-CNM, Campus UAB 08913 Bellaterra, España

⁴CINVESTAV, Phys. D. Apdo 14-740, México, D.F.

E-mail: maceves@ieec.org

Article received on June 18, 2001; accepted on February 19, 2002

Abstract

In these projects the Silicon rich oxide (SRO), or off stoichiometry silicon oxide has been studying from several perspectives. The SRO is a double phase material formed by silicon islands embedded in a SiO₂ matrix, whose final characteristics are related with the silicon excess. The silicon excess is determined by the gases precursor ratio, Ro. The junction SRO/Si has been studied too, and it was found that this structure behaves as different devices depending on the characteristics of the SRO and the Si. Our research led us to understand and explain the electronic behavior of the Al/SRO/Si structure. With this knowledge, we have proposed new devices that use the SRO/Si junction with different characteristics. We can mention two devices developed and tested successfully. One is a surge suppresser, and another one is a radiation sensor. In this paper we present some details, and experimental evidence of the mentioned devices.

Keywords: Silicon rich Oxide, Optical Sensors, Suppressor.

Resumen

Hemos estudiado el óxido de silicio fuera de estequiometría, u óxido de silicio rico en silicio (SRO) desde varios puntos de vista. El SRO es un material de doble fase formado por islas de silicio embebidas en una matriz de óxido de silicio. Sus características están determinadas por el exceso de silicio en el SiO₂. El exceso de silicio se determina por la relación de gases reactivos, Ro, durante su obtención. La estructura SRO/Si también ha sido estudiada, y presenta propiedades que dependen de la Ro del tipo y resistividad del silicio. Como resultado de esta investigación hemos entendido y explicado el comportamiento de la estructura SRO/Si. En este trabajo presentaremos los resultados experimentales obtenidos hasta ahora de dos dispositivos nuevos: uno es la estructura Al/SRO/Si que actúa como un supresor de picos de voltaje en la línea de 60 Hz. El otro es un detector de radiación utilizando la estructura SRO/Si.

Palabras Clave: Óxido fuera de Estequiometría, Sensores Ópticos, Supresores.

I Introducción

The off-stoichiometry silicon oxide, or silicon rich oxide (SRO) also known as semi-insulating polysilicon (SIPOS), is a two-phase material formed by silicon dioxide with excess silicon (Dong et al., 1978). The excess silicon can be as high as 17% for SRO and around 90% for SIPOS (Hamasaki et al, 1978). This material is normally obtained by Chemical Vapor Deposition (CVD) from silane and nitrous oxide as the reactive gases. In this method, the gas flow ratio,

$$Ro = [N_2O]/[SiH_4]$$

is used as a parameter that determines the silicon excess. Lately (Kalnitsky et al., 1990), SRO obtained by silicon implantation into silicon oxide has also been reported.

It has been already proposed that compared to a regular MOS structure (Aceves et al., 1996, Aceves et al., 1999, Aceves, Pedraza, et al., 1999), the devices obtained by deposition of SRO on silicon, and covered with a top electrode, show different properties depending on the characteristics of both materials. That means, the Al/SRO/Si device depends on the SRO silicon excess, Ro, and the type and impurity concentration of the silicon substrate.

One of these behaviors is twofold, i.e., it has a dual compartment: as a MOS capacitor and as a reverse biased PN junction. In such device, that we call Capacitor – NP, the MOS structure will produce an inversion layer in the silicon surface and, as in a reverse biased PN junction, the depleted region will grow. In addition, the leakage current characteristic of a reversed PN junction can be collected through the conductive SRO Layer. So the Capacitor – NP will be able

to detect radiation impinging on it (Aceves, Calleja et al., 1999).

Another application that depends on the Silicon and the SRO attributes is the possibility to use the SRO/Si structure as a surge suppresser for 60 Hz lines (Aceves, Pedraza et al., 1999). For this application, the SRO/Si behaves as a Metal Oxide Varistor (MOV) (Harris 1998), but with the advantage of silicon technology compatibility.

It is also investigated the very interesting possibility of use the SRO film by itself as a radiation sensor. We started studying the emission properties of the SRO to better understand the traps, and then the energetic states, inside of the SRO film (Aceves et al., to be published)

The SRO/Si junction shows new properties that can improve the devices nowadays in use, giving place to new results that justify the research efforts. However, the three mentioned applications have their own advantages besides the silicon technology compatibility, for example, low leakage current, simpler technology and the possibility of developing optoelectronic devices fabricated completely in silicon.

In this paper, experimental results of the research done on the mentioned original applications of the SRO/Si structure are shown. Aspects of the various devices behavior will be presented, and for details on the specific device, references are included. It is important to mention that these original results are consequence of the support received from CONACyT to various projects.

2 Experimenta

2.1 Silicon Rich Oxide

Three methods have been evaluated to obtain SRO. The first method was Low Pressure Chemical Vapor Deposition (LPCVD), and the reactive gases were Silane, 5% diluted in nitrogen, and Nitrous oxide. The deposition temperature was 700 to 750 °C, and the pressure was 1 torr. A hot wall CVD system made in our laboratory was used. Ro's ranging from 10 to 30 were used.

The second method was Ion Implantation. In this case, silicon was implanted into thermal oxide. The SRO films were obtained by Si⁺ implantation with 150 keV (projected range of 228.5 nm), and doses of $1 \times 10^{16} \text{ cm}^{-2}$ and $1 \times 10^{17} \text{ cm}^{-2}$. The thermal oxide films were 550 nm thick, and were grown by wet oxidation at 1100 °C on n type Si substrates (100), 2 to 5 Ω-cm.

The third method was a combination of the two already mentioned. That is, first a layer of SRO was deposited on the silicon substrate and then a Silicon implantation into the

SRO layer was done. The implantation conditions were the same as that for Thermal SiO₂.

For device fabrication the LPCVD method have been used to obtain the SRO film.

2.2 Silicon Wafers

All silicon substrates were <100>, n type and two resistivity were used: 3 to 5, and resistivity > 4000 ohm cm. If needed a n+ diffusion or implantation was done.

2.3 Metallization

Evaporated Aluminum was used for back contacts in all cases. In the front of the devices we used two types of electrodes: aluminum and transparent degenerated metallic oxides, until now, basically FTO (Tin oxide doped with Flour). Aluminum was used for all the application where no transmission of visible light was needed. FTO was used when a transparent and electrically conductive film was essential.

3 Results

3.1 Induced PIN Photodiodes

The structure shown in figure 1 is used as an induced PIN photodiode (Aceves et al., 2000, Aceves, Carrillo et al., 2000) The structure has been tested as a photodetector. Results are shown in figures 2. Until now, the devices have been tested under visible light, but we are trying to extend their sensitivity to X rays. As can be seen the dark current is of some nA by square centimeter @ 100 Volts, that makes the device very sensible.

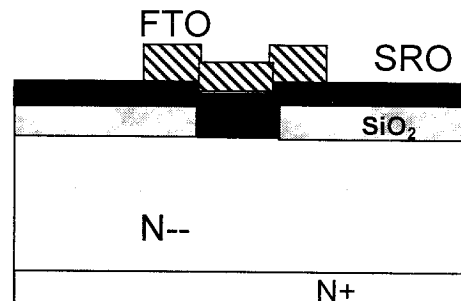


Figure 1. Induced PIN Photodiode structure

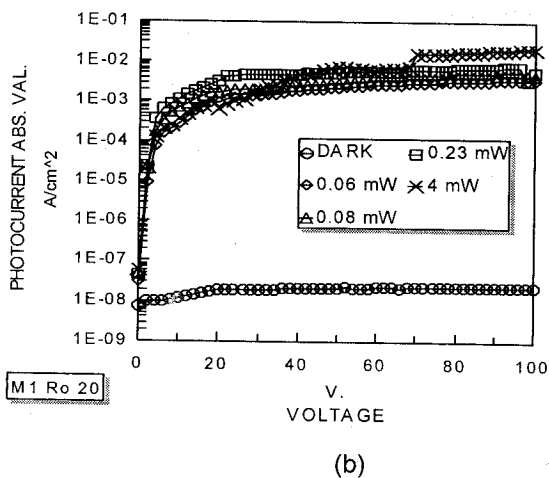
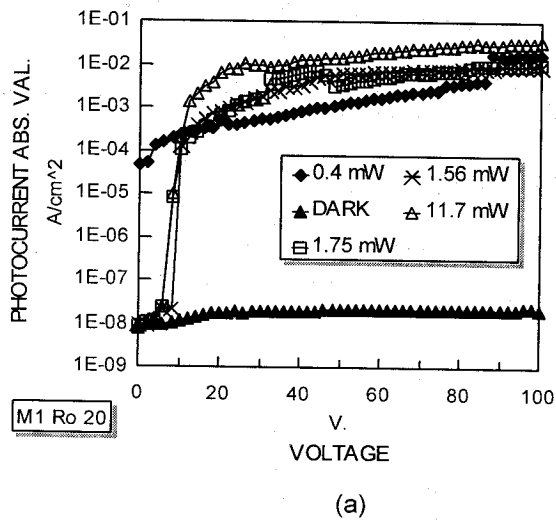


Figure 2 Photocurrent for the structure Al/SRO/Si device shown in figure 1, for (a) 632 and (b) 543 nm wavelength, and various input powers. SRO layers were obtained by LPCVD at a Ro of 20

It is important to say that results obtained are only to experimentally demonstrate that a MOS like structure senses light as a PN junction. That is, the induced PN junction is used in a controllable and stable manner, for the first time. Figure 2 (a) and (b) show how this device responds to two wavelengths; of course more work have to be done to better characterize the device.

To understand how it works, let's think in an N type substrate. When a negative voltage is applied to the FTO an inversion P layer is induced surrounded by a depletion layer. At the beginning, the voltage is not enough to let the electrons tunnel throughout the SiO₂ in the SRO film, so a MOS capacitor behavior is presented by the device. Under these circumstances, even if light shines on the devices a low DC current is sustained. The current is dominated by high resistance of the SRO film. As the voltage is increased, the electrons are able to move between excess silicon islands tunneling the SiO₂. Under these conditions, the current is limited by the leakage current of the P – N induced junction. So, if visible light impinges the device a higher current will be obtained, similar to a standard P – N diode. Then, the device shows a second behavior, that is, as a reverse biased P – N junction, in this case the depletion layer will grow as a function of voltage. A band diagram of the device reverse biased is shown in figure 3.

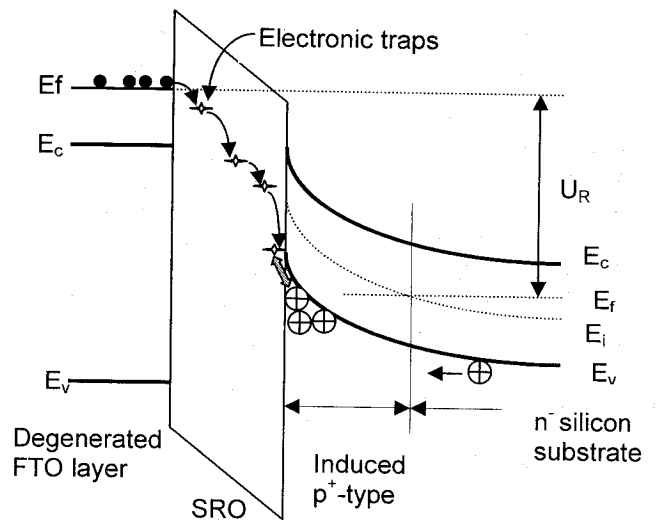


Figure 3. Band diagram of the reverse biased FTO/SRO/Si device

3.2 Luminescence

In order to understand the electronic traps in SRO and to use them to detect radiation, we have studied the emission spectra obtained by photo and cathode – luminescence. For these experiments, SRO layers obtained by ion implantation were used. The studies include the effect of heat treatments (Flores et al., 2000, Flores Gracia et al., 2000, Flores 1 et al., 2000). Figures 4 and 5 show representative emission spectra.

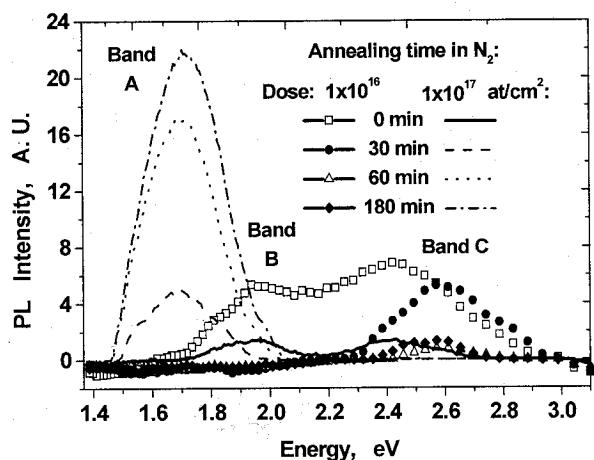


Figure 4. Photoluminescence spectra of Si-implanted thermal oxides. The position of the bands depend on implantation's doses, the PL intensity depends on thermal treatments

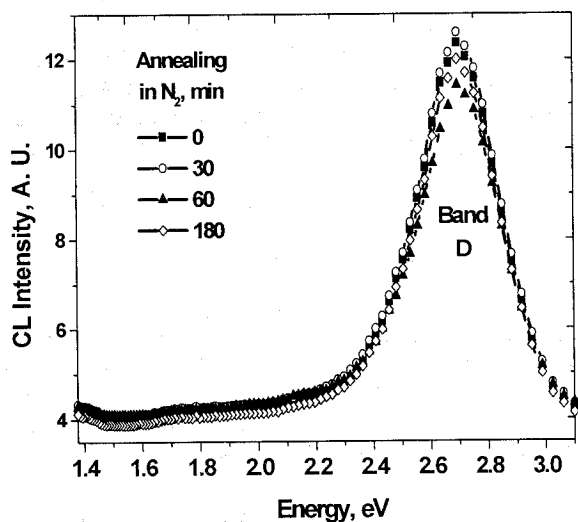


Figure 5. Typical Cathodeluminescence spectra of Si-implanted thermal oxides

Analysis of the results is underway in order to have a better understanding of the emission process, that is a nowadays scientific problem and many research groups are working in this interesting field (Shimizu-Iwayama et al., 1998, Rebohle et al., 1998, Calleja et al., 1995, Ma et al., 1998). However, using our preliminary results, we were able to propose a new emission model (Aceves et al., to be published) (Aceves et al., to be published), and it will be improved as the research progress. Then, the photocurrent, or light emission, generated inside the SRO layer will sense radiation. That is, develop devices that use the SRO film by itself as a detector.

3.3 Surge Suppressor

Figure 6 shows the Al/SRO/Si structure used as a surge suppresser. These devices have a response similar to that of a MOV. The device has been tested under various peak generator models according with the IEEE standards (ANSI/IEEE 1982, ANSI/IEEE 1980). It has been found that two conduction regimens can be distinguished, at low currents a generation current dominates. However, at high current regimen a Poole – Frenkel tunneling dominates (Hielscher and Preier 1968).

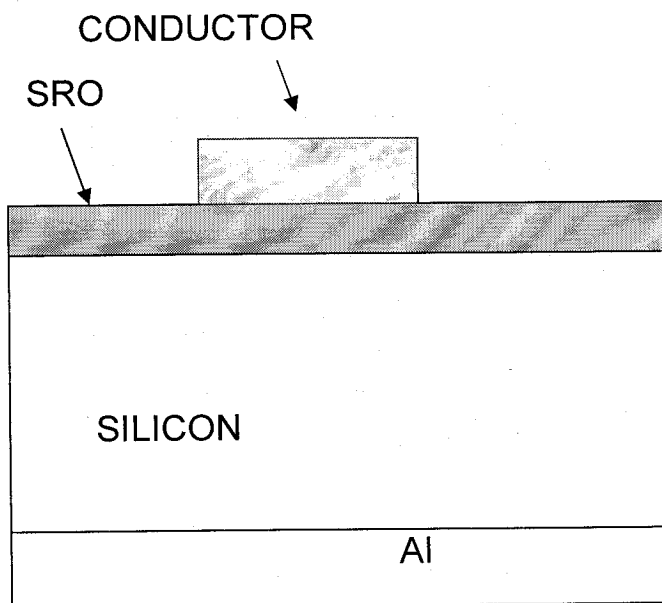


Figure 6. Al/SRO/Si structure used as a surge suppresser

We have been proposed a circuital model (Aceves et al., 2000], and a design method based on the characteristic of the SRO film. We found that the device supports peaks higher than 700 volts, with a clamping voltage around 200 volts. Currently, we are preparing samples designed to support more than 1000 volts (Mendez 2001). Figure 7 shows the model, figure 8 shows experimental and simulated results as a function of time and figure 9 shows the peak and the clamp voltage.

The results of the project are ready to transfer the technology to any industry. Of course, it is not a simple task to get the attention of manufacturing people for scientific developments.

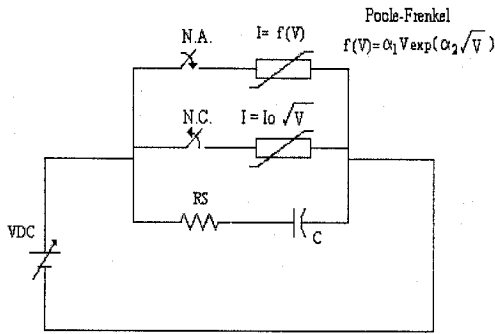


Figure 7. Surge suppresser circuitual model. Two current modes predominate: one is due to generation in a PN junction that is proportional to $V^{1/2}$, and the other is a Poole –Frenkel mechanism

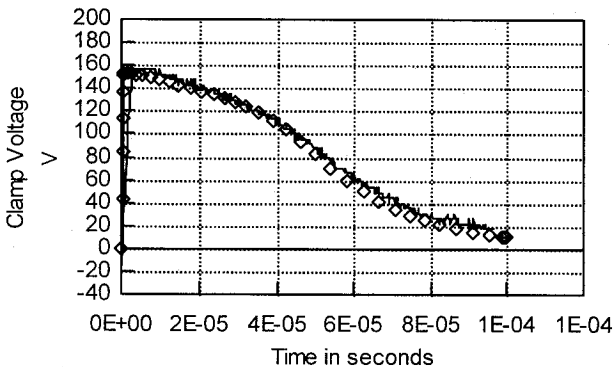


Figure 8. Clamp voltage, simulated and experimental results

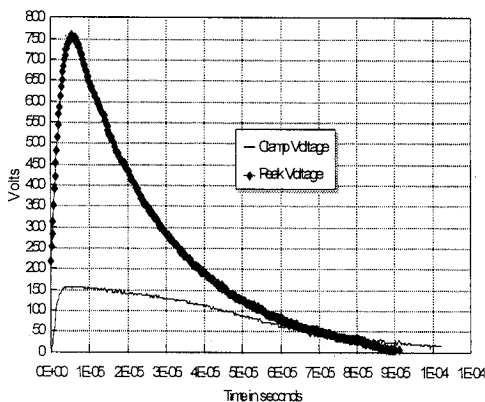


Figure 9. 8 x 20 standard IEEE Applied peak and clamped voltage

4 Conclusions

In the projects supported by CONACyT, we studied the SRO/Si junction from several points of view. The junction's conduction characteristics and its dependence on the properties of the silicon substrate and the excess silicon in SRO were understood. Using this knowledge, we propose new devices, and presented two devices that successfully have been experimentally tested.

One successful device is a photodetector that works in the visible range, and more research is done to extend it to sense X rays. In addition, the SRO emission properties are investigated in order to use the SRO film as a detector.

The other successful device is a surge suppresser that has been tested using the commercial standards. This device is ready to be transferred to the industry.

Acknowledgement.

The authors thank to Pablo Alarcon, Mauro Landa, and Carlos Zuñiga for the preparation of the samples. Also to N. Carlos and Juan M. Alvarez for their help during measurements. This project is supported by CONACyT, México, and ICI, Spain.

References

- "An American National Standard/IEEE Guide for Surge Voltages in Low AC Power Circuits" C62.41 1980.
- "IEEE Standard Test Specifications for Varistors Surge Protective Devices" ANSI/IEEE C62.33 1982
- Aceves, M.; Calleja, W.; Falcony, C.; Reynoso – Hernández, J. A. "The Al/Silicon Rich Oxide/Si P - N Induced Junction As A Photodetector" *Revista Química Analítica*, 18, (Suppl.1):5. (1999)
- Aceves, M.; Carrillo, J.; Calleja, W.; Falcony, C.; Rosales, P. "Duality MOS – PN Junction in the Al/SRO/Si Structure as a Radiation Sensor." *Thin Solid Films*, 373, pp 134 – 136 October (2000)
- Aceves, M.; Falcony, C.; Reynoso, A.; Calleja, W.; Torres, A. "The conduction properties of the silicon /off – Stoichiometric SiO₂ diode" *Solid-State Electronics* 39, 637 (1996).
- Aceves, M.; Flores, J. F.; Carrillo, J.; Domínguez, C.; Falcony, C.; Calleja, W. "On the origin of the visible light emission in SiO₂ implanted with silicon" To be published.

Aceves, M.; Malik, A.; Carrillo, J.; Flores, F.; Carranza,

J. "New radiation sensor using transparent electrode and the induced p - n junction in a silicon rich oxide/Si structure." To be published in proceedings of IBERSENSOR 2000, Buenos Aires, Argentina. Nov. (2000)

Aceves, M.; Pedraza, J.; Mendez, J. "Electronic model of a surge suppressor made of silicon rich oxide and silicon". 3rd. Microelectronics Reliability and Qualification Workshop, 31/Oct. - 1/Nov. Glandale, CA. P5, (2000)

Aceves, M.; Pedraza, J.; Reynoso-Hernandez, J. A.; Falcony, C. and Calleja, W. "Study on the Al/Silicon Rich Oxide/Si structure as a surge suppresser, DC, frequency response and modeling." Microelectronics Journal 30, 855 (1999)

Aceves, M; Falcony, C.; Reynoso, J. A.; Calleja, W.; Pérez, R. "New Experimental Observations on the Electrical Characteristics of The Al/SRO/Si Diode, and Annealing Effects" Material science in semiconductor processing 2, 173 (1999).

Calleja, W.; Falcony, C.; Torres, A.; Aceves, M. and Osorio, R. "Optical properties of non-stoichiometric SiO₂ as a function of excess silicon content and thermal treatments." Thin Solid Films 270 (1995) 114-117.

Dong, D.; Irene, E. A.; Young, D. R. "Preparation and some properties of CVD Si - Rich and Si₃N₄ films" Electrochem. Soc. 125, 819 (1978).

Flores Gracia, F.; Aceves, M.; Carrillo, J.; Domínguez, C.; Falcony, C.; Malik, A. "Comparison of PL and CL characteristics between SiO₂ implanted with Si and SRO films". International Young Scientist Conference Scientific Problems of Optics in XXXI century. October 4th-6th, 2000. . Kiev, Ukrania

Flores, F.; Aceves, M.; Carrillo, J.; Domínguez, C.; Falcony, C., Calleja, W. "Estudio de Foto- y Catodoluminiscencia en películas de óxido térmico con implantación de Si". VI Conferencia de Ingeniería Eléctrica. 6-8 de Sept. de 2000. México, D.F.

Flores, J. F.; Aceves, M.; Carrillo, J.; Domínguez, C.; Falcony, C.; Calleja, W. "Effects of the oxidation in SRO films". XV SBMicro - INTERNATIONAL CONF. ON MICROELECTRONICS & PACKAGING. Sept. 18th-23th, pp. 383 -388 2000. Manaus, Brazil.

Hamasaki, M.; Adachi, T.; Wakayama, S.; Kikuchi, M. "Crystallographic study of Semi insulating Policristallyne Silicon (SIPOS) doped with oxigen atoms" J. Appl. Phys. 49, 3987 (1978).

Harris "Surge suppressor handbook" 1996

Hielscher, F. H.; Preier, H. M. "Non Equilibrium C-V and I-V characteristics of Metal-Insulator-Semiconductor capacitors." Solid State Electronics 12 527 (1968)

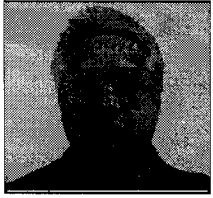
Kalnitsky, A. R. Boothroyd, J. P. Ellul. "A model of charge transport in thermal SiO₂ implanted with Si" Solid-State Electronics 33, 893 (1990).

Ma, Z., Liao, X.; Cheng, W.; He, J. Yue, G.; Wang, Y.; Diao, H. and Kong, G. "A study of strong photoluminescence of SiO_x: h films." Phys. Stat. Sol. (b) 206, 851 (1998).

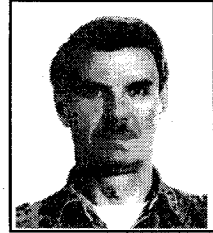
Mendez, J. "Transient characterization of the Al/SRO/Si surge suppresser" Master Thesis INAOE, march/2001.

Rebohle, L.; Von Borany, J.; Grötzchel, R.; Markwitz, A.; Schmidt, B.; Tyshenko, I. E.; Skorupa, W.; Fröb, H. and Leo, K. "Strong blue and violet photo- and electroluminescence from Ge- and si-implanted silicon dioxide." Phys. Stat. Sol. (a) 165, 31 (1998).

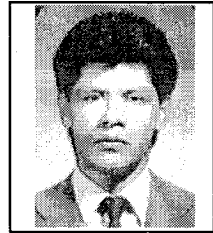
Shimizu-Iwayama, T.; Norihiro Kurumado, Hole, D. E. and Tonswed, P. D. "Optical properties of silicon nanoclusters fabricated by ion implantation." Journal of Applied Physics, Volume 83, Number 11, 1 June 1998



Dr. Mariano Aceves Mijares, has been working in the development of semiconductor devices for more than 20 years. He leads projects supported for various national and international institutions. He is author or co-author of more than 100 paper in technical journals and proceedings. He is part of the academic staff of the postgraduate program of INAOE. He has also expended some sabbatical periods working with the national and international industry.



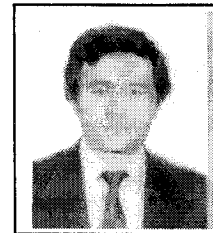
Alexander Malik, received his degree in Physics and PhD in Physics of Semiconductors and Dielectrics from the Chernovtsy University, Ukraine, in 1971 and 1980, respectively. He is the specialist in thin metal-oxide film technology and its applications for optoelectronic devices with 30 years scientific and industrial activity. From 1996 to 1999 years, he worked in Portugal as invited scientist. Since 2000 he works as titular researcher in INAOE, and his activity is connected with the development of novel multi-layered semiconductor detectors and LEDs.



Francisco Flores Gracia, was born in Puebla in 1960. He received the M.Sc. degree from the Universidad Autonoma de Puebla in 1997. Currently, he is working in his Ph.D. thesis at the Instituto Nacional de Astrofísica, Óptica y Electrónica. His early activities were related to bioelectronics researching. Since 1995, he has worked with characterization of optical and electrical properties of silicon rich oxide layers and kinetics of point defects in silicon.



Joel Mendez Morado, was born in Cd. Madero, Tamaulipas in 1974. He studied Electronics Engineering in the Instituto Tecnológico of Cd. Madero from 1992 to 1997. He received the M.Sc. degree from the Instituto Nacional de Astrofísica Óptica y Electrónica in Puebla, México in 2001 with the thesis "Caracterización para transitorios de voltaje de un dispositivo fabricado con la estructura Al/SRO/Si". Automatic Control, Electronic Instrumentation and Metrology are included among his main areas of interest.



Jesús Carrillo López, received the M.Sc. degree in Electronics at the Instituto Nacional de Astrofísica, Óptica y Electrónica in 1979 and Ph.D. degree in Electrical Engineering at the Centro de Investigación y Estudios Avanzados in Mexico city. Since 1979, he is Titular researcher at the Universidad Autónoma de Puebla in Materials Science area. Currently, he is working with Low Pressure Chemical Vapour deposition silicon rich oxides and their applications in radiation sensors and optical and electrical properties of LPCVD silicon oxynitride films.



Carlos Domínguez, received the M.Sc. degree in Chemistry in 1980, and Ph. D. degree in Silicon Epitaxy at Low Pressure in 1985. He is Senior Researcher at the Centro Nacional de Microelectrónica (CNM) since 1991. He has co-authored more than 60 research papers on Solid State Technology, Chemical Sensors and Chemical Processes in Microelectronics. Currently he is co-ordinator of a research group working on integrated optical components based on silicon technology, integrated chemical sensors and application of photocurable polymers for sensors and optoelectronics packaging.

