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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

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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 $\text{SiO}_2$ matrix, whose final characteristics are related with the silicon excess. The silicon excess is determined by the gases precursor ratio, $R_0$. 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 $\text{Al}/\text{SRO}/\text{Si}$ 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: suppressor, 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, a 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 $\text{SiO}_2$. El exceso de silicio se determina por la relación de gases reactivos, $R_0$, durante su obtención. La estructura SRO/Si también ha sido estudiada, y presenta propiedades que dependen de la $R_0$ del tipo y resistividad del silicio. Como resultado de esta investigación hemos extendido 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 $\text{Al}/\text{SRO}/\text{Si}$ 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: Oxido 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,

$$R_0 = \frac{[\text{N}_2\text{O}]}{[\text{SiH}_4]}$$

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 $\text{Al}/\text{SRO}/\text{Si}$ device depends on the SRO silicon excess, $R_0$, and the type and impurity concentration of the silicon substrate.

One of these behaviors is twofold, i.e., it has a dual comportment: 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 suppressor 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 1x10¹⁶ cm⁻² and 1x10¹⁷ 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](image-url)
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 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.

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 García et al., 2000, Flores I et al., 2000). Figures 4 and 5 show representative emission spectra.
3.3 Surge Supresser

Figure 6 shows the Al/SRO/Si structure used as a surge suppressor. 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 regimes can be distinguished, at low currents a generation current dominates. However, at high current regimen a Poole–Frenkel tunneling dominates (Hielscher and Preier 1968).

![Diagram of Al/SRO/Si structure](image)

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.

We have been proposed a circuitual 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.
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 suppressor that has been tested using the commercial standards. This device is ready to be transferred to the industry.

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