Photoconduction in silicon rich oxide films

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Abstract. Photoconduction of silicon rich oxide (SRO) thin films were studied by current-voltage (I-V) measurements, where ultraviolet (UV) and white (Vis) light illumination were applied. SRO thin films were deposited by low pressure chemical vapour deposition (LPCVD) technique, using SiH₄ (silane) and N₂O (nitrous oxide) as reactive gases at 700 °C. The gas flow ratio, Ro = [N₂O]/[SiH₄] was used to control the silicon excess. The thickness and refractive index of the SRO films were 72.0 nm, 75.5 nm, 59.1 nm, 73.4 nm and 1.7, 1.5, 1.46, 1.45, corresponding to Ro = 10, 20, 30 and 50, respectively. These results were obtained by null ellipsometry. Si nanoparticles (Si-nps) and defects within SRO films permit to obtain interesting photoelectric properties as a high photocurrent and photoconduction. These effects strongly depend on the silicon excess, thickness and structure type. Two different structures (Al/SRO/Si and Al/SRO/SRO/Si metal-oxide-semiconductor (MOS)-like structures) were fabricated and used as devices. The photocurrent in these structures is dominated by the generation of carriers due to the incident photon energies (∼3.0-1.6 eV and 5 eV). These structures showed large photoconductive response at room temperature. Therefore, these structures have potential applications in optoelectronics devices.

1. Introduction

Currently, nanoparticles (as silicon nanocrystals, silicon nanoclusters, amorphous silicon and compounds) in different materials have been subjected to an intense study due to their excellent optoelectronics properties, where the absorption-emission mechanism represents one of the most interesting problems in modern solid state physics. Another important problem has been the compatibility of these materials with the silicon technology in order to integrate optoelectronic functions in silicon. One of these materials with nanoparticles, compatible with silicon technology, is the silicon rich oxide (SRO), which is a material with silicon excess formed by multiple phases (SiO₂, SiOₓ and Si-np crystalline or amorphous) [1]. SRO films can be obtained by different techniques, such as chemical vapour deposition (CVD), LPCVD (low pressure), PECVD (plasma enhanced), silicon implantation into thermal silicon dioxide, sol–gel, sputtering, etc [2, 3, 4]. Silicon excess can be controlled with the flow ratio (Ro) between N₂O and SiH₄ (Ro = [N₂O] / [SiH₄]) as the reactant gasses. This material has been studied due to its interesting structural, electrical and optical properties [5, 6],...
which have been applied to different kinds of applications, such as waveguides, non-volatile memory and light detection devices [3-7].

In this work, SRO films were deposited by LPCVD technique. Different photoconductive responses were observed when the silicon excess was varied. An important parameter in this structure is the thickness of SRO films. Thinner films have a better photoconductive interaction with the light on the surface of the film and with the SRO/Si interface. Therefore, due to radiative recombination between the Si-nps and defects [1] within the SRO films when illuminated, the carrier generation is provoked. Electron-hole (e-h) pairs are generated by the fast interaction between incident photons with Si-nps in the SRO films, improving the transport of the photo-excited carriers in SRO thin films towards the contacts. This is clearly observed by the high and fast response of the photocurrent.

On the other hands, we describe the fabrication of Metal-Oxide-Semiconductor-like structures with a single SRO layer (as Al/SRO/Si) and with double SRO layer (as Al/SRO/SRO/Si). In the Al/SRO/SRO/Si structure, the second SRO layer has the purpose of to isolate (as a dielectric) the effects of the silicon bulk.

SRO films with thickness smaller than 75 nm and a large silicon excess (SRO
\[10\]) contain Si-nps (as Si-nc) which interact with light within a wavelength range. White or visible light generates a high photocurrent when the size of Si-nps is larger than 5 nm [7], but for nanoparticles (as Si-nanocluster or compounds) smaller than 1 nm UV light generates the highest photocurrent. In both cases, the measurement of photoconduction is carried out between two contacts of the Al/SRO/Si structures. Using a double layer of SRO it is possible to obtain a larger photoconducto.

2. Experiment

SRO films were deposited on N type Silicon (100) substrates with resistivity of 2-5 Ω-cm. SRO layers were obtained in a horizontal LPCVD hot wall reactor using SiH\(_4\) (silane) and N\(_2\)O (nitrous oxide) as reactive gases at 700 °C. The gas flow ratio, Ro = [N\(_2\)O]/[SiH\(_4\)], was used to control the amount of silicon excess in the SRO films. Ro = 10, 20, 30 and 50 were used for this experiment. The pressure was varied for each Ro from 1.64 - 2 Torr. After deposition, the samples were thermally annealed at 1000° C in N\(_2\) atmosphere for 30 minutes. Aluminum (Al) contacts were made onto the SRO surface by evaporation and standard photo-lithography. The area of the gate electrode was A= 0.089 cm\(^2\). For structures with double layer, which consisted of SRO\(_{10}\)/SRO\(_{30}\) and SRO\(_{10}\)/SRO\(_{50}\), contacts were made with circular gate electrodes of area A= 0.01 cm\(^2\). Ellipsometric measurements were made with a Gaertner L117 ellipsometer to obtain the thickness and refractive index of the SRO films, whose values are shown in Table I.

| Ro  | Refractive index | Thickness (Å) |
|-----|-----------------|---------------|
| 10  | 1.775 ± 0.005   | 720 ± 28      |
| 20  | 1.55 ± 0.03     | 755 ± 25      |
| 30  | 1.46 ± 0.01     | 591 ± 3       |
| 50  | 1.45 ± 0.01     | 734 ± 15      |

Current versus voltage (I-V) measurements were performed at room temperature in dark and under illumination conditions by using a computer controlled Keithley 6517A Electrometer in a screening box. The voltage sweep was done at a rate of 0.1 V s\(^{-1}\). Illumination was performed with an UV lamp (UVG-54) with output power of 6.12 mW/cm\(^2\), and white light (1.7 - 4 eV approximated range) with output power of 2.19 μW/cm\(^2\). Both powers were measured by means of a radiometer (IL1 400A). Photocurrent was measured between two devices in samples with one and two SRO layers, as depicted in Fig. 1 a) and b).
Figure 1. The circuit used for current-voltage measurements for a) one and b) two layers SRO thin films.

3. Results

Figure 1 shows the experimental circuit used for current-voltage measurements under dark and illuminated conditions of the Al/SRO/Si structures with one and two layers of SRO.

Figure 2 a), b) and c) show the dark current density (J_{dark}) of the Al/SRO/Si structure with one layer of SRO under forward and reverse bias. The photocurrent for structures with Ro = 10, 20 and 30, shows an increase due to the photoconduction in the films. Photocurrent density (J_{pc} = J_{light} − J_{dark}) is a function of the wavelength and the applied bias on the SRO films with different flow ratios Ro = 10, 20 and 30, and thickness values of 72 nm, 75 nm and 59 nm, respectively. The thickness and Si-nps contributes with an efficient generation of e-h pairs that allows a better photoconduction when the films are illuminated at different wavelengths. For Ro = 10 and 20, the measured photocurrent has a higher photo-response than the corresponding to Ro = 30. We can see a very important result: the photocurrent for SRO with Ro = 10, 20 and 30 has a symmetric behavior and it can be generated with positive or negative bias.

Figure 2. IV characteristics were taken under dark conditions and with different illumination on Al/SRO/Si MOS like structures. a) SRO_{10}, b) SRO_{20}, c) SRO_{30}.

The current in the Al/SRO_{10}/Si structure increases rapidly to about 4 µA/cm² at 0.5V when it is illuminated with white light and under forward bias. For voltages above 2 V, the current is about 0.19 mA/cm². Beyond 10 V, the current saturates to 1 mA/cm². On the other hand, when the Al/SRO_{10}/Si structure is reversed bias, the current increases rapidly. Beyond -10 V, the current density is 0.1 mA/cm² and it stays at this value. The forward and reverse current ratios with respect to dark current have about 4 magnitude orders. This behaviour is only for SRO_{10} with white light. When the structure is illuminated with UV light, the photocurrent ratio decreases near to 1 magnitude order respect to the value with white light excitation. For structures with SRO_{20} and SRO_{30}, the current have a similar behaviour when they are illuminated with white and UV-light.
Figures 3 a) and b) show the structures with double SRO layer (Al/SRO$_{10}$/SRO$_{30}$/Si and Al/SRO$_{10}$/SRO$_{50}$/Si). For the Al/SRO$_{10}$/SRO$_{30}$/Si structure, the dark current is approximately 0.1 mA/cm$^2$ in forward and reverse bias. When white light is applied the photocurrent increased near two orders of magnitude, while the photocurrent corresponding to UV light increased only 1 order of magnitude. In all ways the behaviour is symmetrical for forward and inverse bias. When white light is applied to the Al/SRO$_{10}$/SRO$_{50}$/Si structure, the forward current decreased to 1.8 pA/cm$^2$ at 1 volts as a discharge. When the SRO film is charging newly, the current rise at 1.2 V, then it increases non-linearly to 0.074 mA/cm$^2$ at 3.2 V. Beyond 17 V, the current saturates to 1.3 mA/cm$^2$. On the other hand, the inverse current with white light applied remains constant at 5 nA/cm$^2$ from 0 to 5 V. The current starts to rise at -7 V, increases non-linearly around 0.721-0.818 mA/cm$^2$ from -8 to -30 V. With UV illumination, the current decreased approximately 1 order of magnitude in relation to current measured under white light illumination. But a high photoconduction is obtained between the two contacts with white light and UV illumination. The photocurrent increases from 4 to 5 orders of magnitude. In all experiment conditions, the SRO films are operating as a photoconductor between the two Aluminium contacts.

![I-V characteristics](image)

**Figure 3.** I-V characteristics under dark conditions, white and UV-light on Al/SRO/SRO/Si MOS like structures. a) SRO$_{10}$/SRO$_{30}$, b) SRO$_{10}$/SRO$_{50}$.

4. Analysis and discussion

We now discuss some possible mechanisms related to the electronic and physical properties of the Al/SRO/Si structures. The dark current is small respect to the photocurrent obtained in each one of the MOS-like structures with SRO films. Furthermore, the dark current is even very small in the two SRO layers structure; it is a direct result of the fact that SRO$_{30}$ and SRO$_{50}$ films have nanoparticles as silicon nanocluster smaller than 1 nm embedded in a SiO$_2$ matrix, they have smaller conduction that SRO$_{30}$ and SRO$_{50}$ layers. In principle there is a very low conduction between the SRO$_{50}$ layers with the silicon bulk. Therefore, the film acts as a good insulator in the dark, but the SRO$_{10}$ film begins to be an excellent conductor of electric current when it is exposed to the light.

This photoconduction is due to the following phenomena. In the case of SRO$_{10}$ with white light exposure, the photons reach the SRO film due to their penetration wavelength on the Al/SRO/Si structure. They produce photo excitation by the interaction between Si-nps (as Si-nc), and e-h pairs are generated and becomes to conductive paths towards the Al contacts. On the other hand, SRO$_{30}$ or SRO$_{50}$ layer devices have the possibility of photoconduction based upon the interaction of defects with Si-nps (nanocluster) with sizes smaller than 2 nm. If e-h pairs are generated in each nanoparticles or defect of the SRO film, this would correspond to a very high electron/hole pairs’ density.
The possible photoconduction mechanisms depend on the silicon excess in the SRO films. Further detailed conduction mechanism study is on course and will be published elsewhere. It’s clear that the enhancement in the photoconduction under irradiation is related with silicon excess and thickness in the structure MOS-like. Therefore, we have the following statements: First, the larger size of Si nanoparticles due to the silicon excess provides a conductive path across the film, allowing high photocurrent with white light illumination, such as in the SRO\textsubscript{10} case. With low silicon excess, we have nanoclusters smaller than 1 nm, they interact with the defects and produce high photocurrent with UV light. Second, the light interacts in better way on the thin films with thickness smaller than 75 nm. The UV light produces an inversion layer, and consequently produces more efficient charge separation and collection surface, which is the case of SRO\textsubscript{20} and SRO\textsubscript{30}. A very simple MOS-like structure that shows high photoconduction in the UV-Vis wavelength range is reported, it is possible the creation of e-h pairs in the SRO layer and in the inversion region generated when voltage is applied. On the others hand, SRO films have a different absorption edge that depends on silicon excess. This absorption edge allows the photons’ absorption at different wavelengths [7]. This result is very important to understand why the SRO films can be excited at different wavelengths and have an excellent photoconduction.

5. Conclusions

We demonstrated that SRO thin films have photoconduction based on Si nanoparticles (silicon excess). They provide high photocurrent between path conductive towards the two contacts under forward and reverse bias when the samples are exposed to UV and White light. It’s clear that there are several key factors as silicon excess, Si nanoparticles size, thickness and MOS-like structure, which allow that SRO films to act as a photoconductor. First, the larger size of Si nanoparticles due at silicon excess provide a conductive path across the film, permitting to obtain high photocurrent with white light illumination, such as in the case of SRO\textsubscript{10}. With low silicon excess, we have nanocluster smaller than 1 nm that interact with the defects permitting to obtain high photocurrent with UV light. Second, the thin films with thickness smaller than 75 nm have better interaction with the light and provoked a inversion layer, this condition allows more efficient charge separation and collection with UV light, which is the case of SRO\textsubscript{20} and SRO\textsubscript{30}. A very simple structure that shows high photoconduction in the UV-Vis wavelength range is reported. The same architecture may be used as a photodetector and light emitter.

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