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Photoconduction in silicon rich oxide films obtained by low pressure chemical vapor deposition

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Photoconduction properties of silicon rich oxide (SRO) thin films were studied under different illumination conditions. In the past, Al/SRO/Si structures showed a high photocurrent in spite of the fact that an opaque Al layer was on the active area. In order to elucidate this observation, new Al/SRO/Si structures were tested, but this time they were also measured horizontally. SRO thin films were deposited on silicon wafers by low pressure chemical vapor deposition technique using SiH_4 (silane) and N_2O (nitrous oxide) as reactive gases at 700 °C. 1%–12% silicon excess was used. Structures with a single SRO layer and with a double layer were fabricated in order to have a barrier to isolate the silicon from the active SRO layer. The results show that all structures have a higher current when light shines on them than when they are in the dark. It is proposed that the photocurrent is produced in the SRO bulk, and an explanation for these observations is given.
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I. INTRODUCTION

Currently, nanoparticles in different materials have been the subject of an intense study due to their excellent optoelectronic 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, compatible with silicon technology, is the silicon rich oxide (SRO), which is a material with silicon excess formed by multiple phases [SiO_2, SiO_x, and crystalline or amorphous silicon nanoparticles (Si-nps)].

SRO films can be obtained by different techniques, such as low pressure chemical vapor deposition (LPCVD), plasma enhanced CVD, and silicon implantation into thermal silicon dioxide.[1–4] In particular, for LPCVD, silicon excess can be controlled with the flow ratio ($Ro=[N_2O]/[SiH_4]$) between N_2O and SiH_4 as the reactant gasses. This material has been studied due to its interesting structural, electrical, and optical properties,[5,6] which are used in different kinds of applications, such as waveguides, nonvolatile memory, and light detection devices.[4–7]

In light sensor applications, SRO devices have shown sensitivity up to the UV region, increasing the Si response.[8] In other reports,[5] SRO devices have shown higher photoresponse in spite of the fact that the devices were covered with opaque Al. It was speculated that the photocurrent was an effect of the Si substrate or that it was an effect of the SRO itself.

In this work, photoconduction of the SRO films is studied. Double and single SRO layer devices were used in order to determine the source of the photoconduction. The double SRO layer has the purpose of isolating the silicon bulk effects from the SRO effect. In both cases, single and double layers, the photonic response was remarkable. Then, for the first time, it is reported that SRO itself shows photoresponse.

II. 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_2O (nitrous oxide) as reactive gases at 700 °C. The gas flow ratio, $Ro=[N_2O]/[SiH_4]$, was used to control the amount of silicon excess in the SRO films. Ro=10, 20, 30, and 50, corresponding to a silicon excess of 12%–1%, were used for this experiment. The total pressure was varied for each Ro from 1.64 to 2 Torr. After deposition, the samples were thermally annealed at 1000 °C in N_2 atmosphere for 30 min. Aluminum (Al) contacts were made on the SRO surface by evaporation and standard photolithography. The area of the gate electrode of structures with a single SRO layer is $A=0.089$ cm^2. For structures with double layer, which consists of SRO_{10}/SRO_{30} and SRO_{10}/SRO_{50} (the subindex indicates the Ro value), Al gate was circular with an

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TABLE I. Refractive index and thickness of the SRO films.

Ro	Refractive index	Thickness (Å)
10	1.78 ± 0.01	720 ± 28
20	1.55 ± 0.03	755 ± 25
30	1.46 ± 0.01	591 ± 3
50	1.45 ± 0.01	734 ± 15

area of $A = 0.01\ cm^2$, and separation between gate electrodes of 0.2 cm. Ellipsometric measurements were made with a Gaertner L117 ellipsometer to obtain the thickness and refractive index of the SRO films before annealing, whose values are shown in Table I.

Current versus voltage (*I-V*) measurements were performed at room temperature in the dark and under illumination using a computer controlled Keithley 6517A Electrometer in a screening box. The voltage sweep was done at a rate of 0.1 V/s. Illumination was performed with an UV (UVG-54, 5–6 eV approximated range) and a white light lamp (1.7–4 eV approximately) with output powers of $6.12\ mW/cm^2$ and $2.19\ \mu W/cm^2$, respectively. The power of lamps was measured using a radiometer (IL1 400A). Dark current and photocurrent were measured between two Al contacts in samples with one and two SRO layers, as shown in Figs. 1(a) and 1(b). The measurements were done at forward biased (+ with respect to the ground) and reverse biased (− with respect to the ground).

III. RESULTS

Figures 2(a)–2(c) show the dark and illuminated current density of the Al/SRO/Si structures with Ro=10, 20, and 30

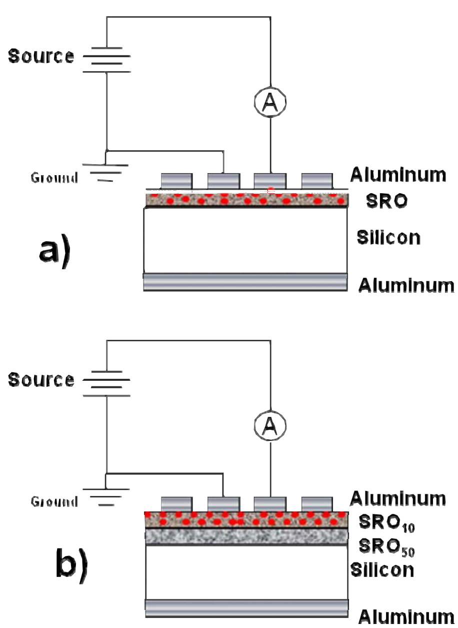

FIG. 1. (Color online) Schematic diagram of the devices and the circuit used to measure the current-voltage characteristics. One of the Al contact is ground as a reference for the bias direction.

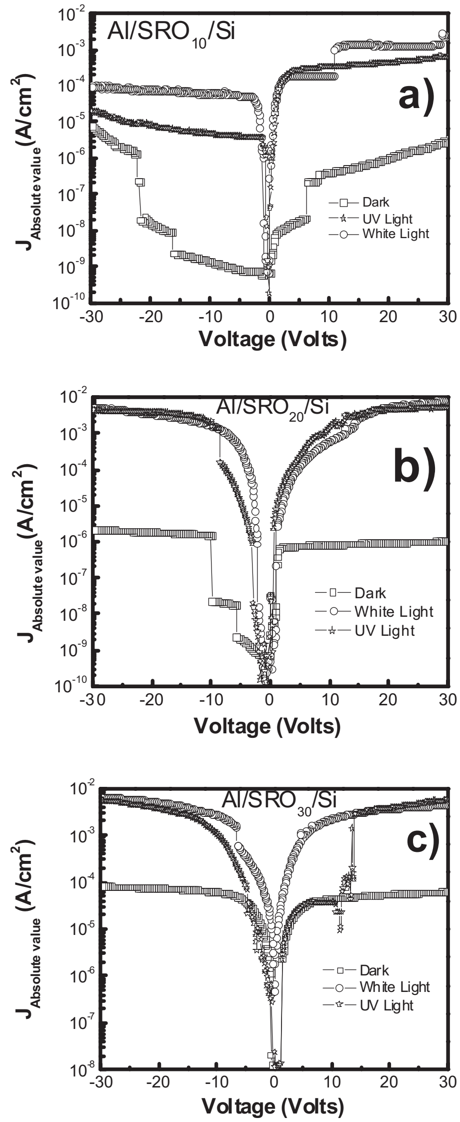

FIG. 2. Dark and illuminated *I-V* characteristics of the Al/SRO/Si MOS-type structures with Ro=(a) 10, (b) 20, and (c) 30.

under forward and reverse biases, respectively. As can be seen, the response to UV and white light is significant for all Ro values. Furthermore, the photocurrent is almost symmetric for both forward and reverse biases.

When the $Al/SRO_{10}/Si$ structure is under forward bias and illuminated with white light, the current increases rapidly to about $4\ \mu A/cm^2$ at 0.5 V. For voltages above 2 V, the current is about $0.19\ mA/cm^2$. Beyond 10 V, the current saturates to $1\ mA/cm^2$. When the $Al/SRO_{10}/Si$ structure is reverse biased and white light shines on it, the current also increases rapidly. Beyond −10 V, the current reaches $0.06\ mA/cm^2$. The forward and reverse current ratios with respect to the dark current are about four orders of magnitude. When the structure is illuminated with UV light, the photocurrent is similar to that obtained with white light; however, a decrease of approximately one order of magnitude is observed. For structures with SRO_{20} and SRO_{30}, the current behaves similar to that of Ro=10, but with a higher

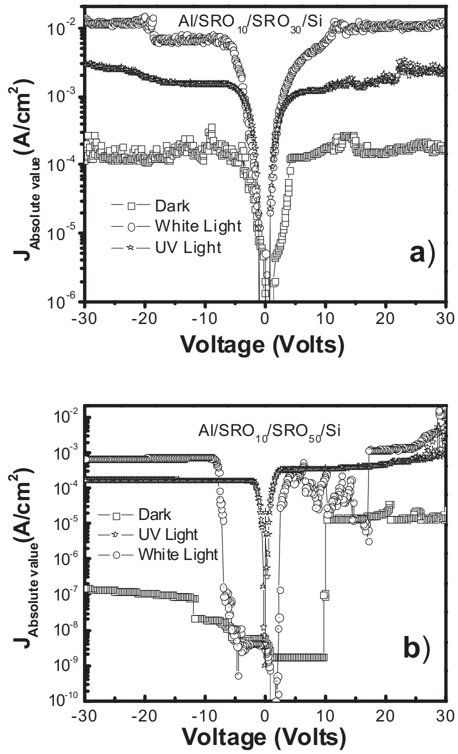

FIG. 3. Dark and illuminated *I-V* characteristics of the (a) $Al/SRO_{10}/SRO_{30}/Si$ and (b) $Al/SRO_{10}/SRO_{50}/Si$ MOS-type structures.

photocurrent, especially in the reverse bias. Also, smaller differences with the different types of illumination are observed.

Figures 3(a) and 3(b) show the current density versus voltage for the structures with double SRO layer ($Al/SRO_{10}/SRO_{30}/Si$ and $Al/SRO_{10}/SRO_{50}/Si$). In the case of the $Al/SRO_{10}/SRO_{30}/Si$ structure, the dark current is approximately 0.1 mA/cm^2 in both positive and negative biases. When white light was applied, the photocurrent increased two orders of magnitude, while for UV light, the photocurrent increased only one order of magnitude, approximately. In both cases the behavior is symmetric. In the case of the $Al/SRO_{10}/SRO_{50}/Si$ structure, the dark forward current is only 1.6 nA/cm^2 at 1 V. Above 10 V, the current jumps to 0.1 $\mu A/cm^2$ and shows other jumps in between. In reverse dark current, the current behaves similar to that in forward bias, but with a maximum current of about 0.14 $\mu A/cm^2$. When white light is applied, the current reaches up to the 0.7 mA/cm^2. Note that for forward bias and white light the current has an erratic behavior jumping up and down to 17 V. When the devices are illuminated with UV, the current decreases approximately one order of magnitude with respect to white light.

IV. ANALYSIS AND DISCUSSION

In previous papers where Al/SRO/Si structures were measured vertically as a photodetector, the electronic conduction through the SRO_{10} was higher than that observed in SRO_{30}.[5] This property is due to the high silicon excess that provides conduction trajectories through "big" Si-nps commonly found in SRO_{10},[9] which produce high dark currents. In contrast to low silicon excess, the density and size of the Si-nps decrease. In SRO_{30} it is not common to find Si-nps, but silicon compounds or silicon clusters of less than 1 nm have been observed.[10] Therefore, a low dark current is obtained.

However, when the light impinges on the $Al/SRO_{10}/Si$ structures, high photocurrent has been observed in spite of the opaque Al that blocks the light in the active area.[5,7] In this case, the current through the SRO can be due to the formation of an induced *p*-*n* junction in the silicon surface, as a consequence of the surface inversion.[11,12] Then, the source of photoelectrons could be the silicon surface. Nevertheless, photons cannot reach the inversion layer because the opaque Al. Therefore, another possibility is that the photoelectrons are generated around the Al; however, only holes generated near to the depletion area edge contribute to the photocurrent. A simple estimation of the diffusion length can be done considering the mobility of holes around 500 $cm^2/V\ s$ (Ref. 13) and using the Einstein relationship at room temperature with a diffusion coefficient of $D = 12.5\ cm^2/s$. A moderate estimation of the recombination lifetime is 1×10^{-6} s. (In our laboratory, we have measured the recombination lifetime around 10^{-8} s in similar conditions as those in this experiment.[14]) So, the diffusion length of holes in the dark is 35 μm. However, under illumination with the injection of carriers, the lifetime can be reduced drastically up to three orders of magnitude.[12] In this way, a conservative estimation will reduce the holes that contribute to the photocurrent to that generated to less than 3 μm away from the depletion layer. Then, the high current obtained in Refs. 5 and 7 for MOS-type structures with opaque Al cannot be ascribed to the holes in the periphery of the devices.

As mentioned, the high photocurrent of the Al/SRO/Si structures cannot be attributed to the electron-hole pairs generated in the Si substrate, so to obtain new information on this phenomenon, horizontal structures were tested, as shown in Fig. 2. It is observed that all structures measured horizontally show photocurrent. Moreover, the photoresponse takes place in both polarities as expected because the symmetry of the device.

On the other hand, the silicon surface should not be affected by the voltage applied between two Al contacts on the SRO, but in the case it does one of the vertical Al/SRO/Si devices have to be in accumulation and the other one in inversion. The fact that photocurrent is observed when the silicon surface in one vertical device is in accumulation and the other one is in inversion, strengthens the argument that the photoresponse is not due to photogeneration in the silicon, or in a voltage induced *p*-*n* junction.

In Fig. 2 the typical *I-V* curves of single layer structures measured horizontally in dark and under illumination are shown. Current jumps are observed in the dark current especially for SRO_{10} and some for SRO_{20}. Similar jumps have been observed in Al/SRO/Si structures measuring the current from the Al gate to the silicon substrate. The jumps are pro-

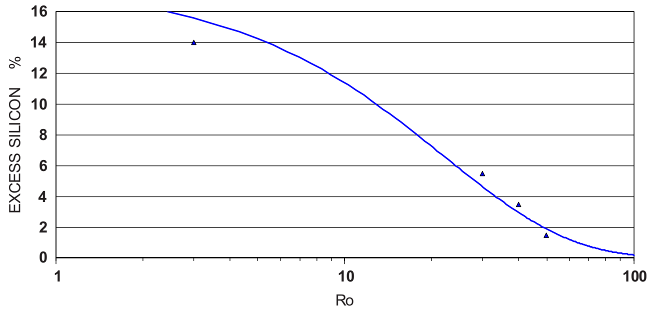

FIG. 4. (Color online) Silicon excess as a function of the Ro. The data were taken from Refs. 1, 23, and 24. A logarithmic fit was done just as visualization support.

duced by the formation of conductive paths.[15] Therefore, the horizontal current measured in this experiment can be ascribed to the conduction in the SRO bulk.

However, the highest dark current observed is for the SRO_{30} contrary to the expected. The SRO_{30} should have the smallest conductivity because of the low silicon excess. Also, *I-V* characteristics of the structure with SRO_{30} do not show current jumps, so another current mechanism is proposed for this structure: surface current. We propose that the total current in the horizontal structures is a combination of bulk current and surface current. When the SRO is conductive enough as in the case of the Ro=10 the current is mainly across the bulk, but if the SRO film is not conductive, as Ro=30, the electrons move easier on the surface.

When the samples are illuminated, the current increases significantly. As shown in Fig. 2, in all the illuminated samples, including SRO_{30}, the current has jumps. Then, the electrons are moving through conduction trajectories in the SRO. That is, the current is due to the SRO bulk. So, under illumination photoelectrons are generated inside the SRO films. The conductive paths reduce their resistance, making the bulk current more likely than the surface current.

In order to find more on the horizontal conduction mechanism, and to assure that the silicon substrate does not take part in the photocurrent, new structures were investigated. This time a barrier was put between the silicon substrate and the highly conductive SRO_{10}, as shown in Fig. 1(b). Two barriers were used, SRO_{30} and SRO_{50}, which have silicon excess of about 5% and 1%, respectively (see Fig. 4). Therefore, these SRO films assure a good electronic barrier, especially SRO_{50}. As shown in Fig. 3, the dark current for these devices have many jumps, implying that the current is in the bulk SRO and it is not due to the silicon substrate.

Under illumination again, the photocurrent is much higher than in the dark for both structures. Particularly, in the Ro_{10}/Ro_{50} structure where the current should be mainly through the SRO_{10} the photocurrent is augmented by four orders of magnitude. Two points have to be mentioned. First is the fact that the photocurrents are different for both polarities, and then at least two different types of traps, conduction paths, are involved. The second is the fact that the SRO is sensitive to wavelengths from UV to visible. The visible lamp used contains a wide range of wavelengths, including some UV. The UV lamp used has its main peak at 254 nm. However, more measurements have to be done to determine the response of SRO as a function of wavelength.

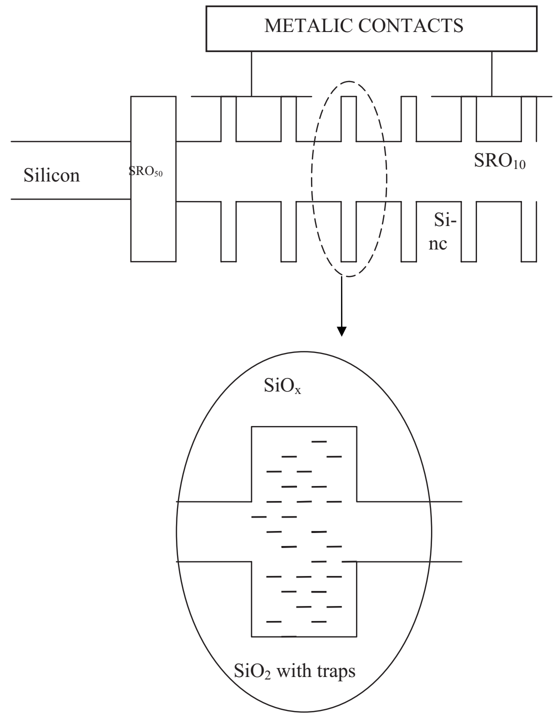

FIG. 5. Band diagram for the structure $Al/SRO_{10}/SRO_{50}/Si$ measured horizontally.

It is well known that SRO is a mix of $Si-(Si_xO_{x-4})$ with x varying from 0 to 4.[16] It has been proposed by various authors that traps exist in SRO that can accept or donate one electron.[17,18] Also, it has been observed experimentally that in SRO_{10} a high electronic conduction is present, but neither high carrier trapping nor high photoemission have been observed. This is due to the existence of the "big nanoparticles" that behave as conductive paths, rather than traps. Then electron-hole pairs generated by light decay but do not emit. In the other case, for SRO_{30} there are not big nanoparticles but perhaps agglomerates of Si, or $Si-(Si_xO_{x-4})$ compounds that allow the trapping of carriers and the emissive decay when illuminated.[19] With these ideas in mind, the band model shown in Fig. 5 is proposed for the $Al/SRO_{10}/SRO_{50}/Si$ structure measured horizontally, but this band diagram could be valid for all other structures. In this model, under an electric field electrons will move in the conduction band of the nanoparticles. Electrons also will move between nanoparticles using the density of traps in the SiO_x, forming conduction paths.[20] When the electric field is applied in the dark, electrons will move through the paths, but some electrons will be trapped, blocking some conductive paths. As the voltage increases, some trapped electrons will be released and new paths will be added increasing the current, i.e., a jump will be registered in the *I-V* curve.

When the device is biased and is under illumination, more electron-hole pairs will be created in the nanoparticles, but

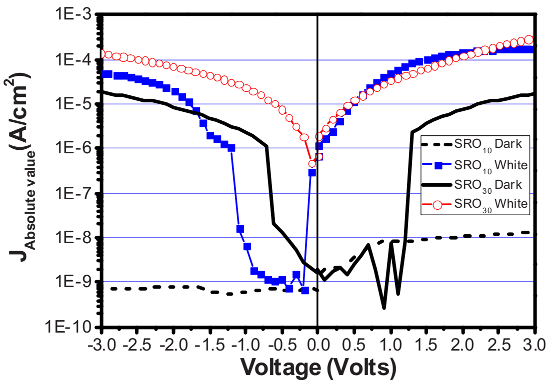

FIG. 6. (Color online) Detail of the current density against voltage for Al/SRO/Si with Ro=10 and 30 single layers, in the dark and illuminated with white light.

also the trapped electrons will be released by energetic photons. As a result, more conductive paths and carriers will contribute to the photocurrent.

The band diagram shown in Fig. 5 can be extended to lower silicon excess films. As the silicon excess decreases, the Si-nps bandwidths decreased and that encircled in the figure increases. At the end, the band diagram of a dielectric with a traps distribution is reached, as proposed in Ref. 19.

Photoelectrons are generated in both the Si-nps and the SiO_x, as already has been stated. However, the fact that in devices with a single layer with different silicon excess, and then different sizes of nps, the current density that is of the same order of magnitude in all the samples does not allow us to distinguish which of the photoelectrons contribute better to the photocurrent: those generated into the Si-nps or those generated in the traps.

Figure 6 reproduces with more detail the curves shown in Figs. 2(a) and 2(c) when the voltage crosses through zero. The photocurrent is observed when the voltage is zero and the structure seems to be photovoltaic (PV). If there is a PV effect, it could be due to the SRO film, as reported in Ref. 21, or could be due to an effect of the silicon. In our case, however, the PV effect was neither observed in the double layer structures, nor in the SRO_{20}. So, no evidence is observed that PV effect is produced in the SRO bulk. Rather, it could be due to an induced *p-n* junction in the silicon surface that serves as a photodetector.[22] The induced *p-n* junction can be provoked by trapped charge in the SRO films.

V. CONCLUSIONS

We demonstrated that the photoconduction is possible in SRO thin films using Al/SRO/Si structures. High photoconduction between two horizontal contacts was obtained under forward and reverse biases when UV and white light were used as excitation sources. Using an electronic barrier, the silicon substrate contribution to the current was eliminated. We believe that there are several key factors for the photoresponse in the SRO films such as silicon excess and Si nanoparticles size, which allow the SRO film to act as a photoconductor. However, more research has to be done in order to understand how these variables modify the photocurrent. A photovoltaic effect was also observed in structures without electronic barrier. However, the PV effect could be attributed to an induced *p-n* junction.

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