

Determination of the energy states of the donor acceptor decay emission in silicon rich oxide prepared by low-pressure chemical vapor deposition

R. López-Estopier,^{a)} M. Aceves-Mijares, and Z. Yu
Department of Electronics, INAOE, Puebla 72840, México

C. Falcony
Department of Physics, CINVESTAV-IPN, Distrito Federal, 07000 México

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Room temperature cathodoluminescence and photoluminescence were used to study silicon rich oxide (SRO) films with 5.5% silicon excess. Intense blue and red luminescence emissions were found. A SRO film was deposited by low-pressure chemical vapor deposition and was annealed at 1100 °C by 3 h in a nitrogen ambient. The emission from the SRO films was modeled as being due to donor-acceptor-pair decay. Calculations have been made to obtain the first estimates of the donor and acceptor energy distributions in SRO films. © 2011 American Vacuum Society.

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I. INTRODUCTION

Since the observation of visible light emission from porous silicon at room temperature,¹ silicon related materials have received enormous interest and have been studied intensively for their potential applications in optoelectronics devices.² A material that has generated great interest is silicon rich oxide (SRO); this material exhibits similar optical properties to porous silicon but is significantly less susceptible to damage.

SRO can be considered as a multiphase material composed of a mixture of stoichiometric silicon oxide (SiO₂), off-stoichiometric oxide (SiO_x, $x < 2$), and elemental silicon. After thermal treatment at temperatures above 1000 °C, the off-stoichiometric oxide, SiO_x ($x < 2$), is separated into silicon nanoclusters (crystalline or amorphous depending on their size), defects (oxidation states), and SiO₂.³ Silicon nanocrystals (Si nCs) have been observed in SRO by transmission electron microscopy corroborating the phase separation,⁴ and the existence and size of nCs depend on the excess silicon and annealing conditions.

Different techniques have been used to obtain SRO, including plasma enhanced chemical vapor deposition (CVD),⁵ low-pressure chemical vapor deposition (LPCVD),³ silicon implantation into thermal oxide,⁶ reactive sputtering,⁷ and others. For CVD, a mixture of SiH₄ (silane) and N₂O (nitrous oxide) can be used as the reactive gases, and the excess Si concentration can be adjusted by the gas ratio $Ro = [N_2O]/[SiH_4]$. Silicon excess ranging from 17% to 0 can be obtained varying the Ro from 3 to >100.

SRO deposited by LPCVD has shown high visible photoluminescence (PL) emission but there is no wavelength shift with the Si nCs' size variation;⁴ this shows that PL emission is not due to quantum confinement. In SRO with a large excess silicon (higher than 10%), Si nCs of ~9 nm have been found; as the silicon excess decreases, the density and

size of the nanocrystals decrease and defects tend to predominate until there are no Si nCs (~5.5% silicon excess).⁴ Samples with ~5.5% of silicon excess have the highest PL emission in spite of the fact that no Si nCs have been observed, and in samples with silicon excess greater than 10%, which are rich in Si nCs, the PL emission is weak.⁸

Extensive studies have been performed in order to find the origin of the visible light luminescence in SRO, although there is considerable uncertainty. Some authors attribute the luminescence to quantum confinement effects in Si nCs embedded in the oxide,^{9,10} interaction between Si nCs and the surrounding oxide,⁶ transition between band tails,^{11,12} and several types of defects in the matrix or the SiO₂/Si nCs' interface.^{13,14} Aceves and co-workers^{15,16} proposed that emission is due to donor acceptor decay (DAD).

On the other hand, SRO has been extensively studied by PL and other characterization techniques but there are only a few studies of cathodoluminescence (CL). PL and CL show similar results with some possible differences associated with the excitation produce by photons or by more energetic electrons.¹⁷ The emission depends strongly on the excitation energy, and not all luminescent centers are excited with the limited energy of the UV photons. CL uses high energy electrons to excite the sample and all luminescence centers present in the material can be stimulated.

In this article, the DAD model is considered as the mechanism of emission of SRO obtained by LPCVD. CL and PL measurements were performed to provide the experimental data in order to estimate the density of states. Then, the energy state distribution is determined from the experimental results. The DAD is characteristic of crystalline semiconductors, and SRO is not crystalline and is not a semiconductor. However, because of its electrical and optical properties, the SRO band gap is conceptualized as that of a crystalline material, and then the DAD mechanism can be applied as proposed by Aceves and co-workers.^{16,15,17-19}

^{a)}Electronic mail: estopier@inaoep.mx

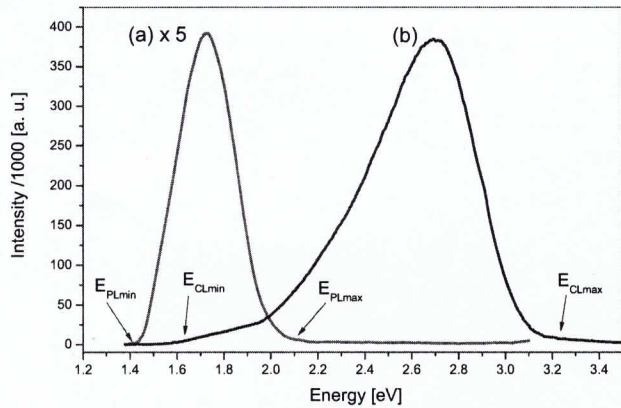


FIG. 1. (Color online) Experimental results of SRO samples: (a) PL and (b) CL. Maximum emissions are centered at ~ 1.75 and ~ 2.71 eV for PL and CL, respectively.

II. EXPERIMENT

SRO film with excess silicon of $\sim 5.5\%$ was obtained by LPCVD, and the partial pressure ratio of the reactant gases, R_o , was fixed at 30, which produces silicon excess of 5.5%. The substrates were *n*-type, (100) silicon wafers and the thickness of the SRO film was ~ 250 nm. After the SRO deposition the sample was thermally annealed at 1100 °C in N_2 atmosphere for 180 min, which has been shown sufficient to produce optically active SRO films.

PL and CL spectra were obtained after thermal treatments. PL spectra were obtained with a Fluoromax-3 spectrofluorometer, and excitation energy of 5 eV was used. In order to obtain CL, the sample was pump up with a luminoscope model ELM2-144 with 5 kV acceleration voltage and 0.3 mA emission current, and the emission spectra were recorded with the spectrofluorometer. CL measurements were also obtained using 10 and 15 keV beam energies.

III. RESULTS AND DISCUSSION

PL and CL spectra from SRO_{30} annealed are shown in Fig. 1. As we can see, maximum emissions are centered at ~ 1.75 and ~ 2.71 eV for PL and CL, respectively. CL emission is asymmetric and extends from 1.6 to 3.1 eV. This difference is because of the higher excitation energy provided by the incident electrons in CL. When photons or cathode-electrons excite the electrons in the SRO to higher energy states, relaxation processes occur and some electrons decay to lower (acceptor) energy states producing light emission. If the excitation energy is reduced, such as in the case of PL measurements, the emission energy is lower. However, if the excitation energy is higher, such as the case of CL measurements, the emission energy is higher. But in both cases the emission energy is lower than the excitation energy. This is confirmed experimentally, as shown in Fig. 1. On increasing the electron beam energy from 5 keV to 10 or 15 keV, we find that the CL emission spectrum is not changed except for small changes in intensity. This result reinforces the idea that 5 keV is sufficiently high energy to populate the

higher energy states. In the remaining discussion, we will concentrate on CL data recorded with 5 keV beam energy.

It is well known that low excess silicon SRO traps more charge and has less conductance than high silicon excess SRO.¹⁶ It is also known that only one electron can be trapped (acceptors) or released (detrapped) in the trapping states.²⁰ So, the DAD model supposes that the overall effect of compounds is to produce energy states in the gap of the SiO_x , and these states can trap electrons under quasistatic condition in the dark. Under illumination, the energy states exchange charge due to the excitation of electrons, and excited electrons will move to higher energy states and then decay to lower energy states, similar to the decay of acceptor-donor pair in a crystalline semiconductor. In Ref. 21 the authors proposed that in SRO-LPCVD the emission could be associated with Si clusters of less of 2 nm and defects' interaction. Also proposed that the band gap is large when the size of the Si cluster is small, and then the energy difference between the defects (localized state) and the Si clusters is big enough to produce the emission. Also, in Ref. 22, nanocrystals of different shapes were studied; in the study of the electronic structure three confinement regimes were used: weak, intermediate, and strong confinements. Under strong confinement in small nanocrystals, the Coulombic interactions are significant, and the optical transition (emission) is between quantum size levels of conduction and valence bands. And the equation proposed to determine the emission is basically the same as that of the DAD. These facts reinforce the proposition of DAD-like in SRO.

Under the assumption that the emissions in both CL and PL are due to the recombination of excited electrons from donor to acceptor states in the SRO, Eqs. (1) can be stated for PL and CL, respectively,¹⁷

$$E_{PL} = E_g - (E_d + E_a)_{PL} + \frac{q^2}{4\pi\epsilon r}, \quad (1)$$

$$E_{CL} = E_g - (E_d + E_a)_{CL} + \frac{q^2}{4\pi\epsilon r}, \quad (1')$$

where $E_{CL,PL}$ are the peak emission energies for CL and PL, respectively; E_d and E_a are the energies of the acceptor and donor pair; and ϵ is the dielectric constant. The last term arises from the Coulombic interaction of the carriers and depends on the pair separation r . Then, the energy of the donor acceptor recombination emission depends on pair separation r .²³

Since E_g , the donor and acceptor energy levels, and r are fixed in a given sample, the CL and PL emission energies can be rewritten as

$$E_{CL} = E_g - (E_d + E_a)_{CL} + \frac{q^2}{4\pi\epsilon r} = E_g - n(E_d + E_a)_{PL} + \frac{q^2}{4\pi\epsilon r}. \quad (2)$$

Because CL emits more energetic photons than PL then $(E_d + E_a)_{CL}$ should be smaller than $(E_d + E_a)_{PL}$, then $n < 1$.

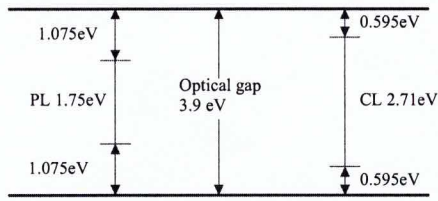


FIG. 2. Band diagram for CL and PL emissions; the donor and acceptor levels were estimated for the maximum peak emissions. This diagram is a simple example of only DAP of one PL and one CL wavelength of the spectrum emitted.

From Eqs. (1) and (2),

$$E_{CL} = E_g - n(E_g - E_{PL} + f) + f, \quad (3)$$

where f is defined as

$$f = \frac{q^2}{4\pi\epsilon r}. \quad (4)$$

Iterating n in Eq. (3), and using the static dielectric constant of SRO₃₀=0.39 pF/cm,^{24,25} f can be obtained, and then r from Eq. (4). So, it was found that the contribution of f to the energy of emission can be neglected. That is so because the only values of r that produces energies big enough to contribute significantly to the emission are related to r values smaller than the interatomic Si distance. For example, if $f = 1.69$ eV, r is 0.19 nm.

Therefore, Eqs. (1) can be reduced to

$$E_{PL} = E_g - (E_d + E_a)_{PL}, \quad (5)$$

$$E_{CL} = E_g - (E_d + E_a)_{CL}. \quad (5')$$

Now it is possible to calculate the energy of the states in the gap. For example, for the PL and CL peak emissions, using $E_{CL}=2.71$ eV and $E_{PL}=1.75$ eV, and the optical band gap ($E_g=3.9$ eV),²⁶ the respective band diagram is shown in Fig. 2 supposing a symmetrical distribution. This diagram represents in a simple way only the donor acceptor pair (DAP) for the maximum emission in PL and the one for the maximum emission in CL.

The whole range of energies of E_d and E_a can be calculated using the whole emission range for both PL and CL, as shown in Fig. 1. E_a and E_d are calculated assuming that the centers are symmetrical. Then for the minimum and maximum emission energies, $|E_{a\min}|=|E_{d\min}|$ and $|E_{a\max}|=|E_{d\max}|$. Using Eqs. (5) we have

$$E_{d\min} = E_{a\min} = \frac{E_g - E_{L\max}}{2}, \quad (6)$$

$$E_{d\max} = E_{a\max} = \frac{E_g - E_{L\min}}{2}, \quad (6')$$

where $E_{L\min}$ is the minimum and $E_{L\max}$ is the maximum luminescent energy in the PL spectrum. Then for PL, the donors are distributed in an energy range 0.9–1.25 eV below the conduction band edge; and the acceptors are distributed in an energy range 0.9–1.25 eV above the valence band edge,

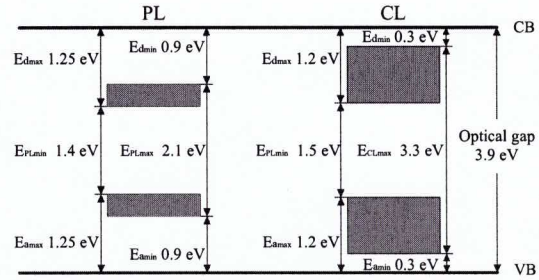


FIG. 3. Energy range of donors and acceptors obtained from PL and CL experimental spectra. $E_{L\min}$ is the minimum and $E_{L\max}$ is the maximum luminescent energy in the spectra; this is the energy range in which the defects (donors and acceptors) are involved in CL and PL emissions.

as shown in Fig. 3. This is the energy range in which the defects (donors and acceptors) can be involved in PL emission. And for CL the E_d 's are distributed from 0.3 to 1.2 eV below the conduction band and for E_a from 0.3 to 1.2 eV above the valence band, as shown in Fig. 3.

IV. DISTRIBUTION OF DAP

The CL and PL spectra of Fig. 1 can be decomposed in Gaussian components, as shown in Fig. 4. Then the spectra can be represented as

$$I(E) = \sum_{i=1}^n I_i e^{-(1/2)((E - \mu_i)/\sigma_i)^2}, \quad (7)$$

where E is energy, I_i is the peak intensity of emission, μ_i is the average of the emission energies, σ_i is the standard deviation, and n is the number of components of the PL and CL spectra, as obtained for each of the Gaussian. The best fit requires $n=3$ and 5 for PL and CL, respectively, as shown in Figs. 4 and 5. Distributions named 1–3 are related to PL range emission, and distributions 3–7 to CL ranges.

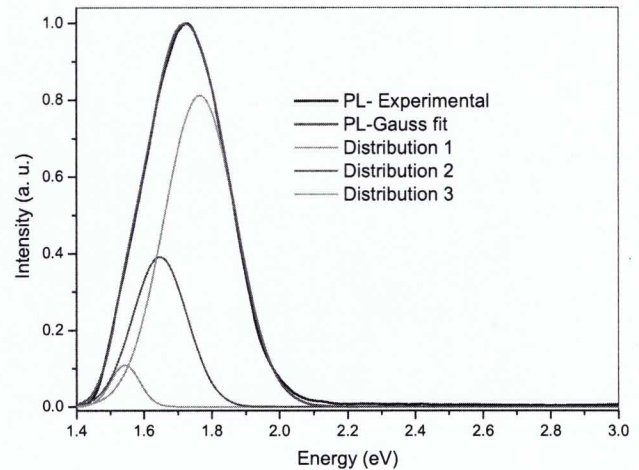


FIG. 4. (Color online) Gaussian fit obtained from PL experimental spectrum; the best fit requires three distributions; the coefficient of determination R^2 is 0.999 68. Distribution number 1 corresponds to the smaller one and distribution number 3 corresponds to the biggest one.

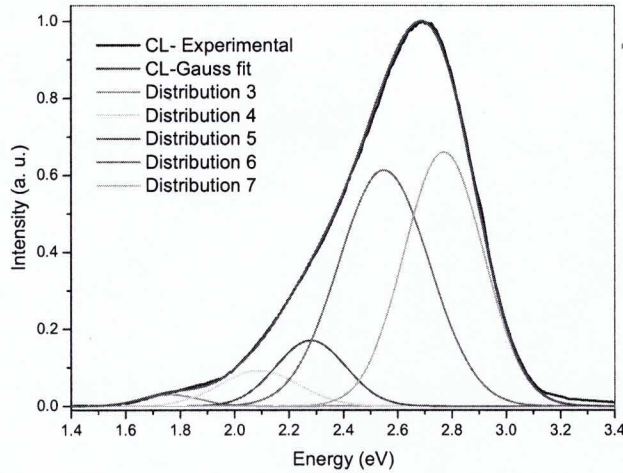


FIG. 5. (Color online) Gaussian fit of CL experimental spectrum; the best fit requires five distributions; the coefficient of determination R^2 is 0.999 71. Distribution number 3 corresponds to the smaller one and distribution number 7 corresponds to the biggest one.

μ_i , σ_i , and I_i values for PL and CL were taken from the fitted curves. The total intensity of $I(E)$ [Eq. (7)] for both CL and PL was normalized to 1. Distribution 3 for both (CL and PL) has the same μ and σ ; the only difference is the intensity. Therefore, emission centered at 1.76 eV shares the same emission center for CL and PL. However, the relative intensity of this distribution is significantly lower in CL due to the high quantity of centers that emits at higher energies in CL. PL distributions 1 and 2 centered at 1.54 and 1.64 eV, respectively, cannot be observed in CL; this could be because most of the excited electrons decay mainly in the high energetic part of the emission spectrum. Therefore, distribution 3 of CL and PL will be considered the same. The intensity of distributions 1 and 2 will be proportional to distribution 3, and their values are shown in Table I.

Furthermore, we suppose that the donors and acceptors have symmetric distributions. Therefore Eq. (1) can be expressed as follows:

TABLE I. Number of distribution (i), average (μ), standard deviation (σ), and peak intensity (I) obtained from resolving into Gaussian components the luminescence spectra. These values were used to obtain the relative donor acceptor distribution.

SRO			
Distribution (i)	μ_i (eV)	σ_i (eV)	I_i
1	1.54	0.043	0.004
2	1.64	0.08	0.0144
3	1.76	0.105	0.03
4	2.09	0.145	0.092
5	2.28	0.128	0.17
6	2.55	0.167	0.613
7	2.77	0.146	0.66

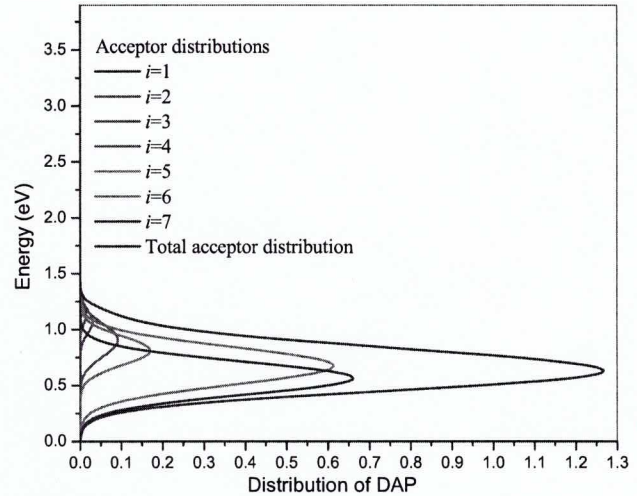


FIG. 6. (Color online) Acceptor distributions and total acceptor distribution calculated for SRO₃₀. Distribution number 1 corresponds to the smaller one and distribution number 7 corresponds to the biggest one.

$$E = E_g - (E_a + E_d) = E_g - 2E_z$$

or

$$E_z = \frac{E_g - E}{2}, \quad (8)$$

where $E_z = E_d = E_a$. That means we only consider the recombination between donors at E_z from the conduction band and acceptors at energy E_z from the valence band. E_g is the energy band gap and E is energy emission.

Once that E_z is known, the average of the distributions of states can be calculated assuming that the donors and acceptors have symmetric distributions with the same variation, which is the same standard deviation for each component, as shown in Table I.

$$\mu_{zi} = \frac{E_g - \mu_i}{2}, \quad (9)$$

where μ_i is shown in Table I.

Then, the whole relative distribution of donors and acceptors is

$$D_{\text{DAP}}(E) = \sum_{i=1}^n I_i e^{-(1/2)((E - \mu_{zi})/\sigma_i)^2}. \quad (10)$$

In order to obtain the distribution of acceptors (or donors), the distribution for each distribution (i) is obtained and then the summation gives the total distribution of acceptors (or donors), as shown in Fig. 6.

Figure 7 shows the total donors and acceptors' distribution for SRO₃₀, that is, the distribution of both DAPs that produces the PL and CL. The distribution was obtained using Eq. (10). In general, the luminescence intensities increase as the concentration of the luminescent centers (DAP) increases. Furthermore, it is important to point out that decay between traps in the film does not always produce an emission, rather a competitive mechanism between emissive and

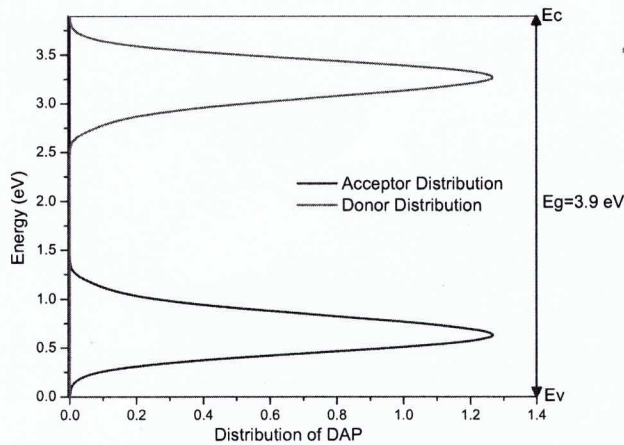


FIG. 7. (Color online) Total donor and acceptor energy distributions in SRO films; the distributions were obtained from Eq. (10).

nonemissive decays takes place. Of course, this mechanism will vary with silicon excess, and that is the cause of the smaller intensity emission in other Ro gas ratios.^{16,15,27} However, determination of the emissive DAP provides a base to simulate the emission of a different Ro film. In a near future, a work on this subject will be presented.

It is well known that electronic traps in SRO are responsible of charge trapping and that the electrical conduction is due to tunneling between these traps.^{25,28} Since electron traps can be both electrically and optically active, characterization of the electronic states in SRO using optical and electrical techniques can shed light on the properties of these important materials. The PL and CL characterizations and energy state models discussed here can be used to gain better understanding of the trapping behavior of these materials.

Under photonic excitation electrons will move to more energetic states leaving behind positive states; that is, positive and negative charges will result in a near neighborhood. So, electrons are able to decay between these traps because of the Coulombic attraction. However, a competition between emissive and nonemissive decays will be present in the SRO films.

A variety of LPCVD-deposited SRO films has been characterized and was found that films with 5.5% silicon excess have the most intense PL and CL emissions. These 5.5% silicon excess films have no detectable Si nCs and higher trap densities; reinforcing that emission is due to recombination from trap states. A DAD model was presented to explain the observed PL and CL emissions. This model can serve as a baseline for future models to improve the fits to the measured spectra.

V. CONCLUSION

In this article, SRO with silicon excess 5.5% was studied. Experimental photo- and cathodoluminescence were obtained, and used to determine the donor and acceptor states in the forbidden gap.

DAD emission model was assumed as valid for SRO obtained by LPCVD. Correlating PL and CL results and the estimation of the donor and acceptor energies was obtained.

The Coulombic interaction was neglected because its contribution to the luminescence is unimportant. The emission DAP's distributions were obtained. It was found that the DAD emission depends on the excitation source and CL excites higher electronic states due to the high excitation energies. SRO₃₀ films with 5.5% excess were found to be well modeled by the DAD emission.

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