A new Global Reaction Model (GRM) has been used to evaluate theoretically the optical properties of nanostructures of Silicon-Rich Oxides (SRO) thin films. In this work we evaluate the optical spectra of a selected set of [Si\textsubscript{n}O\textsubscript{m}] nano-structures (5 ≤ n ≤ 26). We obtain FTIR, Raman and luminescence spectra, besides, we calculate the Orbital Energies plots and propose a plausible mechanism for the generation of this kind of nanostructures which considers the necessary reactions for the formation of different oxide matrices along with the compositional and luminescence spectra changes, before and after the thermal treatment. For the case of luminescence studies, we make comparisons between our theoretical luminescent spectra with those of experimental results.

Thin films made up of materials such as SRO, containing a tetravalent metalloid as silicon, are very relevant because they produce light emission at room temperature when are stimulated. Some novel devices have been proposed and explain correctly the actual molecular structure of SRO, in addition to the optical and electronic properties of this kind of materials. The physical microscopic structure of SRO thin films is still a great interest area of research, and explains why there are still a few models are used to describe a SRO network. This model considers the global reaction mechanisms and explain the actual molecular structure of SRO, so we find in some works that the SiO\textsubscript{x} structure films are assigned to MM. On the other hand, IM was used to describe SiO\textsubscript{x} structures with less than 14 silicon atoms. Likewise, results obtained in this research predict luminescence in visible region for molecular structures with less than 14 silicon atoms. In this case, there should not be any significant variations in the number of oxygen atoms in the vicinity of any given silicon atom, whereby the oxygen content determined by the position of the Si-O\textsubscript{x} stretching mode should be equal to the macroscopic oxygen content. Finally, IM assumes a smooth variation of the chemical composition at the boundaries between silicon clusters and the SiO\textsubscript{2} matrix, leading to a continuous distribution of the oxygen content

In order to explain the accurate molecular structure of SRO, so we find in some works that the SiO\textsubscript{x} structure films obtained by radio-frequency Sputtering and physical vapor deposition were claimed to correspond to RBM, whereas the SiO\textsubscript{x} films obtained by magnetron sputtering, LPCVD, have been assigned to MM. On the other hand, IM was used to describe SiO\textsubscript{x} layers prepared by LPCVD from Si\textsubscript{2}O source at 750 °C. Taking into account the foregoing models focused to study and explain correctly the molecular structure of SRO, in this paper we propose a new Global Reaction Model (GRM) to describe a SRO network. This model considers the global reaction mechanisms of the SiO\textsubscript{x} structure films obtained by thermal oxidation of SiO\textsubscript{2} or some sub-oxides like Si\textsubscript{2}O\textsubscript{3} or Si\textsubscript{3}O\textsubscript{4} and some novel devices have been proposed based on these outstanding properties.

Thermal treatment of SRO thin films can produce light emission at room temperature when are stimulated. Today, only a few models are frequently used to describe a SRO network, namely: the Mixture Model (MM) by Bell and Levy\textsuperscript{10}, the Random Bonding Model (RBM) by Philipp\textsuperscript{11} and the Intermediates Model (IM) introduced in 2011 by Novikov and Grisenko\textsuperscript{12}. MM considers the SiO\textsubscript{x} structure as a mixture of two different phases, one of which is richer in oxygen than the other. RBM describes the SiO\textsubscript{x} as a single-phase structure consisting of a number of homogenously distributed randomly bonded Si-[Si\textsubscript{2-4}O\textsubscript{6-n}] tetrahedron with n = 0, 1, 2, 3, 4. In this case, there should not be any significant variations in the number of oxygen atoms in the vicinity of any given silicon atom, whereby the oxygen content determined by the position of the Si-O\textsubscript{x} stretching mode should be equal to the macroscopic oxygen content. Finally, IM assumes a smooth variation of the chemical composition at the boundaries between silicon clusters and the SiO\textsubscript{2} matrix, leading to a continuous distribution of the oxygen content. Relevant information was reported, in 2012, by Davor et al\textsuperscript{13}, who, in an extensive review, considered that the actual SRO molecular structure seems to be greatly determined by the deposition procedure\textsuperscript{14}. In order to explain the accurate molecular structure of SRO, so we find in some works that the SiO\textsubscript{x} structure films obtained by radio-frequency Sputtering and physical vapor deposition were claimed to correspond to RBM, whereas the SiO\textsubscript{x} films obtained by magnetron sputtering and LPCVD, have been assigned to MM. On the other hand, IM was used to describe SiO\textsubscript{x} layers prepared by LPCVD from Si\textsubscript{2}O source at 750 °C.

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tion presents in a gas mixture of N\textsubscript{2}O and SiH\textsubscript{4}, annealing and secondary reactions when the SRO thin films are obtained by LPCVD technique. By using this model, we analyze a selected set of [Si\textsubscript{x}O\textsubscript{y}N\textsubscript{z}] nano-structures generating their UV-Vis, FTIR and Raman spectra along with dimensions of the silicon-mano-crystals. The outline of this paper is as follows: we describe the GRM in section 2, Section 3 is devoted in presenting experimental results about EL-spectra of SRO thin films obtained by LPCVD and theory about our theoretical as well as we present results of the theoretical studies of the optical properties of a variety of Si\textsubscript{O\textsubscript{x}} structures presumably found in SRO thin films and conclusions.

2.0 The Global Reaction Model

In this model we consider the Global and Partial Reactions which are necessary to generate the oxide matrices [SiO\textsubscript{3}Si\textsubscript{2}O\textsubscript{5}], the annealing reactions for explaining the compositional changes before and after the thermal treatment and consequently the changes in spectra intensity and in a set of secondary reactions of the oxide matrices with the hydrogen produced to obtain the ions that could be associated with the emission in SRO thin films with specific defects.

2.1 Global and Partial reactions

When SRO is prepared by LPCVD, a gas mixture of N\textsubscript{2}O and SiH\textsubscript{4} is habitually used\textsuperscript{7} and the Si excess content can be modified by the gas flow ratio defined as Ro = [N\textsubscript{2}O]/[SiH\textsubscript{4}]. The silicon excess can be as high as 17% for Ro = 3, and the experimentally stoichiometric SiO\textsubscript{2} (a non-free silicon film) can be obtained for Ro ≥ 50.\textsuperscript{10} Theoretically, Ro = 40 corresponds to the stoichiometric silica, when a silane-nitrogen mixture at 5% is used. Experimentally, there is enough evidence that SRO thin films are constituted by a silicon oxide mixture and not only by one of them, and they are independent of the value of Ro, whereby we have the global reaction given by Eq. (2.1):

\[ 7\text{N}_2\text{O}_{\text{gas}} + 11\text{SiH}_4_{\text{gas}} + 6\text{SiO}_2_{\text{solid}} \rightarrow \ ]

\[ \rightarrow \ ]

\[ (1 + x)\text{Si}_4\text{O}_3_{\text{solid}} + (2 + 6 + 2x)\text{Si}_2\text{O}_5_{\text{solid}} + (1 + y)\text{SiO}_2_{\text{solid}} + (2 + 6 + 2x)\text{Si}_2\text{O}_5_{\text{solid}} + (1 + y)\text{SiO}_2_{\text{solid}} \] (2.1)

From this, it is evident that (SRO)\textsubscript{bulk} thin films in equilibrium are always a silicon oxide mixture constituted by the following silicon and silicon oxides quantities:

\[ (1 - x)\text{Si}_4\text{O}_3_{\text{solid}} + (2 + 6 + 2x)\text{Si}_2\text{O}_5_{\text{solid}} + (1 - y)\text{SiO}_2_{\text{solid}} + (2 + 6 + 2x)\text{Si}_2\text{O}_5_{\text{solid}} + (1 - y)\text{SiO}_2_{\text{solid}} \] (2.2)

2.2 Annealing reactions

Depending on the silicon content excess and the post thermal treatment, both the density and size of the embedded Si-nCs can just be controlled through the deposition process, it leads that the electrical and optoelectronic properties can be improved.

When SRO thin films are annealed, some oxides are degraded. The plausible "annealing reactions" proposed are:

In these equations we point out that double arrow notation \[ SI\text{O}_2{\text{solid}} + \text{Heat} \rightarrow (1 - \text{c})\text{SiO}_2{\text{solid}} + (0.5 + 0.5\text{c})\text{Si}_2\text{O}_5{\text{solid}} + \text{Si}_2\text{O}_5{\text{solid}} \] (2.3)

\[ SI\text{O}_2{\text{solid}} + \text{Heat} \rightarrow (1 - \text{c})\text{SiO}_2{\text{solid}} + (2 + \text{c})\text{Si}_2\text{O}_5{\text{solid}} + 2\text{Si}_2\text{O}_5{\text{solid}} \] (2.4)

stands for denoting equilibrium condition, besides, \( \text{c} \) and \( \text{c} \) determine the progress of the annealing reactions.

With GRM is possible to predict as a consequence from reactions proposed in Eq. (2.3) and Eq. (2.4) that, after annealing, the oxides SiO and Si\text{O}_2 along with Si increase in atomic composition and conversely both Si\text{O}_2 and Si\text{O}_2 decrease. We see that this fact agrees with RBM\textsuperscript{11}, along with data obtained experimentally\textsuperscript{6}, see Table 1.

2.3 Side-way or Secondary Reaction

Before performing the first-principles calculations, we take into account that our problem of interest must be modeled with 100 atoms at most; therefore Eq. (2.2) must be rewritten in terms of the number of atoms, leaving the following oxides:

\[ \text{Si}_n\text{O}_{2n} , \text{Si}_2\text{O}_3\text{N}_3, \text{Si}_n\text{O}_3 , \text{Si}_2\text{O}_n \] (2.5)

The reactor effluent is a gaseous mixture of hydrogen, oxygen and nitrogen atoms. The produced hydrogen gas can react as follows:

\[ H_2 = [\text{H}]^+ + [\text{H}^{-}] \] (2.6)

The formed hydrogen react with silicon oxides Eq. (2.5) and after a dehydration reaction has been carried out, it sets up the cations (see oxides in Eq. (2.7))

\[ [\text{Si}_n\text{O}_{2n-1}]^{2+}, [\text{Si}_2\text{O}_3\text{N}_{3n-1}]^{2+}, [\text{Si}_n\text{O}_{n-1}]^{2+} : [\text{Si}_2\text{O}_n\text{N}_{n-1}]^{2+} \] (2.7)

These oxide matrices are nanostructures with oxygen vacancies (3n-1, 2n-1 or n-1 oxygen atoms respectively). As it is widely known, Cervera et al.\textsuperscript{19} have associated the emission in SRO thin films with specific defects, such emissions at 460 nm, 520 nm and 650 nm are related to the oxygen deficiency-related produced Centers (ODC) or oxygen vacancies.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>( Ro=30 )</th>
<th>( Ro=30 )</th>
<th>( Ro=20 )</th>
<th>( Ro=20 )</th>
<th>( Ro=10 )</th>
<th>( Ro=10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{SiO}_2</td>
<td>55.08</td>
<td>47.35</td>
<td>48.28</td>
<td>42.89</td>
<td>48.02</td>
<td>45.96</td>
</tr>
<tr>
<td>\text{Si}_2\text{O}_3</td>
<td>31.60</td>
<td>23.04</td>
<td>34.34</td>
<td>29.39</td>
<td>28.64</td>
<td>19.42</td>
</tr>
<tr>
<td>\text{SiO}</td>
<td>8.18</td>
<td>19.57</td>
<td>9.78</td>
<td>18.23</td>
<td>9.66</td>
<td>13.02</td>
</tr>
<tr>
<td>\text{Si}_2\text{O}_5</td>
<td>3.72</td>
<td>7.94</td>
<td>4.96</td>
<td>6.65</td>
<td>9.73</td>
<td>10.53</td>
</tr>
<tr>
<td>\text{Elemental Si}</td>
<td>1.4</td>
<td>2.10</td>
<td>2.64</td>
<td>2.84</td>
<td>3.95</td>
<td>11.148</td>
</tr>
</tbody>
</table>

Oxides described by Eq. (2.2) may react with the hydrogen in a different way forming the following anions:

The formed anions are different matrices containing oxides

\[ \text{Si}_n\text{O}_{2n-1}\text{O}_2\text{Si}^{3-}, \text{Si}_2\text{O}_3\text{N}_{3n-1}\text{O}_2\text{Si}^{2-} \]

with silicon vacancies or defects, and may or may not be present in the SRO films.

3.0 Discussion of results

As is known, in the EL phenomenon, EL increases the light emission of charge carriers because electrons are injected into the conduction band and holes into the valence band, allowing emission of charge carriers because electrons are injected into the conduction band and holes into the valence band, allowing the electron and holes to recombine radiatively through transitions from higher energy states into radiative centers.\textsuperscript{6}

According to experimental reports\textsuperscript{2,3,22}, EL was tested in devices having an MOS-like structure, using poly-silicon as a gate electrode (LEC, Light Emitter Capacitor). Poly-silicon is enough transparent in the emission range of SRO. On the other hand, EL in SRO, obtained by LPCVD and annealed at 1100 °C, requires applications of high electric fields and also high currents, so that these devices work at the threshold to be electrically damaged. Only devices having high photo-emission display Electroluminescence effects, this requirement is only found in devices with...
a gas flow ratio of Ro=20 as was reported. When electrons are injected into the SRO film, the charge concentration inside the LEC distributes among the agglomeration of defects, which act as superficial and deep traps behaving as emission centers of low and high energy (red and blue centers), respectively. As has also been reported, the mobility of electrons in the SRO is very high compared with that of holes, it makes possible that the emission is attributed to electrons decaying into positive traps. Plausible emission mechanism of an LEC could be quite similar to that observed in organic light emitting diodes containing a high distribution of traps 15.

Likewise, when electrons are injected from anode into the SRO film as a consequence of applied bias voltage, a fraction of the electrons flow within the film moving into the cathode, while the rest will be trapped by defects as already known 15, this phenomenon especially happens in SRO20 (SRO with Ro=20) films. Additionally, as the current increases, the trapped electrons in defects, blockade the conduction paths hindering the charge carrier transport. Therefore, the higher bias voltage, the higher electron energy, so the deep traps are easier reached consequently the emitted photons are more energetic and it leads to the EL intensity is increased.

3.1 Experimental Procedures
In accordance with the interest of this work for correlating the luminescence observed in SRO thin films with that calculated theoretically, here we consider firstly unpublished experimental results included in Figures (1) and (2) (provided by Morales A. et al.). We take luminescent spectra as a reference for comparison with regard to the wavelength values in the emitting regions that are feasible to compare with the theoretical results of our model. To obtain Electro-luminescence in LEC’s made up of SRO, obtained by LPCVD and annealed at 1100 °C, three conditions have to be satisfied: first, the density of SiO molecules in SRO thin films has to be high, second, the energy applied to the LEC has to be enough to reach the different energetic states, and third, there must be high injection of carriers from anode to produce agglomeration of electrons in the conduction trajectories in the film. From the morphological composition approach in SRO20 films, the agglomeration of defects is composed of species or molecules, which require either higher or lower energy to be excited.

Fig. 1 (color on line) Electro-luminescence spectra for SRO film with Ro=20, with applied forward-biased from 44 to 64 Volts.

Fig. 2 (color on line) Electro-luminescence spectra for SRO film with Ro=20, with applied reversed-biased from -50 to -74 Volts.

According to experimental results as shown in Figs. 1-2, by way of explanation, we have that, at low electric fields (or using UV radiation which is not this case) most of electrons will be trapped at lower energy states producing the emission mainly in the red region as indicated in Fig. 1 (forward-biased) and Figure 2 (reversed-biased).

Figure 1 displays EL spectra when SRO20 films were subjected to voltages from 44 to 64 V. The peaks intensity varies with the applied voltage and we observe that step by step each curve shows a peak which increases successively, accompanied by a secondary shifted-peak toward high energies.

From either Figure 1 or Figure 2 it is possible to observe an uppermost peak positioned around of 690 nm, it is similar to the one observed very frequently in PL spectrum found in literature for SRO films deposited by LPCVD. This fact is in good agreement with the theoretically calculated peak corresponding to Si11O11 molecule which has an expected red emission wavelength at 694.37 nm for a triplet excited state, and could correspond with an applied voltage <50V, as well corresponds appropriately with the wavelength calculated whose value is of 699.24 nm for a Si15O7 molecule, nano-structure (see Table 7).

As regards the secondary blue-shift peak, when the applied energy is increased a significant density of electrons are trapped in more energetic states, so when they relax the blue emission appears with an important contribution on the radiative recombination process. Besides, the higher applied reversed-biased, the higher density of electrons trapped in more energetic states consequently higher the blue-shift emission peak. This condition was theoretically found for a Si15O7 molecule where the calculation predicted the highest emission in blue, at 466.83 nm (review Table 7). From Fig. 2 we observe the blue-shift emission wavelength, located approximately around of 675 nm. We stress that no one neutral Si15O7 molecule with this emission wavelength was found.

3.2 Computer-Generated Results
In this work we employed the Density Functional Theory with the aim to evaluate theoretically the opto-electronic properties of a selected set of SiO nano-structures (S5ns26). We include calculations of FTIR, Raman and luminescence spectra. Also, we compute the frontier orbitals, gaps, Mulliken atomic charges, natural charges, bond orders and geometries of all neutral molecules investigated.

3.2.1 Trapping-Charge Mechanism
The interest of this work, as has been mentioned above, is to correlate experimental results with theoretical calculations based on the GRM proposed to explain the origin of the luminescence in SRO thin films. We discuss below the charge trapping mechanism and then show the results of the calculations regarding the charge distribution in molecules suggested. As a routine, the electrical properties of SRO thin films in MOS-like structures have been commonly analyzed experimentally by current versus voltage (I-V) and capacitance versus voltage (C-V) techniques. In a previous work of Morales-Sánchez et al., high current was observed at low negative and positive voltages, but at a certain voltage (Vdrop), the current dropped to a low conduction state until a high electric field again activated a high conduction state. C-V measurements demonstrated a capacitance reduction at the same time as the current dropped, but without appreciable flat-band voltage (Vfb) shifting. The drop in capacitance and current was also observed after applying an electrical stress. These effects are attributed to the annihilation of conductive paths created by Si-nCs. The conduction mecha-
nism was also analyzed by making use of theory about trap assisted tunneling and Fowler–Nordheim tunneling at low and high electric fields, respectively. Fowler–Nordheim tunneling is the wave-mechanical tunneling of an electron through an exact or rounded triangular barrier. Two types of basic situations are recognized: (1) when the electron is initially in a localized state; (2) when the electron is initially not strongly localized, and is best represented by a travelling wave. Emission from a bulk metal conduction band is a situation of the second type, and discussion here relates to this case. It is also assumed that the barrier is one-dimensional [i.e., has no lateral structure], and has no fine-scale structure that causes scattering or resonance effects. To keep this explanation of Fowler–Nordheim tunneling relatively simple, these assumptions are needed; but the atomic structure of matter is in effect being omitted. Hence, starting from the electron one-dimensional Schrödinger equation
\[
\hat{H} \psi(x) = E \psi(x)
\]
rewritten as:
\[
-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x)
\]
With \( \hat{P} \) the kinetic energy operator, \( \psi(x) \) measured from the emitter’s electrical surface \( z \), and \( M(x) \) defined as the electron motive force which can be interpreted as the negative of the electron kinetic energy associated with the motion of a hypothetical classical point electron in the \( x \)-direction which is positive in the confinement barrier. The shape of a tunneling barrier is determined by how \( M(x) \) varies with position in the region where \( M(x) > 0 \). Two models have special status in field emission theory: the exact triangular (ET) barrier and the Schottky–Nordheim (SN) one. For the former \( M^{\text{SN}}(x) = -\hbar^2 \frac{d^2}{dx^2} M \) and for the latter
\[
\int_0^1 \frac{d\bar{x}}{f} \left( \bar{x} \frac{d}{d\bar{x}} \frac{d}{d\bar{x}} \right) \frac{f}{f_0} \psi(x)^2 M(x) = \int_0^1 \frac{d\bar{x}}{f} \left( \bar{x} \frac{d}{d\bar{x}} \frac{d}{d\bar{x}} \right) \frac{f}{f_0} \psi(x)^2 M(x)
\]
here, \( \hbar \) is the zero-field height (or unreduted height) of the barrier, \( e \) is the elementary charge, \( F \) is the barrier field, and \( \epsilon_0 \) is the vacuum dielectric constant. By convention, \( F \) is taken as positive, even though the classical electrostatic field would be negative. The SN equation uses the classical image potential energy to represent the physical effect of “correlation and exchange.” This effect is modeled by using DFT for all analyzed molecules. Besides, the exchange and correlation energy may be written in terms of an average over the Coulomb-coupling-coupling constant:
\[
\langle V \rangle_{\text{XC}} = \frac{1}{2} \int \frac{d\bar{x}}{f} \psi^*(x) \frac{d}{d\bar{x}} \psi(x) - E_H
\]
The exchange and correlation energy defined in Eq. \( \text{(3.1)} \) may also be written in terms of the average exchange-correlation whole density as follows:
\[
\langle V \rangle_{\text{XC}} = \int f^2 dV \langle n^2 \rangle_{\text{XC}} \frac{n^2}{n_0^2} (r, r') \frac{1}{|r - r'|}
\]
The derivative discontinuity is a very important property in describing the gap in insulators. Table 2 lists the calculated HOMO and LUMO energies and the gap energy for \( \text{SiO}_2 \) molecules, where 5s\n26 is the number of silicon atoms in each neutral molecule studied.

An iso-surface is a constant value (in our case the HOMO and LUMO energy) within a volume of space; in other words, it is a level set of a continuous function whose domain is 3D-space.
Using this approach, we evaluate the potential for structures type Si_{12}O_{12}. For example, Fig. 5 displays a slide of potential for the molecule Si_{12}O_{12}. Taking the difference of the two limits when M tends to N from above and to N + 1 from below we have

\[ \epsilon = \frac{\partial V}{\partial n_{+}} - \frac{\partial V}{\partial n_{-}}. \]

Thus, there is a discontinuity in the single-particle kinetic energy. Alike, such discontinuity exists in the exchange-correlation potential which is:

\[ V_{xc} = \frac{\partial E_{xc}}{\partial n_{+}}. \]

We have estimated the band gap through the evaluation of HOMO and LUMO. Besides, we have calculated others Quantitative Structure-Activity Relationships QSAR parameters with the purpose of correlate them with the size of the structures studied.

**Figure 5 Calculated slide of potential for Si_{12}O_{12} structure.**

### Mulliken population analysis

The luminescence phenomena in Si_{12}O_{12} structures could be focused through a trapping charge mechanism but it would be very difficult and complex to make an exhaustive theoretical calculation. Instead of that, in this work we make use of the Mulliken population analysis which permits us that the atomic charge on an atom can be calculated as the sum of the atomic orbital contributions of the atom in the occupied molecular orbital and its nuclear charge. The charge density is related to the chemical reactivity of a molecule, but being a three-dimensional function, is more convenient to define atomic charge density, which is also known as partial charge (atomic charge), approximating the complex distribution by the simplest one in which each atom has a fictive partial charge.

A density matrix is a matrix that describes a quantum system in a mixed state, a statistical ensemble of several quantum states, in contrast to a pure state, described by a single state vector. The density matrix is the quantum-mechanical analogue to a phase-space probability measure (probability distribution of position and momentum) in classical statistical mechanics. Explicitly, we suppose a quantum system may be found in state with probability \( \rho_1 \), or it may be found in state \( \psi_2 \) with probability \( \rho_2 \), or it may be found in state \( \psi_3 \) with probability \( \rho_3 \), and so on. The density operator for this system is \( \rho = \sum \rho_n \). Once the density matrix is determined, one can calculate many properties of the system, particularly, analyze electron density. The Mulliken population analysis, even though represents a rough partition of electronic distribution, can be easily carried out.

Integrating the expression to calculate the charge density, this integral is equal to the number of atoms \( N \), therefore:

\[ N = \sum_{\mu \nu} \rho_{\mu \nu} = \sum_{\mu \nu} \langle \psi_{\nu} | \bar{r} | \psi_{\mu} \rangle = \sum_{\mu \nu} \langle | S_{\nu} | S_{\mu} \rangle = \bar{r} \langle S | S \rangle \]

We see that it is then possible to assign two different ways by which many electrons are placed in each atomic orbital. The first way is that each element of the diagonal of the product is the number of electrons in the atomic orbital. It is easy to see that we thus assign effective charge per each atom if we add the number of electrons in each of the atomic orbital associated with one atom minus the positive charge of the nucleus. This is the essence of the Mulliken population analysis. Making use of this kind of analysis, we calculate the Mulliken charge (in electron unit’s \( e^{-} \)) and the bonds orders (dimensionless) for the structures \( Si_{12}O_{12} \). Particularly, for \( Si_{12}O_{12} \) neutral molecule obtaining results which are shown in Fig. 6, DFT was used in order to get these results.

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**Figure 6 Calculated Mulliken Charge for neutral Si_{12}O_{12} molecule.**
Table 3 Atomic Charges calculated (Mulliken versus Natural charges) for a [Si\textsubscript{18}O\textsubscript{18}] neutral nanostructure.

Additionally, the red highlighted cells, in Table 3, show the four silicon atoms with a Mulliken charge of 1.186 (corresponding to Si\textsubscript{7}, Si\textsubscript{9}, Si\textsubscript{12} and Si\textsubscript{14}). It is noteworthy that silicon atoms identified as Si\textsubscript{8} and Si\textsubscript{13} both exhibit the highest Mulliken atomic charges (+1.298).

The absolute values of the Mulliken charges in the remaining 12 silicon atoms, in this molecule, are less than unity, from which nine have positive charges and three negative ones. The silicon atoms identified as Si\textsubscript{2}, Si\textsubscript{3} and Si\textsubscript{4} forming part of a penta-cycle constituted exclusively of silicon atoms are those that exhibit this unusual behavior in Mulliken charge.

Table 4 Bond Order Mulliken for a [Si\textsubscript{18}O\textsubscript{18}] neutral molecule.
Table 4 lists Mulliken bond orders (dimensionless) for a Si_{\text{O}_n} nano-structure. In this table we point out with blue highlighted cells some bond orders Si-Si which exhibit weak bonds of around 0.07 or 0.04, e.g., Si_{11}-Si_{10}, Si_{14}-Si_{13}, Si_{15}-Si_{14}, and so on. These silicon atoms are joined to each other through oxygen atoms.

We identify, besides, a penta-cycle forming a green highlighted plane in Fig. 7. The red highlighted cells in Table 4 mark some representative silicon atoms which are strongly joined. Si_{11}-Si_{10}, Si_{14}-Si_{13}, Si_{15}-Si_{14}, (Mulliken’s bond order varies from 0.784 to 0.851).

3.2.2 Calculated Fourier Transform Infra-red spectroscopy (FTIR) and Raman spectra

In this work we are interested in studying the normal modes of vibration of the Si_{\text{O}_n} structures for which we make use of DFT in order to compute the Hessian matrix and obtain the FTIR and Raman spectra.

This Hessian matrix contains the second derivatives of the molecular energy (measured with a method of electronic structure) with respect to the molecular coordinates. By diagonalizing this matrix we obtain: (1) the normal modes of vibration which are combinations of the atomic coordinates, they allow an easy description of the vibrational motion of the molecule, because the potential energy associated with the vibrational modes can be decomposed as the sum of harmonic terms, one for each normal mode, (2) the frequencies associated with each normal mode which can be assigned to the frequencies observed in the IR and Raman spectra.

A systemic theoretical study was done recently by Zhan\textsuperscript{16} and Shu-Xian Hu et al.\textsuperscript{13} on the structural and electronic properties of ground-state silicon monoxide clusters (Si-O\textsubscript{n} \textsuperscript{1}/1 ≤ n ≤ 26).

For our case of interest, we apply DFT in order to calculate FTIR and Raman spectra for Si_{\text{O}_n} neutral nanostructures, 5 ≤ n ≤ 26 (excluding n=18, because we have convergence troubles, and n=7, 10 because such structures are either nonexistent or currently unknown. Fig. 8 displays the FTIR spectrum calculated for one of the simplest Si-O structures considered. This molecular structure is constituted by five silicon atoms and five oxygen atoms, and they form two rings of three silicon atoms each one. These rings are linked by a silicon atom and placed in orthogonal planes.

Figure 8 \([\text{Si}_{\text{O}_n}]\) molecular structure formed by two rings placed in orthogonal planes joined by a silicon atom and the corresponding calculated FTIR spectrum (top) and Uv-Vis spectra (bottom)

We identify three outstanding peaks associated with vibrational frequencies located at 987-989 cm\(^{-1}\) (the uppermost peak) overlapped with intensities of 746.87 and 691.98 arbitrary units (A.U.), besides at 939 cm\(^{-1}\) (the middle peak) with 1053.66 U.A. and lastly at 806 cm\(^{-1}\) (the lower peak), besides, the lowest peaks with 157.39 A.U. overlapped with a small vibration of 78.99 U.A. at the same frequency. In figure the filled circles situate the positions of intensity for each peak. The uppermost and middle peaks both correspond to stretching modes Si-O bonds whereas the lower peak corresponds to stretching mode Si-O bonds in cycle that includes a Si-Si bond (see Fig. 8). The two furthest small peaks are associated with rocking mode vibrations in Si-O bonds each one in cycle.

As regards Si_{\text{O}_n} molecule it exhibits photoluminescence both in ultraviolet region (at 303.26 nm) and in visible region (at 581.52 nm). The calculated emission intensity is similar in both regions; refer to Figure 8 (bottom).

On the other hand, it is found that as the agglomerate size is increased, the number of mini-rings formed increases as well. To corroborate this fact, we analyze the Si_{\text{O}_n} molecular structure. This is shown in Figure 9 along with its FTIR spectrum. This nanostructure consists of four cycles each one includes four silicon atoms. Three of them contain Si-Si-Si bonds and the other cycle has only a Si-Si bond. The FTIR spectrum exhibits the highest peak, constituted by five vibrational frequencies (filled circles), and located in the interval of 1001 to 1045 cm\(^{-1}\). Every one of the four cycles generates a specific stretching mode vibration due to Si-O bonds in the cycle, besides, the Si-O bond in cycle together with Si-Si one gives rise to an additional stretching mode.

Table 5 Dimensions calculated corresponding to a silicon nano-crystal embedded in a \([\text{Si}_{\text{O}_n}]\) molecule.

<table>
<thead>
<tr>
<th>Distance calculated Å</th>
<th>Si7</th>
<th>Si2</th>
<th>Si8</th>
<th>Si2</th>
<th>Si3</th>
<th>Si8</th>
<th>Si2</th>
<th>Si6</th>
<th>Si8</th>
<th>Si3</th>
<th>Si7</th>
<th>Si8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.271</td>
<td>3.531</td>
<td>2.559</td>
<td>5.279</td>
<td>3.725</td>
<td>3.166</td>
<td>3.754</td>
<td>3.67</td>
<td>3.531</td>
<td>3.672</td>
<td>5.279</td>
<td>2.559</td>
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</tbody>
</table>

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Figure 9 The FTIR spectrum calculated for \([\text{Si}_{\text{O}_n}]\) molecular structure which consists of four cycles of which three contain Si-Si-Si bonds and the other only a Si-Si bond. Because of the superposition of the rings, it is only possible to identify clearly three of them.

Figure 10 Structure and FTIR calculated for \([\text{Si}_{\text{O}_n}]\) molecular structure along with its FTIR spectrum.
The middle size peak includes overlapped frequencies varying from 889 cm\(^{-1}\) to 977 cm\(^{-1}\). The remaining small peaks have definite frequencies at 820, 665 and 360 cm\(^{-1}\). The corresponding calculated UV-Vis spectrum (not reported) predicts emission in visible region in two regions one of them with two intervals varying from 412.98 to 429.86 nm, and the other from 444.77 to 451.43 nm and the other region with the corresponding wavelengths varying from 546.22 to 694.37 nm respectively.

Figure 11 shows the molecular structure of the Si\(_{13}\)O\(_2\) agglomerate along with its FTIR spectrum. In this case a penta-cycle of silicon atoms is formed, and is green highlighted analogous to that obtained for the case of the Si\(_{12}\)O\(_2\) structure shown in Fig. 7 above, but it is noteworthy that in this case four silicon atoms are approximately located on the same plane and the other silicon atom forms a dihedral angle of -9.6\(^{\circ}\). The FTIR spectrum calculated for the Si\(_{12}\)O\(_2\) agglomerate is quite similar to one obtained for the agglomerate of fifteen silicon atoms. Additionally there is a small shoulder to the left-side of the utmost peak with a frequency of about 1081 cm\(^{-1}\). This noticeable small shoulder not only persists but also shifts for greater agglomerates, such that found in the Si\(_{12}\)O\(_2\) molecule at the vibration frequency of about 1181 cm\(^{-1}\) (refer to Fig. 12).

![Figure11FTIR spectrum calculated for [Si\(_{13}\)O\(_2\)] molecule.](image)

![Figure 12FTIR spectrum calculated for the[Si\(_{12}\)O\(_2\)] structure.](image)

In this case the silicon penta-cycle which is formed in smaller structures is transformed into a pyramid, and the stress on central silicon atom is strongly increased, it yields this structure emits only in ultraviolet region.

Figure 13 displays calculated Raman spectra for the [Si\(_{12}\)O\(_2\)] molecular structure. It forms a nanostructure with five Si-Si bonds formed with six silicon atoms (i.e., Si\(_1\), Si\(_2\), Si\(_3\), Si\(_4\), Si\(_5\) and Si\(_6\)). According to the optical phonon confinement effect in low dimensional structures, the size of silicon nanocrystals can be estimated from both the position and width of the peak localized around of 521 cm\(^{-1}\) following the analysis of Campbell and Fauchet\(^{20}\). In agreement with Sony\(^{33}\) reports as the size of embedded silicon nanocrystals in silica decreases from 2.2 to 1.4 nm, the Raman peak shifts from 511 to 502 cm\(^{-1}\).

We identify in Raman spectrum, displayed in Fig. 13, a small peak at 490 cm\(^{-1}\) likewise at 487 cm\(^{-1}\) in Figure 14. Those vibrational frequencies correspond to Si-Si bonds for sizes 0.38 to 0.51 nm which, in turn, corresponds to the values of the average distance calculated from data in Table 5 and Table 6.

### Table 6 Dimensions calculated for a silicon nano-crystal embedded in a [Si\(_{22}\)O\(_2\)] molecule.

<table>
<thead>
<tr>
<th>Silicon atoms in [Si(_{22})O(_2)]</th>
<th>Distance calculated Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1 – Si2</td>
<td>2.353</td>
</tr>
<tr>
<td>Si1 – Si3</td>
<td>5.675</td>
</tr>
<tr>
<td>Si1 – Si8</td>
<td>5.537</td>
</tr>
<tr>
<td>Si1 – Si12</td>
<td>5.543</td>
</tr>
<tr>
<td>Si1 – Si7</td>
<td>5.208</td>
</tr>
<tr>
<td>Si2 – Si14</td>
<td>5.545</td>
</tr>
<tr>
<td>Si2 – Si9</td>
<td>5.279</td>
</tr>
<tr>
<td>Si2 – Si8</td>
<td>5.676</td>
</tr>
<tr>
<td>Si2 – Si13</td>
<td>5.535</td>
</tr>
</tbody>
</table>

Considering the results obtained in this research, it is possible to fit with the Eq. (3.14) the calculated vibrational frequencies in the molecular structures Si\(_{13}\)O\(_2\), due to silicon nanocrystals versus the number of silicon atoms by the following relation:

\[
v = 37.095 \ln(\text{NSAN}) + 375.54 \quad (3.14)
\]

Where \(v\) is the Raman vibrational frequency in cm\(^{-1}\) and NSAN is the number of silicon atoms in nanostructures type Si\(_{13}\)O\(_2\). This equation reproduces the experimental vibrational frequency data in structures with Si-O bonds, published by Sony\(^{33}\) and Fauchet\(^{20}\) satisfactorily.

As has been done previously we calculated the Si-Si bonds lengths for the [Si\(_{22}\)O\(_2\)] molecule obtaining their values ranging from 2.2479 to 2.5587 Å, the prominent dimensions of nano-crystal formed are calculated and listed in Table 5. We stress that in the [Si\(_{12}\)O\(_2\)] molecule, four silicon atoms form a tetragonal pyramid, Si\(_6\) is located in the center of the crystal, and Si\(_1\) is joined to the pyramid directly to Si\(_6\) and through the oxygen atom O\(_5\) to the silicon atom Si\(_9\).

Figure 14 displays calculated Raman spectra for the [Si\(_{22}\)O\(_2\)] structure, this latter consists of a nano-structure with eleven Si-Si bonds formed with eleven silicon atoms [Si\(_1\), Si\(_2\), Si\(_3\), Si\(_4\), Si\(_5\), Si\(_6\), Si\(_7\), Si\(_8\), Si\(_9\), Si\(_10\), Si\(_11\), Si\(_12\), Si\(_13\), Si\(_14\), Si\(_15\), Si\(_16\), Si\(_17\), Si\(_18\), Si\(_19\), Si\(_20\), Si\(_21\), Si\(_22\)] embedded in Si\(_{22}\)O\(_2\) forms a cycle of fivesilicon atoms and additionally three silicon atoms in cycle have joined two silicon atoms each one.

For the Si\(_{22}\)O\(_2\) molecule, calculated Si-Si bond lengths are in an interval from 2.3534 to 2.3971Å. Dimensions of crystals embedded in a Si\(_{22}\)O\(_2\) molecule are displayed in Table 6.

Considering the results obtained in this work, we report that the number of Si-Si bonds in neutral structures type [Si\(_{22}\)O\(_2\)] is well-fit by Eq. (3.15) with a correlation factor \(R^2\) equal to 0.982.

\[
\text{Number of Si – Si bonds} = 1.053(n)^{0.897} (3.15)
\]

Where 5 ≤ ns ≤ 26 is the number of silicon atoms in the molecular structure.

Nevertheless, the number of Si-Si bonds is an integer number (not a real number), and in consequence, for the structures investigated takes only the following values: \{1, 2, 3, 5, 6, 8, 11 and 14\}. 

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**Research Paper**
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The singlet states take place when all electrons in the molecule are spin-paired and the triplet states when one set of electron spins is unpaired. In Table 7, we have listed results for wavelengths of emission calculated in visible and ultraviolet regions for $\text{Si}_n\text{O}_n$ (structures for molecules with $n \geq 12$ silicon atoms).

Into the software employed, we have chosen options in order to evaluate the triplet states. The intensity of these excitations will be small (zero) but can be useful if we are interested in all lower energy excited states.

### Table 7 Wavelengths of emission calculated in visible and ultraviolet regions for $\text{Si}_n\text{O}_n$ structures.

<table>
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Now, we focus on the UV-Vis spectra calculated for the $\text{Si}_i\text{O}_i$ molecule, they predict, on one hand, emission in the ultraviolet region at 377.58 nm and, on the other hand, emission in the visible region at 699.24 nm (red), whilst for the $\text{Si}_O_m$ molecule, our results predict only one emission peak at 310.16 nm (ultraviolet region), see Figure 15.

In this paper, we make use DFT for evaluating the UV-Vis spectra for $[\text{Si}_O_n]$ structures, where we identify $n$ as the number of silicon atoms. The UV/Vis spectra are carried out by means of the TD-DFT calculation after the main wavefunction has been calculated. In Configuration Interaction based on single-electron promotions only (the so-called CIS method) the absorption energies are the difference between the energies of the Hartree-Fock (HF) ground state and the CIS excited state. The electronic states of most molecules can be divided into singlet states and triplet states.

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</tr>
<tr>
<td>15 Triplet at 444.77-451.43 and 694.37</td>
<td>none</td>
<td>25 325.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 497.63 (max) Doublet at 549.80-556.00</td>
<td>none</td>
<td>26 329.95</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
vibrational level of this same state by losing energy where this lost energy is transferred to other molecules through collisions. The molecule will also partition the excess energy by other possible modes such as vibrations and rotations. For example, fluorescence occurs when the molecule returns to the electronic ground state, from the excited singlet state, by emission of a photon. However, if this molecule does not fluoresce it means that it must have lost its energy by some other way. This process is called radiationless transfer of energy (see Figure 16). On the other hand, a molecule in the excited triplet state may not always use intersystem crossing to return to the ground state. It could lose energy by emission of a photon.

For DFT calculations, excited states are obtained using time-dependent DFT calculations\textsuperscript{35,36}. Our results predict luminescence in the visible region for approximately half of the calculated structures, specifically for \(n \leq 16\) silicon atoms, and large structures with \(n \geq 17\) exhibit luminescence in the ultraviolet region. We display in Figure 17 (a) to (d) some of the calculated UV-Vis spectra and their structures.

4.0 Conclusions

In this report we have employed DFT for evaluating theoretically the structures Si\(_n\)O\(_m\) type structures, where \(5 \leq n \leq 26\) is the number of silicon atoms in such structures, additionally, it has been introduced a new GRM model as a novel approach to explain the physical microscopic structure of the SRO thin films. This model firstly considers the compulsory Global and Partial Reaction(s) to produce the oxide matrices (identified as SiO\(_2\), Si\(_2\)O\(_3\), SiO and Si\(_2\)O), secondly the annealing reactions for elucidating the compositional changes before and after the thermal treatment and subsequently the variations in the intensity of luminescence spectra, furthermore, it describes a set of secondary reactions of the oxide matrices with the hydrogen produced in the reaction chamber to obtain the charged species that could be associated to the emission in the SRO thin films with explicit defects. We point out that in this work we only evaluate the SiO\(_2\) type oxide matrices as suggested by Shu-Xian Huet al.\textsuperscript{31}.

On the other hand, the information obtained from the calculated Raman spectra has permitted us to establish an analytical expression for the vibrational frequencies in theoretically calculated Si\(_n\)-O\(_m\) molecules, due to silicon nanocrystals versus number of silicon atoms. Along with these important results, we have computed the dimensions of silicon agglomerates in the Si\(_n\)O\(_m\) type oxide matrix. Taking into account this information we were able to make comparisons with crystallographic experimental data of the SRO films.

Finally, in the case of the forward-biased SRO obtained by the LPCVD technique, with \(R_o=20\) (SRO20 structure) whose Electro-Luminescence experimental results are known as reported in literature, we compared these results with those ones obtained from our theoretical calculations resulting from this that the observed experimental spectrum peak at \(\approx 690\) nm is in good agreement with the calculated Si\(_n\)-O\(_m\) molecule spectrum peak obtained in theoretical PL studies which presents an expected red emission at approximately 695 nm for a triplet excited state, and it could correspond with an applied voltage \(<50\)V. Also, this corresponds suitably with the calculated wavelength of 699 nm for a Si\(_{11}\)O\(_{11}\) nano-structure.

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