

Theoretical survey of luminescence observed in nanostructured silicon rich oxide films attributed to annealing processes

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ABSTRACT

The motivation of this work is to apply a new model, which we had called the Global Reactions Model (GRM), for the theoretical study of the optical and electronics properties of Silicon Rich Oxides (SRO) structures regardless of the technique used to fabricate such structures. Recently we published the Global Reactions Model (GRM) to describe a set of chemical reactions that could hypothetically occur during the process of obtaining silicon rich oxide (SRO) films, notwithstanding of the technique used to grow such films. Particularly, chemical reactions that occur during the process of growing of SRO films by Low Pressure Chemical Vapor Deposition (LPCVD) and Hot Filament Chemical Vapor Deposition (HFCVD) techniques were emphasized in these models. We suggest and evaluate either some types of molecules or resulting nanostructures and we have predicted theoretically, by applying the density functional theory (DFT), the contribution that they may have to the phenomenon of luminescence. We calculated the luminescent spectra of the as grown and the annealed structures. In this work we focused in siloxanes species presumably found in SRO. Copyright © 2016 VBRI Press.

Keywords: GRM; luminescence; silicon rich-oxide; LPCVD; DFT.

Introduction

The semiconductors and specifically Silicon technology takes over the electronics industry nowadays, so it is highly desirable and profitable the development of silicon-based components compatible with silicon technology, which permits the integration of electrical and optical components on a single device. For many years, one strategy to improve a light emitter based on silicon has been the silicon oxide Rich (SRO), commonly known as off stoichiometric silicon oxide. The interest about the optical properties of SRO has been increased starting from it was confirmed that SRO films exposed to high-temperature annealing exhibit efficient photoluminescence (PL). In general, luminescent properties can provide meaningful information regarding the crystalline structure of a material and, in the case of Silicon Rich Oxides thin films, their luminescence properties are on the whole important since these films can be used to fabricate luminescent devices [1]. The siloxanes are chemicals that have a backbone structure of silicon and oxygen atoms, alternating in occurrence, and have hydrocarbon groups attached to the silicon side chain. In the cyclic siloxanes, the silicon-oxygen atoms are singly bonded and form a ring. Some widely used cyclic siloxanes are displayed of **Fig. 1**. The cyclic siloxanes are used in the manufacture of silicones, in combination or alone in personal care products, and as carriers, lubricants and solvents in a variety of commercial applications. They occur in environmental media, especially in sewage sludge.

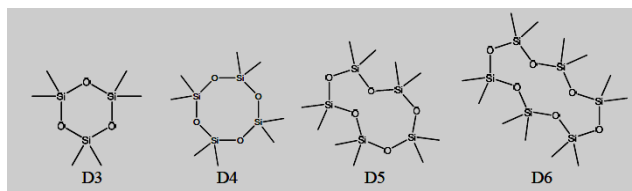


Fig. 1. Common cyclic siloxane structures. hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6).

In studies conducted by the Nordic countries, D5 was the dominant siloxane in all environmental matrices sampled except for air, where D4 dominated. Certain siloxanes are persistent in the environment, resisting oxidation, reduction, and photo-degradation. Published data on D4 and D5, for example, demonstrate hydrolysis in surface water, clay-catalyzed degradation in soil and atmospheric degradation (Durham *et al.* [2] Xu S. [3], Leman *et al.* [4]).

Silicon Rich Oxides films have received important attention of many researches due the generalized idea, that SRO is an ideal substitute of silicon. Silicon rich oxide (SRO) is a silicon compatible material that could solve the light emission limitation inherent to bulk silicon. Aceves-Mijares *et al.* [5] have evidenced that emission in SRO films is due, between others factors, to agglomerates of Si-O compounds. Computational simulations of cyclic chains of SiO were done to calculate the FTIR spectra, UV

Vis emission and HOMO-LUMO densities and they have been found good agreement with experimental data. Those previous results considered a ratio $O/Si = 1.0$. In **Table 1** we present the relative percentages of two kinds of oxides ($SiO_{1.5}$ and SiO) frequently accepted in literature as oxides constituent of SRO films. When SRO films are deposited using the technique of Low Pressure Chemical Vapor Deposition (LPCVD), the partial pressure ratio caused by the flow of reactive gases $Ro = P(N_2O)/P(SiH_4)$ is manipulated to take control the silicon excess.

Table 1. Oxidation states as proposed by Phillips in the Random Bonding Model [6] found in SRO films as grown and after annealing at 1100 °C (adapted from Aceves-Mijares *et al.* cited).

Oxidation state	As grown Ro = 30	Annealed Ro = 30	As grown Ro = 20	Annealed Ro = 20	As grown Ro = 10	Annealed Ro = 10
$SiO_{1.5}$	31.60	23.04	34.34	29.39	28.64	19.42
SiO	8.18	19.57	9.78	18.23	9.66	13.02

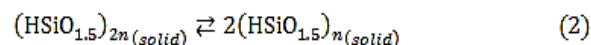
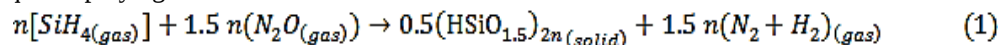
In this work we were focused on evaluating theoretically the contribution to luminescent phenomena of nanostructures with a ratio $O/Si = 1.5$. This interest is due to the relative great abundance of this specific oxide in SRO films. For doing that we evaluated a selected set of structures displayed in **Fig. 2**, which are silsesquioxanes, a bi-cyclic type siloxanes that we suggest could be present in as grown SRO films, derived of the applying the Global Reaction Model (GRM). The physical microscopic structure of SiO_x is still a subject of discussion, and to know its real arrangement is very important to understand the emission mechanism, but unfortunately there are not experimental evidences of molecular structures reported in literature.

In a second part of this investigation, we consider all hydrogen atoms are released from the structures due to thermal annealing, and in consequence we evaluated the possibilities of emission in visible region of thermal treated films.

Formation of siloxanes derivatives

Henderson *et al.* [7] have reported that the preparation of SiO_2 -embedded silicon nanocrystals (Si-NCs) from the thermal processing of sol-gel polymers could be derived from trichlorosilane ($HSiCl_3$). Straightforward addition of water to $HSiCl_3$ generates a cross-linked $(HSiO_{1.5})_n$ sol-gel polymer suitable for the generation of bulk quantities of SiO_2 -embedded Si-NCs. The structural differences between the networks structure $2(HSiO_{1.5})_n$ polymer and hydrogen silsesquioxane (HSQ, $(HSiO_{1.5})_{2n}$) result in controllable differences in the resulting oxide-embedded Si-NCs produced from these precursors.

A well-known fact is that SRO films can be obtained with LPCVD technique employing silane and nitrous oxide.



In the GRM we consider that the reaction of these gases could produce HSQ through Eq. (1) in equilibrium with branched network structure (BNS) as displayed in Eq. (2). **Fig. 3** displays the transformation of siloxane derivatives. Freestanding Si-NCs could be obtained through chemical

etching and/or thermal treatment of the oxide matrix and exhibit tunable PL throughout the visible spectrum. HSQ should produce bigger silicon nano-agglomerates than BNS. Likewise, the present Si-NCs should exhibit size-dependent photoluminescence (PL) in accordance with the principles of quantum confinement.

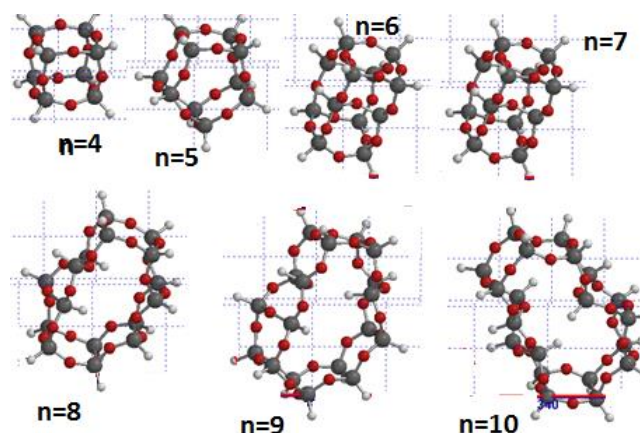


Fig. 2. Molecular Structures of as grown bi-cyclic siloxanes nanostructures modeled from $n = 4$ to $n = 10$ (corresponding to $H_8O_{12}Si_8$, $H_{10}O_{15}Si_{10}$, $H_{12}O_{18}Si_{12}$, $H_{14}O_{21}Si_{14}$, $H_{16}O_{24}Si_{16}$, $H_{18}O_{27}Si_{18}$, $H_{20}O_{30}Si_{20}$).

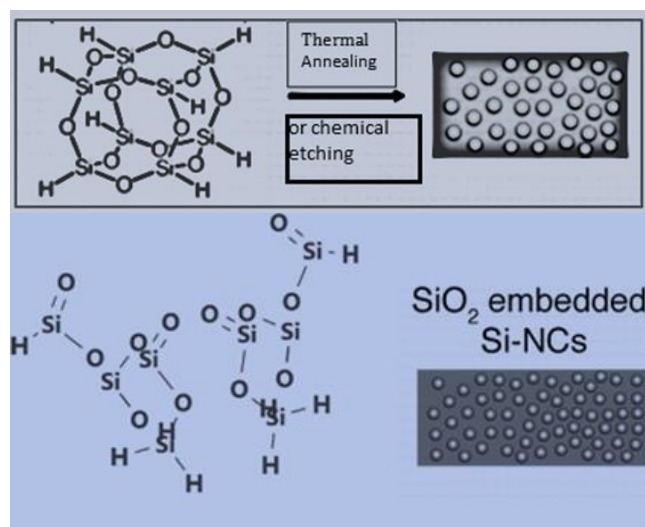


Fig. 3. Siloxane derivatives for $n = 4$. Cage structure of hydrogen silsesquioxane $(HSiO_{1.5})_{2n}$ (left), and with two branched network structures $2(HSiO_{1.5})_n$ (right).

Results and discussion

The SRO films exhibit characteristic infrared absorption peaks related with the Si–O–Si bonds in embedded SRO films. The FTIR absorbance spectra of SRO samples have

been identified experimentally and can be found in widely investigations in literature, see by example [8, 9]. Typical values reported are: (1) Si–O rocking at approximately 450 cm^{-1} , (2) Si–O bending at 808 cm^{-1} , (3) Si–H bending

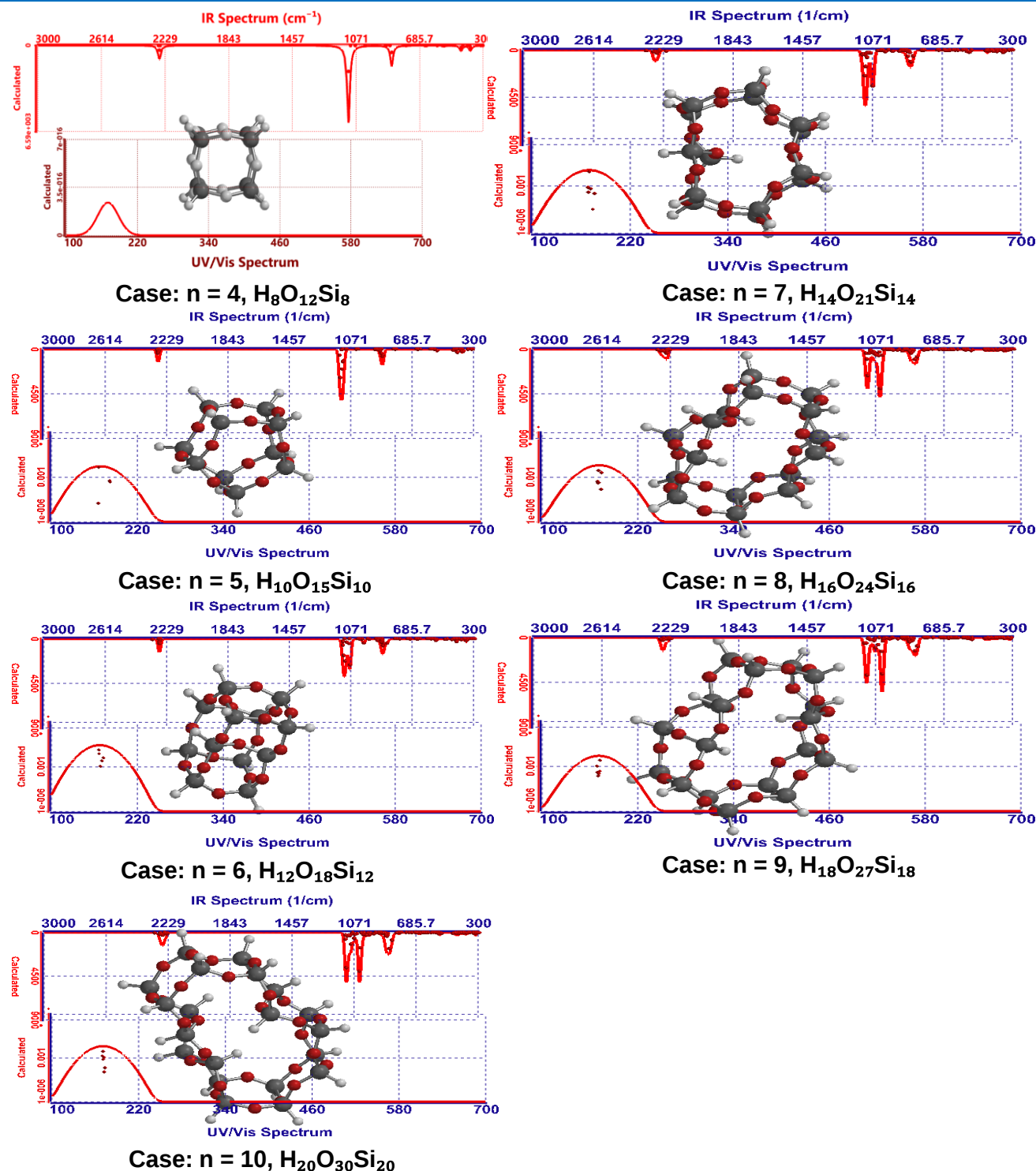


Fig. 4. Calculated UV Vis, FTIR spectra and molecules structures of as grown structures type: $\text{Si}_{2n}\text{O}_{3n}\text{H}_{2n}$, from $n = 4$ to $n = 10$.

at 883 cm^{-1} , (4) Si–O symmetric stretching vibration from 1055 to 1082 cm^{-1} and (5) Si–O asymmetric stretching at 1170 cm^{-1} .

The experimental as-deposited samples described in the literature exhibit the characteristic IR absorption due to the stretching vibration of the Si–O–Si bonds about 1035 – 1080 cm^{-1} .

Theoretically we have evaluated the FTIR spectra displayed in Fig. 4. FTIR spectra correspond with upper

plots in each case shown, whereas the plots presented in bottom for each case represent the UV Vis spectrum for each case of as grown structures, type: $\text{Si}_{2n}\text{O}_{3n}\text{H}_{2n}$, from $n = 4$ to $n = 10$. A small peak appears in the interval 2263 – 2275 cm^{-1} in all the studied cases.

These vibration frequencies are motivated by Si–H bonds. The theoretical values obtained for Si–O asymmetric stretching vibration was (1116 , 1118 , 1116 , 1114 , 1116 , 1114 and 1114 cm^{-1}) while for Si–O symmetric stretching vibration were: (1075 , 1097 , 1080 , 1070 , 1055 ,

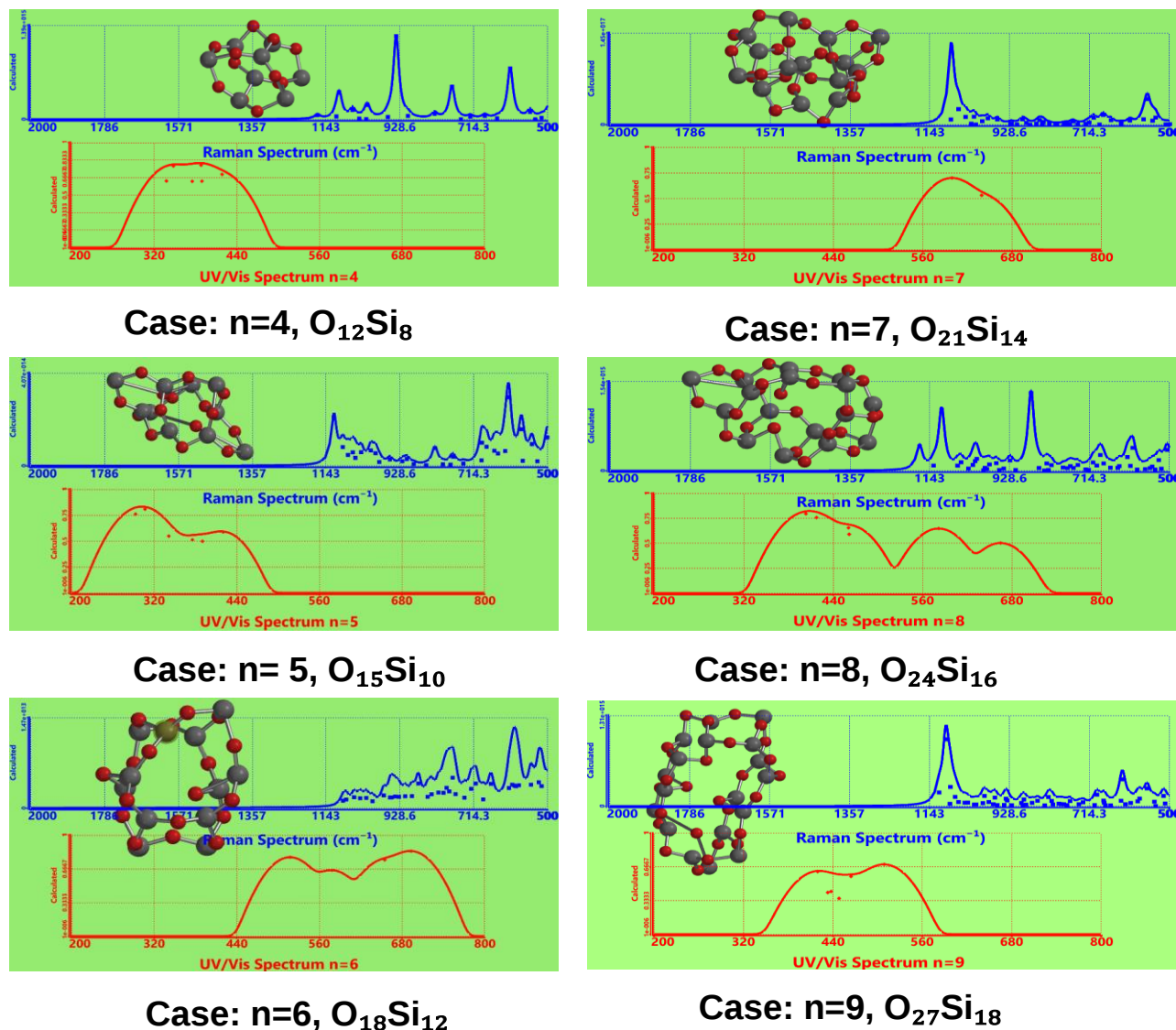
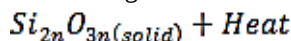


Fig. 4. Calculated UV Vis, FTIR spectra and molecules structures of as grown structures type: $\text{Si}_{2n}\text{O}_{3n}:\text{H}_{2n}$, from $n = 4$ to $n = 10$.

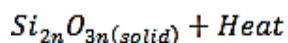
1072 and 1071 cm^{-1}). Excepting for the smallest structures, i.e, $n = 4$ and $n = 5$, in all cases the peaks corresponding to the symmetric and asymmetric cases are clearly separated.

A third smaller peak appears in FTIR spectra at: (854, 872, 870, 860, 850, 849 and 850 cm^{-1}) which corresponds to Si-H bending mode. Calculated vibrations were sorted from smallest to highest nano-structures.



$$\rightleftharpoons 2(1 - \xi')\text{Si}_{n-m}\text{O}_{(n-m)(\text{solid})} + (0.5 + \xi')\text{O}_{2(n-m)(\text{gas})} + 2\xi'\text{Si}_{(n-m)(\text{solid})} \quad (3)$$

And



$$\rightleftharpoons (1 - \xi'')\text{Si}_{2(n-m)}\text{O}_{(n-m)(\text{solid})} + (1 + 0.5\xi'')\text{O}_{2(n-m)(\text{gas})} + \xi''\text{Si}_{(n-m)(\text{solid})} \quad (4)$$

Based on the results obtained, they had predicted that the structures as they were deposited (as grown), they would have only luminescent emission in the UV region. For each one of the structures type $\text{Si}_{2n}\text{O}_{3n}:\text{H}_{2n}$ modelled, we predict only one wide band emitting in UV region. Calculated numerical values for most intense emissions

correspond with the wavelength of: (166.76, 181.40, 172.80, 176.15, 174.51, 172.46 and 173.69 nm), arranged from smallest to highest structure.

When $\text{Si}_{2n}\text{O}_{3n}:\text{H}_{2n}$ structures are treated thermally it occurs induced loss of hydrogen atoms. New structures will form with condensate formulas $\text{Si}_{2n}\text{O}_{3n}$. These nano structures were modelled and the results of the prediction

are presented in the seven cases of Fig. 5. As we will discuss below, we expect that silsesquioxanes (the bi-cycle-siloxane structures in Fig. 5) are able to emit in visible region. In fact, we have found that this is one of the mechanisms of emission present in SRO films.

If annealing process is extended in time, degradation of oxides (SRO films) would be possible, giving place to

silicon nanocrystal apparition. Quantity and size of silicon nano-agglomerates expected could be obtained from a generalization done in accordance with the GRB, and the proposed annealing reactions could be:

where, ξ' and ξ'' are the progress parameters of the annealing reactions and $0 \leq m \leq (n-1)$.

As we can see in the cases reported in the **Fig. 5**, where calculated Raman spectra are presented in the plots in blue, there is an intense peak at 939 cm^{-1} for case $n = 4$.

This frequency corresponds to stretching vibration of Si-O-Si bonds for specific oxygen atoms, I mean, those which join pair of silicon atoms of cyclic siloxanes. In the case for $n = 5$, unexpected Si-O distances greater than $2.0 \text{ \AA}$, including a bond with $5.18 \text{ \AA}$ was predicted in equilibrium structure, giving as result vibrations bands instead of vibrations peaks.

A similar situation occurs for case $n = 6$, i.e., disperse frequencies of vibration of low intensity are produced by Si-O bonds, except that we didn't found bond length bigger than $2.36 \text{ \AA}$. For case $n = 7$, the most intense peak in Raman spectrum appears at the frequency of 1085 cm^{-1} . This peak is the result of the constructive interference of three vibration frequencies in 1066 , 1085 and 1086 cm^{-1} . Case for $n = 8$ display two intense peaks, at 1111 and 871 cm^{-1} .

A predicted intense peak at the frequency of 1099 cm^{-1} for structure with $n = 9$ ($\text{O}_{27}\text{Si}_{18}$) complement the analysis or calculated Raman spectra. As the size of the cluster increases, a shift to towards higher frequencies is observed in the calculated most intense vibration frequency. Graphs shown in red (bottom) for different cases exhibited in **Fig. 5** illustrate that silsesquioxane structures, contained presumably in SRO films, will be able to emit in visible region of electromagnetic spectrum. One or more overlapped bands can appear. Shift in wave-length of most intense emission seems be random, i.e., it does not obey a defined pattern.

Conclusion

We have applied the Global Reaction Model in order to predict the theoretical luminescent behavior of bi-cycle-siloxanes hypothetically contained in nanostructured Silicon Rich Oxide films. Applying Density Functional Theory, we evaluate optical, geometric and electronic properties of structures type $\text{Si}_{2n}\text{O}_{3n}\cdot\text{H}_{2n}$, from $n = 4$ to $n = 10$ and we have found that these isolated structures could emit only in UV region. When SRO films are treated thermally, hydrogen atoms are released, forming structures type $\text{Si}_{2n}\text{O}_{3n}$ which are able to emit in visible region. We suggest the annealing reactions that can occur, doing a refinement of GRM, when SRO films are exposed to thermal treatment for a long time. Formation of silicon nanocrystals is predicted for long annealing times. This study was complemented with a discussion of vibration frequencies calculated by means of FTIR and Raman spectra.

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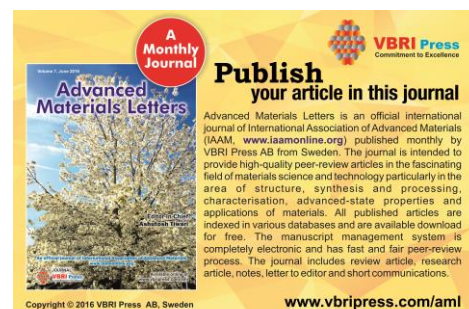
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Author contributions

NDET conducted the modeling of nano-structures and wrote the draft manuscript. JALL provided studies and advised the film growth procedures. JFJFG provided the idea and supervised the study. DHL provided the background and support in the modeling process and corrected the draft manuscript. JMJ carried out the PL interpretation in siloxane structures. All authors read and approved the final manuscript and contributed to the analysis and discussion of results. Authors have no competing financial interests.

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