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Abstract

Silicon oxycarbide (SiC$_{x}$O$_{y}$) has been extensively investigated due to its wide use in the Si semiconductor industry in applications that include low-k dielectrics, passivation layers, and etch-stop layers. Furthermore, SiC$_{x}$O$_{y}$ research has been exploring its prospective use in numerous other technological usages, such as lighting, energy, and biological applications. The latter include white light-emitting materials, hydrogen storage materials, gas sensors, anode materials for lithium batteries, and biomedical devices. SiC$_{x}$O$_{y}$ materials can intensively luminescence in a broad emission spectral range that spans the ultraviolet, the visible, and even the near-infrared spectrum, when doped with erbium. Herein, we present pertinent results on the material behaviors from chemically synthesized SiC$_{x}$O$_{y}$ thin films and nanowires. Moreover, their light-emitting properties and underlying mechanisms for light emission are explored in conjunction with data from their thin film counterparts, which are also employed as baseline comparison metric. We further highlight major challenges and promises of such materials.

Keywords: silicon oxycarbide, SiC$_{x}$O$_{y}$, Si-O-C, Si-C-O, nanowires, thin films, luminescence, CVD, e-beam lithography, structural properties, optical properties, band tails, disorder

1. Introduction

In silicon (Si) complementary metal-oxide-semiconductor (CMOS) chip technology, silicon oxycarbide (SiC$_{x}$O$_{y}$) materials have been extensively employed to serve multiple purposes. For example, SiC$_{x}$O$_{y}$ materials have been the focus of extensive study due to their applicability
as low-k dielectrics, passivation layers, and etch-stop layers to name a few [1, 2]. SiC$_x$O$_y$ materials have also been the focus of studies due to their potential application in a plethora of other technological applications (e.g. light emission, energy, and bioapplications). In particular, they have been proposed as candidates for white light-emitting materials [3–5], filters, porous adsorbents, and catalytic supports [6, 7], as hydrogen storage materials [8], gas sensors [9], negative electrode materials for lithium batteries [10, 11], and in biomedical devices [12]. Additionally, it has been also shown that SiC$_x$O$_y$ can be utilized as a host material to optically active impurities (rare earth ions). To this end, europium (Eu$^{2+}$)-doped SiC$_x$O$_y$ thin films synthetized by RF magnetron sputtering [13] as well as erbium (Er$^{3+}$)-doped SiC$_x$O$_y$ thin films for near-infrared (IR) emission at the commercially useful telecommunication wavelength of 1540 nm have been recently reported [14–16].

The fabrication of luminescent Si-based nanostructured materials for light emission applications is highly desirable, similarly to how Si-based nanophotonics has undergone great advancements in recent years [17, 18]. Due to the seamless integration of Si-based materials with process protocols and technologies developed for semiconductor CMOS technology, manufacturing costs and process complexity could be also reduced. Furthermore, the extreme down-scaling methods achieved by CMOS technology offer the opportunity to study new compelling properties owing to possible confinement effects in one (1D) or two (2D) dimensions (e.g., the reduction of exciton-phonon interactions, the increase of extraction efficiency of spontaneous emission, and suppression of Auger recombination) [19, 20]. Therefore, the functionality of such nanostructured materials and their devices can be employed in a ubiquitous way in light emission applications [21]. To this extent, SiC$_x$O$_y$ nanowires (NWs) have been recently shown to exhibit strong room-temperature visible luminescence [22–24].

In parallel, the identification and elimination of potential obstacles that could deteriorate the luminescence efficiency of such materials (e.g., temperature and excitation power density) needs to be taken into consideration. Indeed, the luminescence efficiency is known to be influenced by environmental fluctuations in temperature and pump-power-density changes [25, 26]. These fluctuations can become critical in luminescence applications such as light-emitting diodes (LEDs). In these applications, the operating temperature and power density can reach respectively ~150°C and ~200 W/cm$^2$, thus greatly influencing the light output and color chromaticity.

Silicon oxycarbide films have been grown predominantly through low-temperature plasma-enhanced chemical vapor deposition (PECVD) using an array of silane-based precursors for the needs of semiconductor industry [27–30]. However, the incorporation of source precursor fragments and decomposition byproducts in the resulting films has led to the observation of enhanced stress levels and increased defect density, both of which have detrimental effects on the optical performance of resulting materials and device structures. Recently, Lin et al. prepared amorphous SiC$_x$O$_y$ using a very high-frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) technique [31]. The resulting films exhibited intense room-temperature blue luminescence, characteristic of Si-related neutral oxygen vacancy defect centers. Ryan et al. and Vasin et al. showed that a wide variety of SiC$_x$O$_y$ with a continuous range of compositions could be produced by reactive RF-magnetron sputtering [32, 33]. Karakuscu et al. and Abbass et al. have reported sol-gel-prepared SiC$_x$O$_y$ thin films [34, 35], while Vasin
et al. have reported a-Si$_x$C$_{2-x}$O$_y$:H thin films growth by low-temperature oxidation of carbon-rich a-Si$_x$C$_{2-x}$:H thin films [36].

Nevertheless, it is desirable to identify alternative deposition methods, which can inhibit or minimize processing induced structural and/or compositional damage to SiC$_x$O$_y$ materials due to phase separation owing to the non-stoichiometric composition. Herein, key findings are summarized pertaining to the development of a thermal chemical vapor deposition (TCVD) strategy for the growth of SiC$_x$O$_y$ thin films approximating the SiC$_x$O$_{2(1-x)}$ ($0 < x < 1$) stoichiometry for light emission applications [37, 38]. These studies led to the identification of a deposition process window for the growth of SiC$_x$O$_y$ thin films with strong room-temperature light emission [3]. Additionally, we present the findings pertaining to room-temperature visible photoluminescence (PL) from SiC$_x$O$_y$ sub-100-nm nanowire materials fabricated by electron beam lithography (EBL) and reactive ion etching (RIE). These metal-free non-toxic Si-based nanostructured materials may offer an alternative and environmentally friendly pathway toward efficient visible light-emitting materials and devices.

2. Synthesis and fabrication of silicon oxycarbide thin films and nanostructures

2.1. SiC$_x$O$_y$ materials grown by thermal chemical vapor deposition: composition control

SiC$_x$O$_y$ thin films and their nanostructures are deposited on Si(100) or SiO$_2$ substrates in a hot-wall quartz tube reactor by thermal CVD at 800°C. A single source oligomer (2,4,6-trimethyl-2,4,6-trisila-heptane (C$_7$H$_{22}$Si$_3$)) is utilized as the source precursor for silicon and carbon atoms and ultra-high purity oxygen (O$_2$) and argon (Ar)/nitrogen (N$_2$) are also employed as co-reactant and dilution gases. The composition of the resulting amorphous SiC$_x$O$_{y≤1.73}$ (0.11 < $x$ < 0.65) thin films is regulated by modifying the oxygen flow rate and, hence, the oxygen partial pressure in the reaction zone. The films are deposited onto three types of substrates: single-crystal silicon (c-Si) (100), for composition, structural and optical analysis; double-polished intrinsic Si and high-quality UV transparent fused silica, for infrared and optical studies. A subset of the as-deposited SiC$_x$O$_y$ films was annealed for 1 h in different ambient (e.g., O$_2$, Ar, N$_2$, or forming gas (FG, 5% H$_2$ and 95% N$_2$)) at temperatures in the range from 500 to 1100°C. Detailed description of the deposition and annealing processes can be found elsewhere [37, 38]. The resulting samples were subsequently employed in a comparative analysis of as-deposited and post-annealed films to determine the effects of thermal treatment on film structural and optical properties as well as their photoluminescence performance.

Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS) were employed to determine the Si, C, and O content in the SiC$_x$O$_y$ materials and they were separated in three different classes, defined by their composition: SiC-like ([O] < 5 at.%), Si-C-O, and SiO$_2$-like ([C] < 5 at.%). The compositional evolution of the SiC$_x$O$_y$ thin films was plotted in the Si-C-O ternary diagram of Figure 1a along with the SiC$_x$O$_{2(1-x)}$ ($0 < x < 1$) line, with the latter representing stoichiometric silicon oxycarbide without any excess of carbon. The upper and lower limits in SiC$_x$O$_{2(1-x)}$ correspond to SiC and SiO$_2$, for, respectively, x = 1 and 0 [39, 40].
As is shown in Figure 1a, the composition of the thermal CVD-grown SiC\textsubscript{x}O\textsubscript{y} was properly tailored to closely follow the pure stoichiometric oxycarbide formula over the whole range of the synthesis process parameters. The SiC\textsubscript{x}O\textsubscript{2(1−x)} behavior observed in the samples produced herein suggests the substitution of two divalent oxygen atoms by one tetravalent carbon atom as the C concentration in the SiC\textsubscript{x}O\textsubscript{y} materials increases. The latter will be further discussed in Section 3.1. Furthermore, the observed small deviation from the stoichiometric SiC\textsubscript{x}O\textsubscript{2(1−x)} trend suggests that there is much less excess of C compared to non-stoichiometric compositions reported for SiC\textsubscript{x}O\textsubscript{y} with SiC/SiO\textsubscript{2} phases and free carbon, as it is shown in Figure 1 of reference [39].

Due to the presence of methyl groups in the CVD reactants, it is expected to have hydrogen atoms in the grown silicon oxycarbide thin films whose concentration cannot be quantified by the RBS or XPS techniques. Instead, the nuclear reaction analysis (NRA) was conducted by using the \( ^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \gamma \)-ray resonant nuclear reaction at 6.835 MeV [41]. Figure 1b shows the NRA-derived hydrogen concentration measurements of the silicon oxycarbide films as a function of post-deposition annealing temperature \( T_a \) [37]. After the 900°C annealing step, the hydrogen content is significantly reduced to 5, 2.2, and 4.5 at.%, respectively, for the SiC-like, Si-C-O, and SiO\textsubscript{2}-like samples. For annealing temperatures above 1000°C, the hydrogen content was not detectable (>1 at.%) in all three different types of samples.

The mass density \( \rho \) (g/cm\textsuperscript{3}) of thin films was calculated using the elemental compositions determined by RBS and XPS and the thicknesses measured by scanning electron microscope (SEM) by employing the following equation:

\[
\rho = \frac{D \times 10^{15}}{d} \times 1.66 \times 10^{-24} \frac{(A_{\text{Si}} + xA_C + yA_O + zA_H)}{(1 + x + y + z)} \text{(gr/cm}^3) \tag{1}
\]

where \( D \) is the thickness in rump units, which is related to the planar density, \( d \) is the film thickness, \( A_{\text{Si}}, A_C, A_O \), and \( A_H \) are the atomic weights of Si, C, O, and H, respectively, and \( x, y, \) and \( z \) are the normalized fractional contents, respectively, of C, O, and H.
The density of the silicon oxycarbide films was observed to increase with higher annealing temperature, due at least partly to the reduction in hydrogen concentration, as shown in Figure 1c. More specifically, the densities of the as-deposited films are 2.8, 2.2, and 2.1 for, respectively, SiC-like, Si-C-O, and SiO$_2$-like films. After annealing at 1100°C, the densities were measured to be significantly higher, with values of 3.3, 2.6, and 2.4 g/cm$^3$ for, respectively, SiC-like, Si-C-O, and SiO$_2$-like films.

2.2. Nanofabrication of silicon oxycarbide nanostructures

SiC$_x$O$_y$ nanofabricated systems were fabricated by electron beam lithography and reactive ion etching, namely periodically ordered sub-100-nm nanowire arrays. A representation of the baseline nanofabrication scheme of the SiC$_x$O$_y$ NW arrays is schematically depicted in Figure 2. Following the synthesis of SiC$_x$O$_y$ thin films, negative hydrogen silsesquioxane (HSQ) (6% HSQ in methyl-isobutyl-ketone solvent) resist is spun onto SiC$_x$O$_y$ wafer pieces—deposited on Si (100)—at 1000 rpm, followed by a bake procedure for 4 min at 80°C. Line patterns are exposed using electron beam lithography and then the resulting wafer piece is developed in a chemical solution bath (low concentration (2.38%) of tetramethylammonium hydroxide (TMAH) developer), yielding 2D-nanowire HSQ patterns. The HSQ patterns then underwent a hardening annealing process in Ar/N$_2$ ambient at 500°C, followed by a fluorine-based (e.g., combination of CHF$_3$ and CF$_4$ gases) anisotropic RIE to transfer the pattern into the SiC$_x$O$_y$ thin films. The HSQ residue is then removed by wet etching in buffered hydrofluoric (BHF) acid, resulting in periodically well-defined NWs [22].

Pertaining to the NW fabrication, certain samples underwent a sidewall image transfer (SIT) process which was performed by conformal deposition of a thin silicon carbide (SiC) hard mask (sidewall layer) on the patterned photoresist followed by anisotropic RIE [23]. This allowed for a significant reduction of the critical dimensions as, during the SIT process, the NW width is defined by the thickness of the SiC layer rather than the resolution of the
lithography step. The SiC$_x$O$_y$ NWs underwent different post-fabrication thermal treatments for up to 2 h at annealing temperatures in the range of 50–700°C in Ar, O$_2$, or forming gas (5% H$_2$ and 95% N$_2$) atmospheres.

3. Bonding configuration of silicon oxy carbide materials and nanowires

3.1. Fourier transform infrared spectroscopy (FTIR) characterization of silicon oxy carbide thin films

Figure 3a shows the Fourier transform infrared spectroscopy (FTIR) data of SiC$_x$O$_y$ thin films in the 400–1700 cm$^{-1}$ range. The spectra are characterized by three absorption bands and a shoulder assigned to the Si-O-C rocking, Si-C stretching, and Si-O transverse and longitudinal-stretching vibration modes, centered at, respectively, ~440, ~800, ~1000, and ~1150 cm$^{-1}$ [22, 37, 38].

More specifically, the Si-O-C vibration mode (~440 cm$^{-1}$) is caused by the $\equiv$Si-O-Si$\equiv$ rocking mode due to out-of-plane motion of O in O$_{1-x}$C$_x$$\equiv$Si-O-Si$\equiv$C$_y$O$_{(3-y)}$ and is unaffected by the Si-O-Si-bridging bond-angle variation [42–45]. For samples with C content higher than 20 at.%, the density of $\equiv$Si-O-Si$\equiv$ bonding groups decreased significantly, as dictated by the SiC$_x$O$_{2(1-x)}$ stoichiometry, suggesting that the backbone-bonding network related to the SiO$_4$ tetrahedral in SiC$_x$O$_y$ changed toward SiC-like structures with significant presence of SiC$_4$ tetrahedral. The replacement of O atoms by C atoms with increasing C/O content in films is reflected in the monotonic increase of the bond area ratio of [Si-C] and [Si-O] as clearly depicted in Figure 3b.
Additionally, incorporation of the less electronegative C atoms leads to a reduced Si-O-Si bond angle between tetrahedral (see Figure 3c) [30, 44]. As a result, the density of the as-grown films is expected to increase with increasing C content, which is in agreement with the density values shown in Section 2.

Figure 4 displays the FTIR spectra collected in the range from 400 to 2300 cm\(^{-1}\) for the three classes of as-deposited silicon oxycarbide materials and for their annealed counterparts at 900 and 1100°C [37].

Deconvolution of the FTIR spectra reveals several bonding components in the as-deposited SiC\(_x\)O\(_y\) material systems [30, 37, 45, 46]. In particular, the deconvolution of the absorption bands in the range of 400–1400 cm\(^{-1}\) for the SiC-like film indicates the presence of a weak C-H mode at \(~530\) cm\(^{-1}\), a major Si-C-stretching absorption mode at \(~764\) cm\(^{-1}\), and a shoulder assigned to the Si-O-stretching mode at \(~960\) cm\(^{-1}\). The hydrogen-related absorption bands (Si-H and C-H) are located at \(~2100\) and \(~2900\) cm\(^{-1}\), respectively. Finally, the absorption observed at \(~1846\) cm\(^{-1}\) is attributed to a C-O-stretching mode.

As seen in Figure 4b, the IR spectrum of Si-C-O film has three characteristic absorption band regions, originating from the Si-C and Si-O functional groups [37]. In comparison to the SiC-like matrix films, a new absorption peak is seen at \(~440\) cm\(^{-1}\), attributed to the Si-O-C vibration mode discussed above. The IR region from 600 to 1300 cm\(^{-1}\) is broader compared to that in the SiC-like films, and its deconvolution shows the presence of four peaks centered at 663, 816, 1002, and 1114 cm\(^{-1}\) attributed to Si-C-H, Si-C stretching, and to the transverse optical (TO) and longitudinal optical (LO) asymmetric Si-O-stretching modes, respectively. Compared to the SiC-like films, the position of the Si-C absorption peak shifted from 764 to \(~816\) cm\(^{-1}\), owing to the addition of more electronegative O atoms in the network [47].

The FTIR absorption spectrum of the SiO\(_2\)-like film is characterized by an intense Si-O-Si mode (rocking), centered at \(~440\) cm\(^{-1}\); a Si-O mode (bending) located at \(~815\) cm\(^{-1}\), and an intense Si-O vibration mode (stretching) at \(~1100\) cm\(^{-1}\). The hydrogen-related vibration modes for C-H and O-H are observed at, respectively, \(~2900\) cm\(^{-1}\) and in the 3100–3700-cm\(^{-1}\) range.
The findings outlined above describe the evolution of the as-deposited films from silicon carbide-like to silicon dioxide-like films as the amount of C decreases. Regarding the annealed samples up to 700°C, the IR absorption behavior remains similar to the case of their as-deposited counterparts, and it is worth mentioning that changes took place at annealing temperatures beyond 900°C [44–46].

In the case of the SiC-like sample annealed at 900°C (Figure 4a), the Si-C- and Si-O-stretching modes show minor changes. However, both hydrogen-related modes appear with reduced intensities, as expected from the NRA results shown in Figure 1b. After the 1100°C annealing, the Si-C absorption band increased drastically in intensity and its line shape changed from Gaussian to mix of Gaussian and Lorentzian, suggesting the presence of longer-range order (Lorentzian). Additionally, all hydrogen-related vibration modes are no longer present in the films owing to hydrogen desorption.

Similarly, for the 900°C-annealed Si-C-O a small intensity increase of the Si-C-stretching mode was observed, while further annealing at 1100°C led to an overall absorption intensity increase accompanied with a blue shift of the Si-O stretching (Figure 4b). Finally, the annealing studies on the SiO$_2$-like material (Figure 4c) revealed a significant intensity increase of the Si-O-Si-rocking and the Si-O-stretching modes.

The bond density is directly proportional to the area of the IR band absorption, and can be estimated as in reference [37] using the inverse absorption cross section found in literature (3 × 10$^{19}$ cm$^{-2}$ for Si-C [48], 1.4 × 10$^{20}$ cm$^{-2}$ for Si-H [49], and 1.35 × 10$^{21}$ cm$^{-2}$ for C-H [50, 51]). The Si-C bond density for the as-deposited SiC-like sample is ~2.2 × 10$^{23}$ cm$^{-3}$ while for the as-deposited Si-C-O sample is ~5.5 × 10$^{22}$ cm$^{-3}$. The dependence of Si-C bond density with annealing temperature for both SiC-like and Si-C-O is presented in Figure 5a. It shows a constant concentration up to 700°C annealing temperature. At higher temperatures, the Si-C bond concentration increases owing to the densification of the materials and hydrogen desorption, which contributes to the increased availability of Si and C atoms formerly bonded to hydrogen. Indeed, as seen in Figure 5b, the bond density of the Si-H and C-H bonds decreases with annealing temperature $T_a \geq 900$°C for both classes of materials.

As shown in Figure 5c, the total concentration of hydrogen atoms as determined by the NRA measurements is greater than the total content of hydrogen as calculated by FTIR. Each H-related bond corresponds to one H atom; therefore, the H-related bond density corresponds to the H atomic density. The total atomic density is determined by RBS measurements. This finding suggests that some H atoms are incorporated during CVD growth and are not chemically bound to other elements. These non-bonded H atoms may be present in the form of molecular hydrogen formed during the decomposition of the precursor [37].

### 3.2. FTIR characterization of silicon oxycarbide nanowires

Large SiC$_x$O$_y$ NW structures were fabricated on intrinsic Si substrates in order to perform bonding configuration analysis [22]. The normalized absorbance FTIR spectra of both the as-deposited SiC$_{0.34}$O$_{1.52}$ thin film and the as-fabricated NWs are shown in Figure 6. It was found that the bonding configuration of the SiC$_{0.34}$O$_{1.52}$ NW system was maintained after nanofabrication as the relative intensities of Si-C and Si-O absorption bands remained the
same with respect to the as-deposited thin film. A slight absorption increase of the Si-O shoulder at ~1200 cm$^{-1}$ may be due to surface oxidation induced on the as-synthesized NWs.

3.3. XPS characterization of silicon oxycarbide thin films

The information about the bonding configuration in silicon oxycarbide thin films extracted by the means of FTIR analysis was also independently assessed by XPS studies [37]. The XPS analysis focused on examining the electronic environment (chemical bonding) of the Si 2p, C 1s, and O 1s core energy.
In the case of the as-deposited samples, the Si 2p spectrum of the SiC-like matrix (Figure 7) is composed of a center peak at 100.3 eV assigned to Si-C bonds and two shoulders centered at 99.2 and 101.2 eV assigned to Si-H- and Si-C-O-type bonding [37, 52]. In the case of the Si-C-O material, the Si 2p peak broadened and shifted to higher binding energies. The peak deconvolution showed the presence of three components centered at 100.8, 102.1, and 103.2 eV which are attributed to the Si-C, Si-C-O, and Si-O bonds, respectively [37, 46, 52]. This result agrees with the FTIR findings where, for both Si-C- and Si-O-stretching modes, the vibration frequencies increased with increasing O content (incorporation of more electronegative atom).

![Figure 7. XPS spectra of the Si 2p peaks for the as-deposited SiC-like, Si-C-O and SiO$_2$-like samples [37].](image_url)

In the case of the as-deposited SiO$_2$-like material, the Si 2p spectrum shifted to even higher binding energy and yielded two peaks centered at 102.3 and 103.5 eV which are related to two different Si-O electronic configurations [37, 53, 54].

4. Optical properties of silicon oxycarbide materials

The structural evolution of the as-deposited silicon oxycarbide materials along the SiC$_x$O$_{2(1−x)}$ stoichiometry was also reflected in their optical properties. The evolution of the index of refraction and the optical gap as a function of the C content of the materials and upon annealing treatments will be addressed in the following subsections.

4.1. Refractive index

The refractive index ($n$) of SiC$_x$O$_y$ is found to exhibit a linear relationship with increasing the [Si-C]/[Si-O] bond area ratio (Figure 8a). The linear increase of $n$ versus [Si-C]/[Si-O] over the
range analyzed is found to be partly associated with an increase of mass density in SiC\textsubscript{x}O\textsubscript{y} with increasing [Si-C]/[Si-O] \cite{37}. To understand this behavior, someone can correlate the refractive index (n) or the dielectric constant (\(\varepsilon = n^2\)) with the structural parameters through the Lorentz-Lorenz (L-L) equation \cite{55}.

![Graph](image)

**Figure 8.** (a) The index of refraction at 800 nm of different SiC\textsubscript{xy} given as a function of the [Si-C]/[Si-O] bond-area ratio. The solid line is the linear fit of the displayed data and (b) plot of index of refraction (n) at 800 nm as a function of annealing temperature \cite{22, 37}.

The FTIR measurements in **Figure 3** show a decrease in the Si-O-Si bond angle with C addition, which is expected considering the difference in the electronegativity between C and O. The mass density and Si atomic content (Si atoms possess higher electronic polarizability than O) of samples with higher carbon concentration is larger as opposed to SiO\textsubscript{2}-like samples \cite{56}. It is therefore suggested that the increased index of refraction with increasing [Si-C]/[Si-O] ratio is due to the variations in bond angles, larger mass density, and higher Si content. Further increase of the refractive index of all three classes of silicon oxycarbide materials is also observed upon post-deposition annealing beyond 900°C (**Figure 8b**). This behavior is expected considering the densification of SiC\textsubscript{xy} materials upon annealing as shown in **Figure 1c** \cite{22, 37}.

### 4.2. Optical gap

The observed increase in the refractive index \(n\), as C concentration increases along the SiC\textsubscript{2(1-x)}\textsubscript{2-x} stoichiometry, correlates well with the decrease in the optical gap of the films. For example, the \(E_{04}\) gap, which corresponds to the energy where the absorption coefficient \(\alpha\) is equal to \(10^4\) cm\(^{-1}\) \((\alpha(E_{04})= 10^4\) cm\(^{-1}\)), is found to decrease with increasing [Si-C]/[Si-O] ratio (**Figure 9a**). The Tauc optical gaps, \(E_{g}\), were also calculated from the optical absorption measurements using Tauc’s law, \((\alpha h\nu)^{1/2} = B(\nu-E_g)^n\), where \(\alpha\) is the absorption coefficient and \(\nu\) is the photon energy \cite{38}.
Similar to $E_{04}$, the $E_g$ values decrease with increasing [Si-C]/[Si-O]. This behavior can be explained by considering the larger splitting energy difference between the bonding and anti-bonding electronic states in Si-O bonds in comparison to Si-C bonds [22, 38, 57].

In addition, as seen in Figure 9a, $E_{04}$ values are generally higher than their $E_g$ counterparts, similar to other hydrogenated disordered systems [58]. This could be explained by taking into account that Tauc’s optical gap refers to the optical transitions between extended states close to the band edge, while $E_{04}$ is related to transitions of the extended states away from the band edge [38, 58].

As seen in Figure 9b, both the $E_{04}$ and $E_g$ gaps decrease with increasing annealing temperature. It is worth mentioning that the decrease in the optical gap is more pronounced in the films with higher O concentration. For example, the decrease of the Tauc gap values between the as-deposited and post-1100°C annealed films are ~0.5, ~0.6, and ~1.4 eV for, respectively, the SiC-like, Si-C-O, and SiO$_2$-like classes of SiC$_x$O$_y$. It is suspected that the possible precipitation of carbon in the high O-containing systems could be responsible for this phenomenon at high annealing temperatures. The Si-C bond length (~1.88 Å) is longer than the Si-O bond length (~1.63 Å). Consequently, a high degree of strain may accumulate in the Si-C sites within the SiO$_2$ network (e.g., in the SiO$_2$-like sample with <5 at.% C). Thermal annealing may result in strain relaxation, with the subsequent structural rearrangements perhaps favoring the formation of carbon clusters, as reported in a previous study [59]. Their optical gap values may vary between ~0.6 and 3 eV, depending on the cluster size [58, 60]. Consequently, it would be expected that the precipitation of carbon in O-rich samples (e.g., SiO$_2$-like) could be relatively facile, with the optical gap in these samples decreasing more rapidly with increased annealing temperatures.

Furthermore, the decrease in optical gap with increased annealing temperatures seems to correlate well with the loss of hydrogen. As seen in Figure 9c, hydrogen reduction is accompanied by
a decrease in the energy band gap in the annealed SiC$_x$O$_y$ films. The presence of Si-H bonds (~2000 cm$^{-1}$) can be an indication of dangling-bond passivation in the material, while the presence of other hydrogen-bonding configurations may be responsible for forming recombination centers and increasing the degree of structural disorder [61, 62].

In the as-deposited high C content samples, the Si-H$_n$ stretching mode is found at ~2100 cm$^{-1}$ (insets of Figure 4(a–c)). These peaks are attributed to Si-H-related bonds [63, 64]. Considering the absence of any Si-H$_n$ bonding (2000–2200 cm$^{-1}$) in the Si-C-O- and SiO$_2$-like samples, it is suggested that any dangling bonds in the films remained unsaturated, resulting in enhanced structural disorder. Furthermore, hydrogen desorption upon annealing would likely contribute to the formation of additional dangling bonds and defect states, which lead to the increased density of localized states below the mobility edge, thereby decreasing the optical gap. This mechanism seems to be taking place in all thermally grown CVD SiC$_x$O$_y$ films in this study.

4.3. Structural disorder and dangling bonds

Regarding the electronic structure of amorphous materials, it is common to expect the presence of band-tail states and localized defect states. These states exist due to the structural disorder in materials and may have a significant effect on the material’s performance even at low concentrations. Therefore, it is important to elaborate on the degree and impact of structural disorder in the CVD-grown SiC$_x$O$_y$ systems.

As it was discussed earlier, thermal annealing causes lowering of the optical gap owing to the increased optical absorption observed in the SiC$_x$O$_y$ materials grown by CVD. The latter is true even at photon energies well below the optical gaps. The enhanced sub-band-gap absorption is a result of an increased density of band-tail states and localized defect states [31]. One of the proposed mechanisms responsible for the increased density of band-tail states upon annealing is the annealing-induced enhanced bond-angle disorder due to structural reconfiguration and/or strain relaxation [65]. In this context, the FTIR full-width half maximum (FWHM) values for both the Si-O- and Si-C-stretching modes in the TCVD SiC$_x$O$_y$ films, with the exception of the 1100°C-annealed SiC-like sample, increased after annealing, suggesting that thermal treatments indeed enhance bond-angle distortion (see Figure 4(b and c)).

In the case of SiC-like material annealed at 1100°C, the FTIR spectrum shown in Figure 4a suggests that a significant amount of crystallization takes place resulting in the Lorentzian line shape of the infrared absorption band. This suggests that the bond-angle disorder is dramatically reduced. However, the optical absorption for the SiC-like films annealed at 1100°C is further increased compared to its as-deposited counterparts [38]. This suggests that, in addition to bond-angle variation, a different type of disorder is also present. Such behavior is known for amorphous covalent materials where both topological and compositional disorders are present simultaneously [66].

Furthermore, the deviation of the CVD-grown SiC$_x$O$_y$ films from the purely stoichiometric SiC$_{2(1-x)}$O$_x$ shown in the ternary diagram of Figure 1 suggests that there is a small excess of carbon that can form homonuclear bonds upon annealing. Also, this deviation increases for
high C concentration materials, toward the SiC-like class regime. The electronic states associated with the homonuclear bonds would exist as localized states within the gap due to their relatively weak bond strength [67, 68].

In this context, electron paramagnetic resonance (EPR) studies on SiC$_x$O$_y$ materials, grown by CVD, showed the presence of unpaired electrons (dangling bonds) [5]. The same study proposed that one of the major EPR signals may be originated from ($\equiv$Si$_3$)$_3$C radicals or associated defects with different backbone atoms bonded to C atom, such as in C-Si-O configuration [69]. The SiC$_{x}$O$_{2(1-x)}$ stoichiometry trend of SiC$_{x}$O$_{y}$ (SiC$_{x}$O$_{2(1-x)}$) suggests that two divalent oxygen atoms are replaced by one tetravalent C, further supporting the presence of ($\equiv$Si$_4$)$_3$C radicals in our films, originating from oxygen incorporation into ($\equiv$Si$_4$)$_3$C structures. Consequently, the density of such radicals is expected to increase following thermal oxidation of ($\equiv$Si$_4$)$_n$CH$_n$ groups, as it was observed, which have not been completely dehydrated during the film deposition [70]. Similarly, the oxidation of ($\equiv$Si$_4$)$_n$CH$_n$ groups with one or two back-bonded C atoms to Si may also lead to an increased density of Si-dangling bonds in SiC$_{x}$O$_{y}$. Such dangling bonds may also contribute to the formation of band-tail states in SiC$_{x}$O$_{y}$ [5].

5. Photoluminescence properties of silicon oxycarbide thin films and nanowires

5.1. Visible luminescence emission from SiC$_x$O$_y$ thin films

The room-temperature photoluminescence spectra for SiC$_x$O$_y$ samples with different C concentrations under excitation at 300 nm are shown in Figure 10a. The spectra are characterized by a broad emission in the whole visible range (350–800 nm). The photoluminescence excitation (PLE) intensity (Figure 10b) shows the presence of a shoulder at low excitation energies (<3.5 eV) and a steep increase at high excitation energies (>~3.7 eV). This was fit linearly and the intercept of the fitted line at the photon energy abscissa was taken as the PLE edge. As shown in Figure 10c, a strong correlation was observed between the values of $E_{04}$ and the PLE edge, suggesting that the PL emission energy in the SiC$_{x}$O$_{y}$ samples may be related to their optical gap [5].

Based on optical, FTIR characterizations, passivation experiments and electron paramagnetic resonance measurements, defect-related mechanisms and small sp$^2$-carbon clusters that could be attributed to white luminescence from SiC$_{x}$O$_y$ thin films were excluded [3, 5]. For example, structural defects typical seen with EPR measurements in silicon oxides, which cannot be explicitly controlled by material processing and are not directly related to the stoichiometry and material characteristics, such as Si-related neutral oxygen vacancies or non-bridging oxygen-hole centers, were ruled out. Instead, the observed intense white luminescence originates from the recombination of photogenerated carriers between the energy bands and at their tail states associated with the Si-O-C/Si-C bonds, as indicated by the direct correlation between the integrated luminescence intensity and the Si-O-C bond density (see Figure 11) [3].
On this, the integrated red and green PL emission bands were added and their normalized integrated values were plotted along with the intensity of the red-shifted Si-O-rocking (related to Si-O-C bond density) mode as a function of C content (Figure 11) [3]. A strong correlation between the emitted luminescence and the Si-O-C bond density in SiC_yO_x was revealed. This suggests that the emitted luminescence can be directly associated with the Si-O-C structure in the materials [5]. Additionally, the PL/PLE analysis revealed a strong similarity in the PLE behavior for the green/blue band emissions between the SiC control and SiC_yO_x, suggesting...
that C-Si/C-Si-O bonding may be also responsible for the excitation path of the observed luminescence in SiC$_x$O$_y$.

5.2. Band-tail recombination model

Representative forming gas-annealed SiC$_x$O$_y$ samples were additionally studied with means of PL and PLE analyses as presented in Figure 12 [22].

The evolution of the PL peak position in SiC$_x$O$_y$ was supported by the band-tail states recombination model, typical of amorphous materials [71]. Upon excitation, the photogenerated carriers thermalized to lower energies associated with band edges (hopping edge) before they recombined radiatively (energy plateau in Figure 12b). The PL peak position increased with the excitation energy up to the $E_{\text{exc,on}}$ value, as the electron population at high-lying band-tail levels of the conduction band increasing with higher excitation energy. The red shift of $E_{\text{exc,on}}$ seen with increasing C content in SiC$_x$O$_y$ can be ascribed to the observed linear decrease of the optical gap ($E_g$) with increasing [Si-C]/[Si-O] and their values almost coincide with the $E_g$ values of the films [22].

PL dynamics experiments showed a fast decrease of the PL intensity, suggesting the existence of fast recombination mechanisms in SiC$_x$O$_y$ and the PL decay spectra followed a stretched exponential law [23]. These findings further support a band-tail states recombination model, in which carriers recombine by tunneling between spatially separated conduction and valence band-tail states. Due to the diffusivity/tunneling of the photogenerated carriers during thermalization in the band-tail states before they recombine and the inhomogeneous
constitution of the band-tail states related to C-Si/Si-O-C bonding, where each state contributes with a slightly different PL lifetime, a distribution of lifetimes is expected, hence the stretched exponential behavior. This is inherent in disordered semiconductors, such as amorphous Si:H, C:H, SiC, and SiN, due to the broad and variable spatial density of these states [72–74].

To further elucidate on the band-tail states recombination model in SiC, the PL luminescence decay at different emission energies was additionally investigated. The time evolution of the PL line shape is presented in Figure 13a. It can be seen that during the first 1 ns of the luminescence decay, the integrated intensity substantially decreased and a red shift, equal to $\Delta E = 0.31$ eV, in the PL emission peaks occurs for the SiC thin film with 12 at.% C. This red shift is found to be less for samples with higher C concentration [23].

![Figure 13.](image)

Furthermore, the PL lifetimes increased as the emission energy was decreased, in agreement with electron-hole (e-h) hopping within lower-energy tail states, as the rate of thermalization decreases significantly due to the rapidly decreasing density of band-tail states [75]. Similar behavior was observed in amorphous semiconductors where the luminescence lifetime increase is attributed to e-h hopping [74]. Upon FG annealing, the average lifetimes exhibited higher values compared to their as-deposited counterparts (Figure 13c). Furthermore, the integrated PL intensity of the FG-annealed films increased significantly along with a blue shift in peak position (e.g., six times for the sample with 21 at.% C with 0.2 eV blue shift). This change in lifetimes and PL intensity can be attributed primarily to the passivation of non-radiative recombination centers present in lower-energy portion of the band-tail states of the as-deposited films.

The increase in the luminescence lifetime in SiC with low C content can be attributed to the decrease of non-radiative recombination paths compared to their high C content counterparts. As the SiC composition evolves from SiC-like to SiO$_2$-like, a decrease of the local disorder is
expected. As presented above herein FTIR measurements suggest that the degree of bond-angle disorder decreases with decreasing C content in the chemically grown SiC$_x$O$_y$ films. Additionally, it is expected that in the case of high C content samples, the density of band-tail states should increase as indicated by their increased sub-bandgap absorption [15, 76]. Therefore, for SiC$_x$O$_y$ films with higher C content (C >14 at.%), a higher density of band-tail states and enhanced disorder is expected, which results in faster thermalization of the photogenerated carriers yielding higher decay rates and a tighter lifetime distribution (Figure 13b) [23].

5.3. Visible luminescence from SiC$_x$O$_y$ nanowires

Figure 14a and b shows the normalized room-temperature PLE and PL emission spectra of SiC$_{0.34}$O$_{1.52}$ nanowire arrays. To better understand the visible light emission in SiC$_x$O$_y$ NWs, their PL and PLE properties were explored in conjunction with data from the thin film of the same composition. The PL emission spectrum of SiC$_{0.34}$O$_{1.52}$ NWs exhibits broadband characteristics ranging from blue to deep red, while the PLE spectrum monitored at the peak luminescence emission (~550-nm) spans from near-UV to blue/green regions of the spectrum.

![Figure 14](image)

Figure 14. (a) Room-temperature PLE spectra of 120-nm-thick SiC$_{0.34}$O$_{1.52}$ thin film and its corresponding NWs measured at its emission peak. Almost identical PLE emission spectra between NWs and thin films were observed, suggesting that there is no change in the excitation path and emission origin of the observed luminescence in SiC$_{0.34}$O$_{1.52}$ nanowires, (b) ensemble steady-state normalized PL spectrum of the SiC$_x$O$_y$ NWs array along with the normalized PL spectrum of its thin film analog (E$_{exc}$ = 4.1 eV) and (c) average lifetimes of the SiC$_{0.34}$O$_{1.52}$ NW array with 12 at.% C and its thin film analog at different PL emission energies [22, 23].

PLE analysis suggested that the observed luminescence from SiC$_x$O$_y$ NWs is related to radiative recombination of photo-excited carriers in band-tail states associated with C-Si/Si-O-C-bonding groups [5, 22]. Furthermore, a supplementary mechanism, in addition to the proposed band-tail states recombination process, may be needed in order to take into account the reduced dimensionality of SiC$_x$O$_y$ NW. In the case of the NW structure with spatially confined volume, the statistics of the lowest energy states due to Si-C bonds may be excluded [77]. Furthermore, by nanostructuring the recombination volume is reduced, thus, the tunneling
probability of a carrier between adjacent states at similar energy is expected to decrease. Consequently, the carriers will be exposed to a smaller number of non-radiative sites [23, 77, 78], resulting in enhanced PL efficiency, PL blue shift, and faster lifetimes with a tighter distribution as observed in SiC$_{0.34}$O$_{1.52}$ (12 at.% C) (Figure 14c). However, it is important to emphasize that the effects of NW-related surface recombination and optical scattering may not be ruled out.

5.4. Photo-stability upon thermal oxidation and excitation power density

In addition to PL and PLE studies, the luminescence performance of the SiC$_{0.34}$O$_{1.52}$ NW arrays was investigated as a function of oxidation temperature and excitation power density [22].

The oxidation treatments up to 250°C (Figure 15a) did not cause any change in the composition and bonding configuration of the SiC$_{0.34}$O$_{1.52}$ material. Consequently, the emission intensity and line shape, from SiC$_{0.34}$O$_{1.52}$ nanostructured arrays, did not reveal any changes, suggesting the absence of luminescence degradation due to thermal oxidation. This stability can be attributed to the similarity of the oxidation rates and activation energies of SiC$_{x}$O$_{y}$ materials to those of SiC [79]. Hence, SiC$_{x}$O$_{y}$ materials (with higher carbon content) appear to be significantly more resistant to oxidation annealing, compared to its SiO$_2$-like counterparts (with very low carbon content) [3].

Figure 15. (a) PL spectra of the AD and 2-h-oxygen-annealed SiC$_{0.34}$O$_{1.52}$ NW at various temperatures (excitation wavelength $\lambda_{\text{exc}} = 457$ nm). The inset shows the integrated PL intensity versus annealing temperature and (b) room-temperature PL spectra of the 70-nm-width SiC$_{0.34}$O$_{1.52}$ NWs for different CW excitation probing power densities (excited at the $\lambda_{\text{exc}} = 457.9$ nm of an Ar ion laser). The inset shows the linear behavior of the integrated PL intensity as a function of the excitation power density [22].

The excitation power dependence study (Figure 15b) showed a linear behavior in the integrated PL with respect to the power density (up to ~800 W/cm$^2$). Similar to the thermal-oxidation study, the peak position and the line shape of the PL in the nanowires remained unchanged, suggesting good emission stability at high excitation intensity [22]. The latter is more supporting evidence suggesting the absence of defect-related localized emission in the proposed origin of the visible luminescence from SiC$_{x}$O$_{y}$ nanowires, as no PL saturation at high powers was observed (e.g., due to state filling of the localized states) [80, 81].
6. Concluding remarks

The optical and luminescence properties of silicon oxycarbide thin films and nanostructured (e.g., NW) arrays are correlated to their synthesis routes, structural properties, and bonding configuration. The composition of the chemically CVD-grown SiC$_{x}$O$_{y}$ thin films approximate the SiC$_{x}$O$_{2(1-x)}$ ($0 < x < 1$) stoichiometry. The index of refraction increases linearly as the [Si–C]/[Si–O] bond-area ratio increases, accompanied by a linear decrease of the optical gap. The white (red, green, and blue) emission can be achieved simultaneously from the same SiC$_{x}$O$_{y}$ film following a single-deposition process, without the complications encountered in the case of using nanocrystals (e.g., Si, SiC). In particular, it was determined that the white PL emission of SiC$_{x}$O$_{y}$ thin films is strong enough to be seen with the naked eye under bright room conditions. Based on the PL, FTIR, and EPR analyses, typical structural defects in oxides were ruled out as the mechanism for white luminescence from SiC$_{x}$O$_{y}$. Instead, the observed intense visible luminescence originates from the recombination of photo-generated carriers between the energy bands and at their tail states associated with Si-O-C/Si-C bonds. In this regard, the potential advantages offered by our proposed approach of SiC$_{x}$O$_{y}$ thin films and NWs range from color tunability, thermal/photo-stability to enhanced light extraction efficiency and from cost reduction to environmental considerations. To this end, these compelling behaviors may provide a pathway for further controlling and enhancing the thermal stability and PL yield of white light emission from such films and nanostructured materials through optimal engineering of Si-O-C/Si-C bonds in the matrix.

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Author details

Spyros Gallis*, Vasilios Nikas and Alain E. Kaloyeros

*Address all correspondence to: sgalis@sunypoly.edu

Colleges of Nanoscale Sciences and Engineering, SUNY Polytechnic Institute, Albany, NY, USA

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