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Visible photoluminescence in amorphous SiO$_x$ thin films prepared by silicon evaporation under a molecular oxygen atmosphere

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A simple reactive evaporation method is proposed to prepare light-emitting amorphous SiO$_x$ thin films. By evaporating pure silicon in a controlled molecular oxygen atmosphere, it is possible to obtain a very large composition range. By changing the pressure in the preparation chamber, $x$ can be varied from 0.7 to 1.85. The composition and the structure of the films were investigated using energy dispersive x-ray, infrared absorption and x-ray photoelectron spectroscopies. The samples contain amorphous silicon clusters dispersed inside an insulating silicon oxide matrix. The room-temperature photoluminescence properties were then measured. By conveniently choosing the oxygen pressure, the as-deposited films exhibit visible photoluminescence without any annealing post-treatments. The luminescence intensity initially increases with excess silicon concentration and then disappears for a too-high silicon excess. The above effect is interpreted in terms of confinement of the amorphous silicon clusters in the insulating matrix. © 2003 American Institute of Physics.

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Silicon-based materials are currently of interest for optoelectronic devices due to their light-emission properties in the visible range at room temperature. Because of low-cost manufacturing and compatibility with the optoelectronic industry, silicon oxide films have particularly been studied. Several techniques are used for the production of such films: plasma-enhanced chemical vapor deposition,$^{1,2}$ sputtering,$^3$ Si ion implantation into SiO$_2$.$^{4,5}$ In particular, our group has prepared amorphous SiO$_x$ thin films using the evaporation technique either by evaporating a SiO powder$^6$ or by co-evaporating silicon and a SiO powder.$^7$ The as-deposited samples exhibited photoluminescence (PL) in the visible range at room temperature. The PL is attributed to a confinement effect of silicon clusters embedded in a silicon oxide matrix. After annealing treatments, the PL energy shifted toward smaller energies, which is induced by the growth of the amorphous silicon clusters. In order to obtain a high PL intensity, it is necessary to create a strong confinement of the carriers. Consequently it would be interesting to improve the barrier efficiency by increasing the oxidation of the matrix. In our previous works, the evaporation of SiO and the co-evaporation of Si and SiO gave rise to as-deposited SiO$_x$ samples with $x$ values equal to 0.95 and lower than 0.95, respectively. In order to improve the PL properties, the evaporation of pure silicon under a molecular oxygen atmosphere is investigated. Few studies$^{8,9}$ on such films have been performed, and no visible PL at room temperature was found before crystallization of silicon. Moreover, in the work of Cheylan et al.,$^9$ an argon/oxygen plasma was used instead of a molecular oxygen atmosphere. In the present work, it is shown that the preparation method used enables one to obtain either Si-rich films or O-rich close to SiO$_2$ films, by controlling the oxygen pressure. For a determined oxygen pressure range, the as-deposited samples show the PL phenomenon in the visible domain. The PL properties are interpreted in relation with the composition and the structure of the films. The origin of the PL, attributed to the carriers recombination in the amorphous silicon clusters confined in the oxide matrix, is briefly discussed.

The SiO$_x$ thin films have been prepared by silicon evaporation under a controlled molecular oxygen atmosphere. Silicon is provided by an electron-beam gun. The deposition rate is controlled by a quartz microbalance system and is equal to 1 Å/s. Four different oxygen pressures have been used: 2×10$^{-6}$ Torr (film A), 7×10$^{-6}$ Torr (film B), 2×10$^{-5}$ Torr (film C), and 7×10$^{-5}$ Torr (film D). The silicon substrates were maintained at 100 °C. The film thickness was 2000 Å.

Electronic diffraction experiments show the amorphous character of the samples, which is expected with a substrate temperature equal to 100 °C. The average chemical composition $x$ of the SiO$_x$ films was analyzed by energy dispersive x-ray spectroscopy (EDXS) using quartz SiO$_2$ as reference. Four measurements were performed on each sample to determine the average composition. The evolution of the atomic structure and of the oxygen bonding configurations was followed by Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) experiments. The IR transmission measurements were carried out with a FT spectrometer with a resolution of 4 cm$^{-1}$. The spectra were all background subtracted. XPS measurements were performed using a VG MKII analyzer with a monochromatized Mg K$_{\alpha}$ source (overall resolution energy of 1 eV). All XPS spectra were corrected for any charging effects by fixing the C 1s binding energy at 285 eV. PL measurements were carried out with a Raman spectrometer equipped with a 300-grooves mm$^{-1}$ grating. The multichannel detector was a charge coupled camera cooled at 140 K. The 488-nm
Excitation light source was emitted from an argon laser and the incident power was around 10 mW/mm².

The EDXS technique gives the average composition \( x \) of the SiO_x. This composition is equal to 0.7, 1.3, 1.6, and 1.85 for the samples prepared with oxygen pressures equal to \( 2 \times 10^{-6} \), \( 7 \times 10^{-6} \), \( 2 \times 10^{-5} \), and \( 7 \times 10^{-5} \) Torr, respectively. Sample A contains a large silicon excess, while sample D is close to silica.

Infrared absorption spectra over the range 400–1400 cm⁻¹ are shown in Fig. 1. Characteristic Si–O bands are observed at 1000–1100 and 800 cm⁻¹. They are assigned to the asymmetric and the symmetric stretching modes of Si–O bonds, respectively. The Si–O rocking vibration band is also present near 450 cm⁻¹. The absorption intensities of the Si–O assigned bands all increase with the oxygen partial pressure due to a higher Si–O–Si bonds number. In the same time, the frequency of the main peak shifts toward higher wave numbers from 1043 cm⁻¹ for sample A to 1072 cm⁻¹ for sample D as the oxygen content increases. This effect has already been observed by several groups which have showed that the peak frequency \( n \) of this band and the composition \( y \) of the silicon oxide phase are linked by a linear relation. In our group, such a relation was determined using reference samples: \( y = (n - 918)/81 \). The difference between the values obtained by this formula and those obtained by the formula proposed by Pai et al.¹⁰ is lower than 3%. The composition values obtained by the IR absorption and by EDXS techniques are compared in Fig. 2. The discrepancies observed between the two values, especially for the Si-rich films, suggest that the films are made of a pure silicon phase and a silicon oxide one. Indeed, the EDXS technique gives the global composition of the films while the FTIR spectroscopy gives the composition of the silicon oxide phase, but does not detect the Si–Si bonds. This explains that the composition values obtained by FTIR spectrometry are higher than those obtained by the EDXS technique. The Si-richer film SiO_1.85 contains amorphous silicon clusters embedded in a SiO_1.3 silicon oxide matrix. As the oxygen content increases in the as-deposited films, the pure Si fraction decreases and for the oxygen-richer film, the two values are quite equal, which suggests that the pure Si fraction is very weak.

XPS experiments have been carried out in order to confirm the presence of a-Si clusters. Si 2p core level spectra of the four as-deposited samples are compared in Fig. 3. The characteristic spectra of a SiO_2 reference is also added. The Si-richer film spectrum exhibits two clearly separated peaks located at 99.4 and 103.2 eV, which are attributed to a pure silicon phase and a silicon oxide phase close to silica, respectively. As the oxygen content increases, the pure silicon phase peak intensity decreases and the silicon oxide peak position slightly shifts toward higher binding energies, indicating an oxygen enrichment of the silicon oxide phase. These results corroborate the presence of two phases. With increasing oxygen pressure in the preparation chamber, the volume fraction of the pure silicon phase decreases and the silicon oxide phase becomes close to SiO_2.

The PL spectra of the a-SiO_x films are compared in Fig. 4. The oxygen-richer film SiO_1.85 exhibits a weak visible PL at room temperature with a maximum at 625 nm. The PL intensity increases with the silicon excess and the PL wavelength shifts to 650 nm. For the Si-richer film SiO_0.7, the PL disappears. The PL evolution could be explained thanks to the structural investigation. Indeed, PL in the visible range is generally attributed to the presence of silicon clusters with an

![FIG. 1. Infrared absorption spectra of the a-SiO_x samples. The oxygen pressure during the evaporation was 2 x 10^{-6} Torr (film A), 7 x 10^{-6} Torr (film B), 2 x 10^{-5} Torr (film C), and 7 x 10^{-5} Torr (film D).](image1)

![FIG. 2. Comparison between the composition values obtained by EDXS and FTIR spectroscopy.](image2)

![FIG. 3. XPS spectra of the Si 2p core level for the a-SiO_x samples.](image3)
enlarged band gap due to a quantum confinement effect. The passivation of these clusters is also a crucial factor because defects such as dangling bonds are nonradiative recombination centers that suppress the PL. The results allow us to assume that the films contain well-passivated amorphous silicon clusters embedded in a silicon oxide matrix. For the oxygen-richer film, the pure silicon fraction is very weak. There are few silicon clusters, which explains the weak PL intensity. With the increase of the silicon fraction, the silicon clusters become more and more numerous which explains the PL intensity increase. The PL disappearance for the Si-richer film is due to the fact that the silicon domains are very large and contain defects which quench the PL.

As a conclusion, the use of a very simple technique such as evaporation of silicon under a molecular oxygen atmosphere enables to produce a large scale of amorphous silicon oxide films suitable for the fabrication of Si-based emitters. By conveniently choosing the oxygen pressure during the evaporation, it is possible to obtain films which exhibit a visible PL at room temperature without any annealing post-treatments. The PL is attributed to the carriers recombination in the amorphous silicon clusters. For films with a too-large excess of silicon or films close to SiO₂, the PL will be absent or very weak.


FIG. 4. PL spectra of the α-SiOₓ samples obtained with a 488-nm light source.