Photoluminescence and Stability of Sputtered SiO$_x$ Layers

Seyed Mohammad Ali Hosseini-Saber,* Ruslan Muydinov, Najme Ahmadi, Josefa Ibaceta-Jaña, Zainab Kazemi, Stefan Seeger, Heiko Gundlach, Ulrich Gernert, Bernd Szyszka, and Hans Joachim Eichler

1. Introduction

Silicon (Si) is the most important semiconductor material used in photovoltaic, microelectronic, and photonic devices. It is an ideal platform for monolithic integrated optoelectronic systems because it is nontoxic and inexpensive compared to the widely used III–V semiconductors.$^{[1–3]}$ However, Si was considered to be an unsuitable material for effective light generation. Its indirect bandgap stipulates weak light emission resulting from optical or electrical excitation. In 1981, quantum confinement was observed in silicon nanocrystals.$^{[4,5]}$ This effect was interrelated with an energy shift of optical absorption. Furthermore, light emission from Si nanocrystals (SiNCs) and porous Si was achieved.$^{[6]}$ Subsequently, SiNCs have drawn significant attention. As a result of the Heisenberg principle, the electron momentum distribution becomes broadened when the particle size decreases to a nanometer scale, thus providing a way for quasi-direct electronic transitions. It results in effective light generation in SiNCs via photoluminescence (PL).$^{[6]}$ The recombination of electrons and holes in SiNCs causes a bright PL signal at room temperature.$^{[7]}$ Changing the size of nanocrystals allows tuning the energy of the PL maximum.$^{[4,8]}$ Among the parameters affecting light emission from SiNCs in SiO$_x$ layers are the following: the impact of oxygen and chemical degradation in the ambient atmosphere, defects in the SiO$_x$ layers, substrate effects.$^{[9–11]}$ In addition, light emission may originate also from the substrate by laser-induced nonbridging oxygen hole centers (NBOHCs).$^{[12]}$ Achievement of efficient and controllable light emission in SiNCs would drastically enhance the development and use of Si-based optoelectronic devices due to their compatibility with mature Si-based electrical circuits.

Various methods have been proposed so far to produce SiNCs embedded in different layers, such as plasma-enhanced chemical vapor deposition (PECVD),$^{[13–15]}$ electron beam (e-beam) evaporation,$^{[16,17]}$ ion implantation,$^{[18,19]}$ and sputtering.$^{[20–22]}$ Depending on the material and plasma settings, sputtering can provide homogeneous amorphous or crystalline layers with settable density. Therefore, it is also widely used in the fabrication of semiconductor and optical coatings on an industrial scale. SiNCs can form in amorphous Si-containing, e.g., SiO$_x$, layers using annealing, which can be conductive or radiative thermal ones. It is known that
laser-induced heat produces more ordered and isolated SiNCs in comparison to conventional thermal annealing in Si-based layers.\textsuperscript{[24,25]} Yet, it is difficult to achieve uniform large-scale crystallization via laser annealing; furthermore, this would demand expensive equipment. In comparison, broadband xenon flash annealing can provide a more uniform scalable heat treatment.\textsuperscript{[24,25]}

In this work, we deposited SiO$_x$ layers with different O/Si ratios using magnetron sputtering. The O/Si ratio was determined by energy-dispersive X-ray analysis (EDX). The refractive index was calculated based on optical transmission spectra. In addition, layer thickness was estimated and confirmed by scanning electron microscopy (SEM). Then, the fabricated layers were annealed using 2.7 ms pulses of the Xe irradiation with different energy densities (1, 2, and 20 J cm$^{-2}$). The annealed SiO$_x$ layers were investigated by Raman spectroscopy and PL measurements, which provided an estimate of the SiNCs’ size distribution and the light emission properties of the films. We also detected a blueshift of the PL signal after about 6 months of storage of the chosen sample in ambient air. This effect was probably caused by progressive oxidation and hydrolyzation.

2. Preparation of the Layers

Four SiO$_x$ thin layers were deposited by the RF sputtering method (Denton Desktop Pro) with the RF power of 30 W. As shown in Table 1, we use two kinds of substrates, namely, quartz and B270 glass. In addition, we used a pure Si wafer as a target. The layer thickness was controlled during deposition using an oscillating quartz measurement system. The basic pressure in the chamber was 3 × 10$^{-6}$ Torr. Ar gas with a purity of 99.9999% was flown to the chamber. Therewith the process pressure was 7 × 10$^{-3}$ Torr. After accomplishing the deposition and turning off the pumps, the pressure was changed inside the chamber. Figure 1 shows the chamber pressure in our sputtering system after turning off the pumps. It shows that the pressure increases almost linearly with time (about 0.03 Torr h$^{-1}$), which means an airflow leak into the chamber during the deposition procedure would affect the O/Si ratio of the layers.

Flash lamp annealing (FLA) was performed in the FLA 100 system (DTF, Germany). A single light pulse was generated by an array of four xenon lamps (160 × 50 mm$^2$). Their exact irradiation spectrum was to some extent determined by an adjustment of the capacitor charging (energy density) and the inductance of the inductor–capacitor (LC) circuit (pulse length). The FLA treatment took place in a vacuum to avoid the influence of water and oxygen during heating. The pulse time was fixed as 2.7 ms, whereas the energy density was varied (see Table 1). Other preparation conditions are also shown in this table.

As-deposited layers were analyzed using EDX to identify the O/Si atomic ratio in the coated layers. SEM investigation was performed on a Hitachi SU8030 SEM microscope with a cold field emitter gun (CFEG) and EDX analyzer EDAX TEAM system having a 30 mm$^2$ Octane silicon drift detector (SDD). Table 2 shows the EDX results.

Using the ZEISS Gemini SEM500 NanoVP microscope, the thickness and morphology of layers were investigated. The as-deposited layers were found to be rather smooth and continuous, and revealed no contrast characteristic for crystalline media as shown in Figure 2. A Perkin-Elmer UV–vis spectrophotometer Lambda 19 was used to estimate the thickness and refractive index of the layers. Raman and PL spectrum measurements were done by the HORIBA LabRAM HR800, using the excitation wavelength of 532 nm with the power of 30 mW.

We deposited an extra sample (test sample) to calibrate the sputtering machine thickness measurement system. The test sample thickness was measured during the deposition by the quartz oscillating system embedded inside the chamber. After the deposition and transmission spectra measurement, the layer was diced until it could be put in the SEM. The SEM result was used to calibrate the oscillating quartz system inside the chamber by finding the tooling factor. The SEM image of the cross-section of the test sample is shown in Figure 2. In this test sample, the SEM measured thickness is 892 nm, whereas it measured 65 nm during the deposition by the oscillating quartz. Therefore, the tooling factor of the oscillating quartz was calculated to be 13.72. After finding the tooling factor, we could make samples with almost exact thicknesses using the oscillating quartz measurement multiplied by the tooling factor.

![Figure 1. Chamber pressure after turning off the pumps. The red line is a linear fit line to the measured data. The pressure increases from $3 \times 10^{-6}$ to $4 \times 10^{-2}$ Torr in 90 min almost linearly.](image)

| Sample | Substrate       | Sputter time [min] | FLA energy density [J cm$^{-2}$] |
|--------|-----------------|--------------------|----------------------------------|
| S1     | Quartz glass    | 480                | 2                                |
| S2     | B270            | 610                | 20                               |
| S3     | B270            | 230                | 1                                |
| S4     | B270            | 180                | 2                                |
| Test   | B270            | 540                | –                                |

Table 2. Results of the EDX measurements recalculated to the 100% sum.

| Sample | Si [at%] | O [at%] | x in SiO$_x$ |
|--------|----------|---------|--------------|
| S1     | 39.4     | 60.6    | 1.54         |
| S2     | 49.8     | 50.2    | 1.00         |
| S3     | 50.0     | 50.0    | 1.00         |
| S4     | 47.6     | 52.4    | 1.10         |
3. Layer Thickness and Refractive Index

In addition, optical transmission spectra give valuable information that helps to find the effective refractive index and the thickness of the layers based on the oscillation of the spectra. The transmission spectra oscillate because of the passing beam’s interference through the sample. We estimated the layer’s refractive index by considering the passing beam and the one-time reflected and passed beam and neglected other inner reflections (Figure 2).

The transmitted electrical field is the interference of \( \vec{E}_1 = t_{l-s}\vec{E}_0 \) and \( \vec{E}_2 = t_{l-s}r_{l-s}r_{l-s}\vec{E}_0 \), where \( l \), \( s \), and \( a \) represent the layer, substrate, and air, respectively. In these equations, \( r_{l-s} = (n_l - n_s)/(n_l + n_s) \) and \( r_{l-s} = (n_l - 1)/(n_l + 1) \) are the reflection coefficients of the electrical field from the borders of the layer–substrate and layer–air respectively and \( t_{l-s} \) is the field transmission coefficient from the layer–substrate border. Also \( n_l \) and \( n_s \) are the refractive indices of the layer and substrate, respectively. The maxima and minima of the transmitted intensity can be written as

\[
\begin{align*}
I_{\text{max}} &= t_{l-s}^2I_0 + r_{l-s}^2I_0 + 2r_{l-s}t_{l-s}I_0 \\
I_{\text{min}} &= t_{l-s}^2I_0 + r_{l-s}^2I_0 - 2r_{l-s}t_{l-s}I_0
\end{align*}
\]

where \( I_0 = (\vec{E}_0)^2 \). Therefore, the contrast of the transmission spectra oscillation, \( \nu = (I_{\text{max}} - I_{\text{min}})/(I_{\text{max}} + I_{\text{min}}) \), can be written in terms of the refractive indices of the layer and the substrate (see Figure 3). By doing some calculations, the refractive index of the layer is calculated as

\[
n_l = q \pm \sqrt{q^2 - n_s^2}
\]

where \( q \) is an auxiliary parameter, which is defined as

\[
q = -\frac{1}{2}(1 + n_s) \left[ \frac{1 + \frac{1}{\sqrt{q^2 - 1}} \sqrt{q^2 - 1}}{1 - \frac{1}{\sqrt{q^2 - 1}} \sqrt{q^2 - 1}} \right]
\]

From Equation (2), \( n_l \) has only one acceptable answer and the refractive index of the layer can be estimated simply from the optical transmission spectra by having the refractive index of the substrate. As the refractive index of the substrate and the oscillation rate are functions of wavelength, the refractive index of the layer is also a function of the wavelength. Figure 3 shows an optical transmission spectrum of the test sample. The oscillations rate is calculated with the help of upper (violet) and lower (red) limit dashed curves that are obtained from interpolation of the maximum or minimum points, respectively. In the sample spectrum (Figure 3), the refractive index of the substrate in the wavelength of \( \lambda = 623 \) nm is \( n_s = 1.523 \) and the spectral oscillation rate (\( \nu \)) is about 0.016. Therefore the refractive index of the sample in this wavelength is estimated as \( n_l = 1.63 \). In addition, we estimate the layer thickness from the spectral oscillation. As shown in Figure 2, the light path difference between the two transmitted beams at normal incidence is \( \Delta(\lambda) = 2n(\lambda)d \), where \( d \) is the layer thickness.

On the other hand, a peak of intensity occurs when the light path difference is equal to the correct number of the wavelength, i.e., \( 2n(\lambda)d = m\lambda \), where \( m \) is an integer number. By changing the wavelength of the spectrometer source, the next peak occurs at \( \lambda \), where \( 2n(\lambda)d = (m - 1)\lambda \). One can solve the integer \( m \) from these two relations. Subsequently, the layer’s thickness will be derived in terms of the wavelength and its corresponding refractive index at two successive peaks of the transmission spectra as

\[
d = \frac{1}{2} \left[ \frac{n(\lambda)}{\lambda} - \frac{n(\lambda')}{\lambda'} \right]^{-1}
\]

Table 3 shows the obtained refractive indices and thicknesses of the samples calculated by Equation (2) and (4). The obtained...
thickness of the test sample (see Figure 2) shows that the estimations are acceptable compared to the SEM measurement, with about a 10% difference. The estimated $n(\lambda)$ is the effective refractive index of the layer that depends on the ratio $x$ of Si and O atoms inside the layer. As the refractive indices of Si, SiO, and SiO$_2$ are about 3.5, 2, and 1.5, respectively, it can be assumed that the layer consists of SiO and SiO$_2$ compounds more than pure Si atoms. Therefore, the coated layers can be named SiO$_x$ layers with $1 < x < 1.54$ (Table 2).

4. Raman Spectra and NC Size

After treatment by the flash lamp, the samples’ PL and Raman spectrum were measured to investigate the Si-crystal sizes formed inside the SiO$_x$ layers during the flash lamp treatment. As the Raman shift of the SiNCs is related to their size,$^{[26]}$ the SiNC sizes embedded in the SiO$_x$ layer can be estimated from the layers’ Raman shift. It is reported in Paillard et al.$^{[27]}$ that the frequency shift of the SiNCs concerning the crystalline Si (521 cm$^{-1}$) can be written as

$$\Delta \omega = -A \left( \frac{\theta}{L} \right)^\gamma$$  \hspace{1cm}(5)$$

where $A = 52.3$ cm$^{-1}$, $\gamma = 1.586$, $a = 0.543$ nm the Si lattice parameter, and $L$ is the diameter of the nanocrystals. The results of the Raman spectroscopy of the samples S1, S2, S3, and S4 are shown in Figure 4a–d respectively, and the estimation of the SiNCs’ size is shown in Table 4. Changing Raman shift to low frequency is in agreement with other research and this occurs due to the quantum confinement in NCs.$^{[26,28]}$ Therefore, as shown in Table 4, the flash lamp power of 1 J cm$^{-2}$ (for sample S3) was not enough for the nanoscale crystallizing of Si according to Equation (5). On the other hand, the formation of SiNCs triggers asymmetry in Raman spectroscopy. Figure 4a,c has asymmetry in the low-frequency tail that could correspond to near-surface bonds at the grain boundaries of SiNCs, which are strained as reported in the other research.$^{[29,30]}$ However, it seems that it is not enough for validating SiNCs’ formation in the samples, and PL measurement also is necessary to confirm the Raman spectrum results.

5. Photoluminescence and Discussion

Figure 5a shows the denoised PL spectrum for sample S1 with a PL peak at 705 nm. The spectrum is decomposed to a strong main peak at 680 nm (blue line) and two small Gaussian spectra with the maxima at 718 nm (red line) and 829 nm (violet line). We estimated the SiNCs’ size based on previously published data. Figure 5b shows the dataset extracted from the literature.$^{[31,32]}$ The orange dashed line is the fit curve based on the $d^{-1.19}$ law.$^{[33,34]}$ where $d$ is the SiNC diameter. The blue stars in Figure 5b are placed corresponding to the position of PL peaks. It shows that the PL peak of 680 nm (1.82 eV) corresponds to the SiNC size of about 1.4 nm, which is close to our estimation by Raman spectroscopy 1.2 nm.

### Table 3. Refractive index of the samples and thickness obtained from the transmission spectra peaks.

| Sample | $n(\lambda)$ | $d$ [nm] |
|--------|-------------|---------|
| Test   | 1.63        | 983     |
| S1     | 1.71        | 850     |
| S2     | 1.72        | 1084    |
| S3     | 1.84        | 412     |
| S4     | 1.86        | 327     |

### Table 4. Estimation of the SiNC sizes according to Equation (5).

| Sample | $\omega_{\text{peak}}$ [cm$^{-1}$] | $L$ [nm] |
|--------|----------------------------------|---------|
| S1     | 506.7                            | 1.2     |
| S2     | 502.5                            | 1.1     |
| S3     | 521                              | –       |
| S4     | 516.9                            | 2.7     |
The difference might come out of the interface stress, which can affect the Raman peak position of SiNCs.\textsuperscript{[35]} Two additional PL peaks at 718 nm (1.72 eV) and 829 nm (1.49 eV) can be ascribed to the mean particle size of 1.7 and 2.7 nm. There are also some different estimations of SiNCs' size in the literature.\textsuperscript{[36,37]} For instance, different PL peaks versus the SiNCs' mean size in comparison to previous studies\textsuperscript{[31,32]} were reported by Kothemann et al.,\textsuperscript{[4]} which are shown in Figure 5b (square data points and purple dashed line in Figure 5b). Their deposition method (PECVD) and the chemical environment (SiON matrix) were in that case however different.\textsuperscript{[4]} This difference could originate from the various ligands and surface chemistries, which can change the crystal field effect, crystal strain, and number of dangling bonds that can break degeneracies and separate energy states.\textsuperscript{[38]} Moreover, the broadening of the PL spectra could be related to the surface defects.

Figure 6 shows the PL of samples S2, S3, and S4 in different scales compared to Figure 5. As shown in Figure 6, samples S2, S3, and S4 reveal low PL intensity in comparison to S1. The PL maxima in the S2, S3, and S4 samples are at 718, 727, and 730 nm, respectively. Figure 6d shows the PL for the B270 glass substrate used in S2, S3, and S4. The broad PL peak at 700 nm that can be observed in samples S2, S3, and S4 can be attributed to the vibration modes in bridging oxygen or the random network of Si–O bonds.\textsuperscript{[112]} We explain the weakness of the PL signal in S2 by the too high power used (20 J cm\textsuperscript{-2}). This could cause damage to the layer. Conversely, the weak PL intensity in S3 could result from too low power impact of the Xe flash lamp (1 J cm\textsuperscript{-2}). Although we used the same flash lamp power for treating samples S4 and S1, the layer thickness in the former case was about half of the thickness of sample S1. Thinner films absorb less energy of Xe radiation. Therefore, a few SiNCs may be formed inside the layer during the annealing. In addition, the substrate material must be taken into account when fabricating SiNC-based devices by means of our method. By considering the results of the Raman and PL spectra, we can observe that sample S1 has both asymmetric broadening and the peak changing to low frequency in contrast to the other samples. It shows that for validating the formation of the SiNCs both asymmetric broadening and the peak changing to low frequency need to be considered. The observed PL in Figure 5a is the slow-band transition because CW lasers are used for the excitation of the SiNCs.\textsuperscript{[39,40]} The slow-band transition is the required transition for lasing action because it has an interface state between the valence and conduction band edges that can produce population...
inversion to lase. This indicates that the produced SiO<sub>2</sub> layers are able to be used as laser gain materials. In addition, to study the effect of oxidation and degradation, the PL of sample S1 was measured after long storage in ambient air at room temperature. Figure 7 shows the evolution PL of sample S1 during the near 6 months when it was exposed to air. The peak position of the PL shifted to shorter wavelengths. The red spectrum is for the PL of the as-prepared sample and the peak is on 733 nm. After 70 days, the PL peak shifted to 705 nm, as demonstrated by the yellow spectrum. Then, the PL peak shifted to 666 nm in the next 105 days (blue spectrum). It seems that the blueshift occurred due to the degradation and formation of the oxide layers around SiNCs and their effective sizes became smaller.

6. Conclusion

SiO<sub>2</sub> layers were fabricated by sputtering silicon onto SiO<sub>2</sub> and B270 glass substrates in a chamber containing leaked air. The O/ Si atomic ratio of 1 < x < 1.54 was measured by EDX. Only silicon and oxygen atoms were detected in the layers. The optical transmission spectra of the layers were measured, which exhibit interference oscillations. The distance of the oscillations gives the layer thicknesses 327-1084 nm and the oscillation contrast results in the refractive indices of the layers from 1.63 to 1.86. The SiO<sub>2</sub> layers were annealed using a Xe flashlamp to produce PL that is assumed to originate from SiNCs. Their mean diameters were estimated between 1.1 and 2.7 nm by Raman spectra. The Raman spectrum of sample S1 shows both asymmetric broadening and the peak changing to a lower frequency, which is required to validate the formation of SiNCs as mentioned in other research. Continuous irradiation with the 532 nm laser resulted in PL bands with 500 to 900 nm wavelengths. The layer coated on the quartz substrate, S1, shows more than ten times stronger PL intensity with respect to the other layers deposited on B270 substrates. The broadband PL intensity indicates a wide size distribution of nanocrystals. Main SiNC size of sample S1 was assessed as 1.4 nm by the fitted curve to the PL peak datasets reported in previous research.

Si NCs dispersed in hydrogen silsesquioxane (HSQ) thin film layers were used in 2018 to construct optically pumped lasers with emission at about 775 nm wavelength. We expect that sputtered SiO<sub>2</sub> layers with embedded Si nanocrystals produced by flash lamp annealing could provide an alternative active medium for silicon-based lasers. The well-established electronic silicon technology may provide a pathway to realize electrically excited Si nanocrystalline lasers.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Scholarship Becas Chile-DAAD 2017/91645541. Photoluminescence and Raman measurements were done by the support of Prof. Wagner, Dr. Maximilian Daniel Cedric Reis, and Dr. Harald Scheel in the Institute of Solid State Physics at the Technical University Berlin. M.Sc. Alexandre Novikov checked the paper draft.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

flash lamp annealing, photoluminescence, Raman spectroscopy, Si nanocrystals, SiO<sub>2</sub> layers

Received: May 11, 2021
Revised: July 16, 2021
Published online: August 18, 2021

[1] J. Liang, C. Huang, X. Gong, ACS Sustainable Chem. Eng. 2019, 7, 18213.
[2] M. Hollenbach, Y. Berencén, U. Kentsch, M. Helm, G. V. Astakhov, Opt. Express 2020, 28, 26111.
[3] C. L. Wu, G. R. Lin, IEEE J. Quantum Electron. 2011, 49, 1230.
[4] R. Köthemann, N. Weber, J. K. Lindner, C. Meier, Semicond. Sci. Technol. 2019, 34, 095009.
[5] D. Timmerman, I. I. Izeddin, T. Gregorkiewicz, Phys. Status Solidi A 2010, 207, 183.
[6] L. T. Canham, Appl. Phys. Lett. 1990, 57, 1046.
[7] L. Khomenkova, M. Baran, J. Jedrzejewski, C. Bonafos, V. Paillard, Y. Venger, I. Balberg, N. Korsunsksa, AIMS Mater. Sci. 2016, 3, 538.
[8] M. Schnabel, C. Weiss, P. Löper, P. Wilshaw, S. Janz, Phys. Status Solidi A 2015, 212, 1649.
[9] S. Dutta, S. Chatterjee, K. Mallem, Y. H. Cho, J. Yi, Renew. Energy 2019, 144, 2.
[10] F. Maier-Flaig, J. Rinck, M. Stephan, T. Boeskrocker, M. Bruns, C. Kubel, A. K. Powell, G. A. Ozin, U. Lemmer, Nano Lett. 2013, 13, 475.
[11] J. Chen, J. Suwardy, T. Subramani, W. Jevasuwan, T. Takei, K. Toko, T. Suemasu, N. Fukuta, Cryst. Eng. Commun. 2017, 19, 2305.
[12] D. Tan, X. Sun, J. Qiu, Opt. Mater. Express 2021, 11, 848.
[13] A. M. Hartel, D. Hiller, S. Gutsch, P. Löper, S. Estradé, F. Peiró, B. Garrido, M. Zacharias, Thin Solid Films 2011, 520, 121.
