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# Temperature dependent radiative and non-radiative recombination lifetimes of luminescent amorphous silicon oxynitride systems

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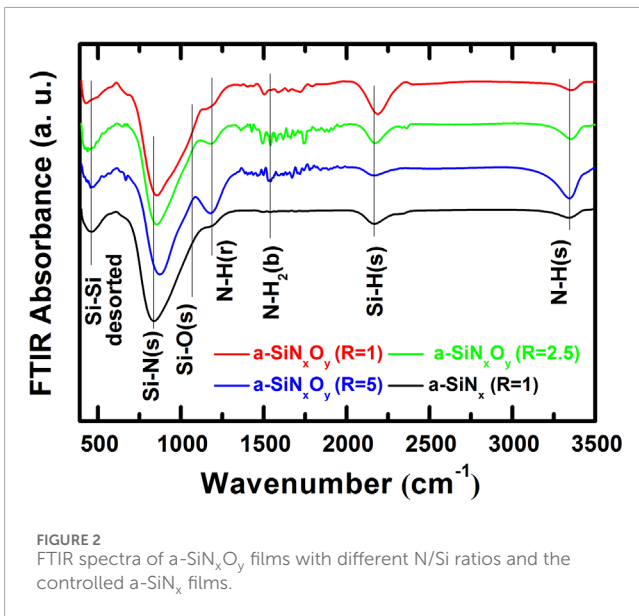
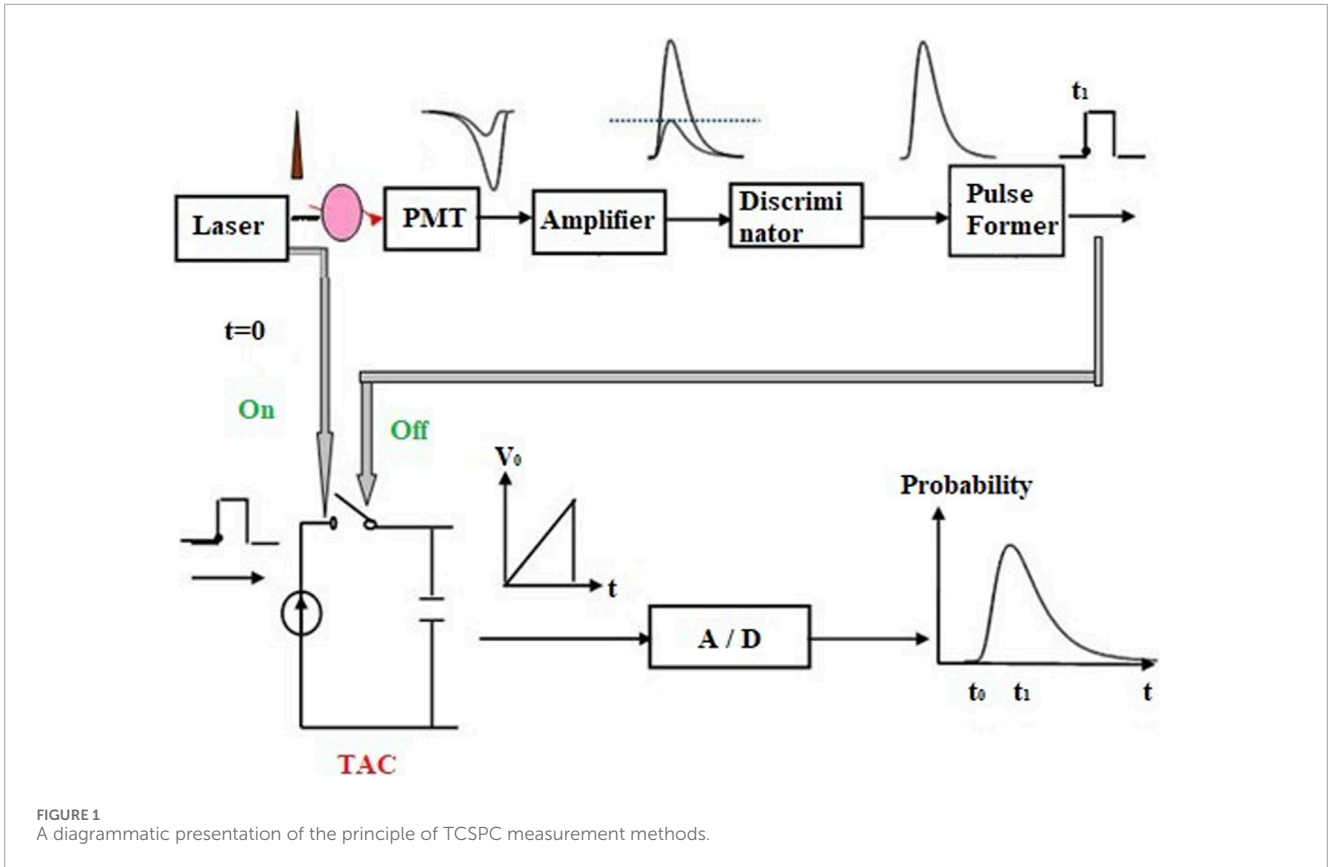
In our previous work, we deeply researched the absolute photoluminescence (PL) quantum yields of luminescent modulating a-SiN<sub>x</sub>O<sub>y</sub> films with various N/Si atom ratios under different measurement temperatures. In this work, we further systematically studied the temperature dependent kinetic processes of radiative and non-radiative recombinations in a-SiN<sub>x</sub>O<sub>y</sub> systems in the visible light range. First, we investigated the structure of a-SiN<sub>x</sub>O<sub>y</sub> films and obtained the concentrations of both trivalent Si and N-Si-O defects related dangling bonds through XPS, FTIR and EPR measurements. Then we further tested the transient fluorescence attenuation of a-SiN<sub>x</sub>O<sub>y</sub> films detected at different emission wavelengths. We found that the PL lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> films vary with the change of N-Si-O defect state concentrations, which is different from the typical PL decay characteristics of band tail related a-SiN<sub>x</sub> films previously reported. By combining the resulting PL IQE values with the ns-PL lifetimes, we further intensively redetermined the radiative and non-radiative recombination lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> systems. The related radiative recombination rates were obtained ( $k_r \sim 10^8 \text{ s}^{-1}$ ), which can be compared to the results in the direct band gap.

## KEYWORDS

a-SiN<sub>x</sub>O<sub>y</sub>, PL lifetimes, defect states, radiative recombination rates, non-radiative recombination lifetimes

## 1 Introduction

To realize Si-based monolithic photoelectric integration, the most critical task of various components in the related integration manufacturing processes is to realize Si-based light sources with highly efficient luminescence. However, due to the indirect band gap of Si, the related luminescent efficiencies are very low. Therefore, based on improving the absolute photoluminescence quantum yields (PL AQYs) and PL internal quantum efficiencies (PL IQE), the study of the PL properties and the related dynamics processes in Si-based high-efficient luminescent

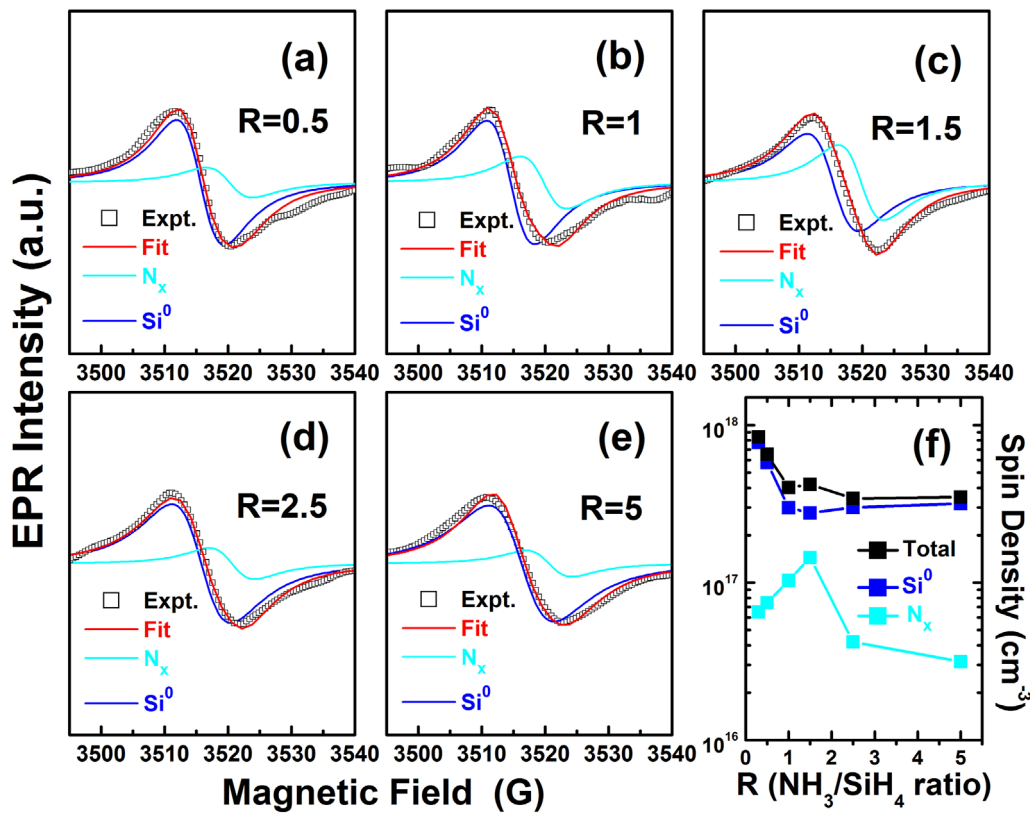


materials has become one of the research hotspots for more than 2 decades [1, 2].

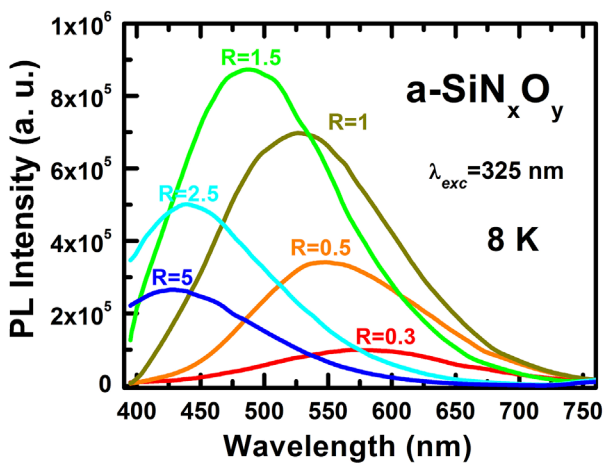
Most of the previous researches on the luminescence mechanisms and the related PL decay processes has focused on Si nanostructured materials, such as porous silicon (PS Si) [3, 4], colloiddally passivated Si quantum dots [5–9], and nc-Si

embedded Si-based films [10–15]. Only a few reports were talked about Si-based compounds, such as amorphous silicon carbide (a-SiC<sub>x</sub>) [16, 17], amorphous silicon nitride (a-SiN<sub>x</sub>) [18, 19], and amorphous silicon nitride oxide (a-SiO<sub>x</sub>N<sub>y</sub>) [20–25]. And they found that the PL lifetimes of a-SiN<sub>x</sub> and a-SiO<sub>x</sub>N<sub>y</sub> films are generally in the nanosecond range [15–18, 20]. Yang’s group studied the luminescence characteristics of a-SiN<sub>x</sub> films with tail states under different components and found that PL lifetime is related to luminescence peak position (E<sub>PL</sub>) [18]. Kato et al. studied in detail that the PL dynamics of a-SiN<sub>x</sub> and a-SiO<sub>x</sub>N<sub>y</sub> with tailed luminescence and found that the fluorescence decay time scale is in the range of 10<sup>-8</sup> to 10<sup>-4</sup> s. The E<sub>PL</sub> of transient fluorescence spectra changes over time in the nanosecond (~100 ns) to microsecond time scales [20].

In the previous work, we deeply researched the absolute PL quantum yield of light-emitting modulating a-SiO<sub>x</sub>N<sub>y</sub> films in the visible range under different test temperatures, and briefly analyzed their luminescence origins [23]. In this paper, we combined temperature dependent PL (TD PL) and time-resolved PL (TR PL) spectroscopy to further systematically study the kinetic processes of radiation recombination and non-radiative recombination processes of a-SiN<sub>x</sub>O<sub>y</sub> films with various N/Si atom ratios under different test temperatures. First, we investigated the structure of the a-SiN<sub>x</sub>O<sub>y</sub> films through XPS and FTIR measurements, and obtained the concentrations of both silicon and N-Si-O defects related dangling bonds by EPR measurements. Then, we studied the transient fluorescence properties at different detection wavelengths, and found that the luminescence lifetimes of



**FIGURE 3** The measured EPR and the related deconvoluted signals of the a-Si<sub>x</sub>N<sub>x</sub>O<sub>y</sub> films with (A) R = 0.5; (B) R = 1; (C) R = 1.5; (D) R = 2.5; (E) R = 5. (F) The spin densities of total defects, Si DBs, and N<sub>x</sub> defects vs R.



**FIGURE 4** PL spectra of a-Si<sub>x</sub>N<sub>x</sub>O<sub>y</sub> films with different R at 8 K under 325 nm He-Cd laser excitation.

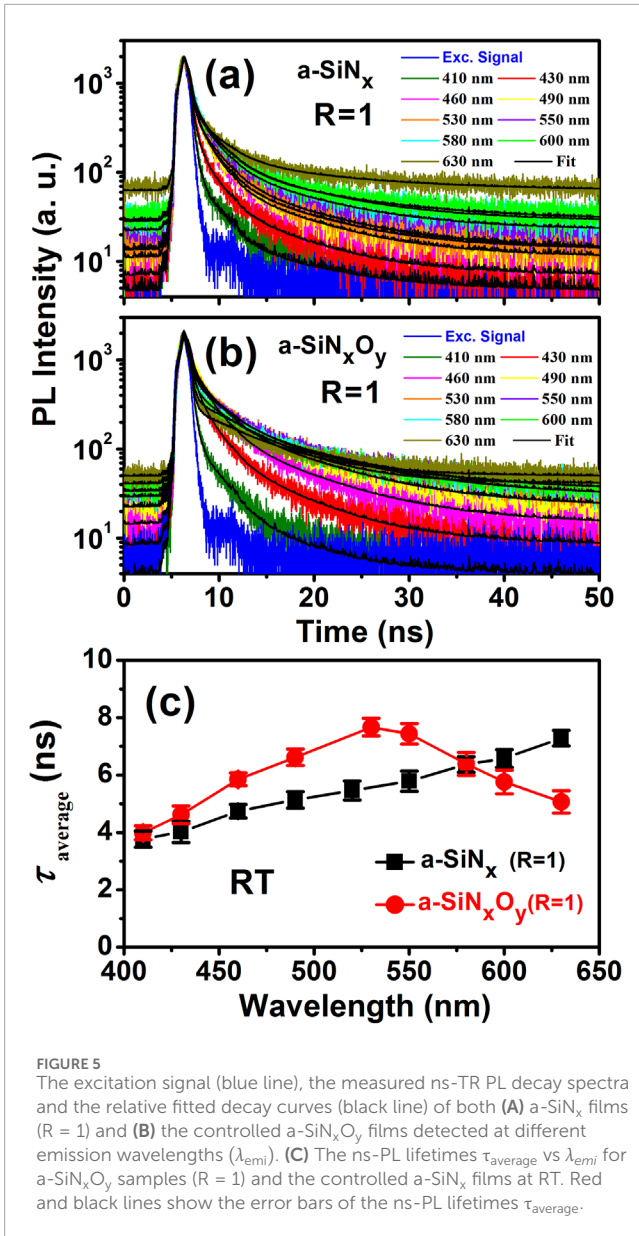
samples changed with the variation tendency of the concentrations of N-Si-O defect states, which was different from the typical band tail luminescence kinetic characteristics reported in the past. Furthermore, we tested the PL lifetimes of a-SiO<sub>x</sub>N<sub>y</sub> films at different

temperatures, and analyzed the related radiative and non-radiative recombination processes. Based on the measured PL lifetimes of the a-SiO<sub>x</sub>N<sub>y</sub> films at different temperature range, combined with the PL IQE values obtained earlier, we calculated the radiative and non-radiative recombination lifetimes of a-SiO<sub>x</sub>N<sub>y</sub> films at different temperatures. At last, we deeply analyzed the change law between the radiative recombination processes of a-SiO<sub>x</sub>N<sub>y</sub> films and the concentration of N-Si-O defect states. We found that the radiation recombination rates of the films are almost unchanged over the whole temperature range. The obtained radiative recombination rates  $k_r \sim 10^8 \text{ s}^{-1}$  can be compared with the results in the direct band gap (such as CdSe nanocrystals).

## 2 Materials and methods

### 2.1 Material fabrication

The a-Si<sub>x</sub>N<sub>x</sub>O<sub>y</sub> films (~500 nm) were deposited on polished Si substrates in a plasma-enhanced chemical vapor deposition (PECVD, OXFORD Plasmalab 80PLus, Oxford, UK) system with a silane, ammonia, and nitrogen gas mixture. The gas flow ratios R ( $R = \text{NH}_3/\text{SiH}_4$ ) and the related fabrication parameters were well controlled through the whole fabrication processes, both of which were described in our previous work last year in detail [23]. After

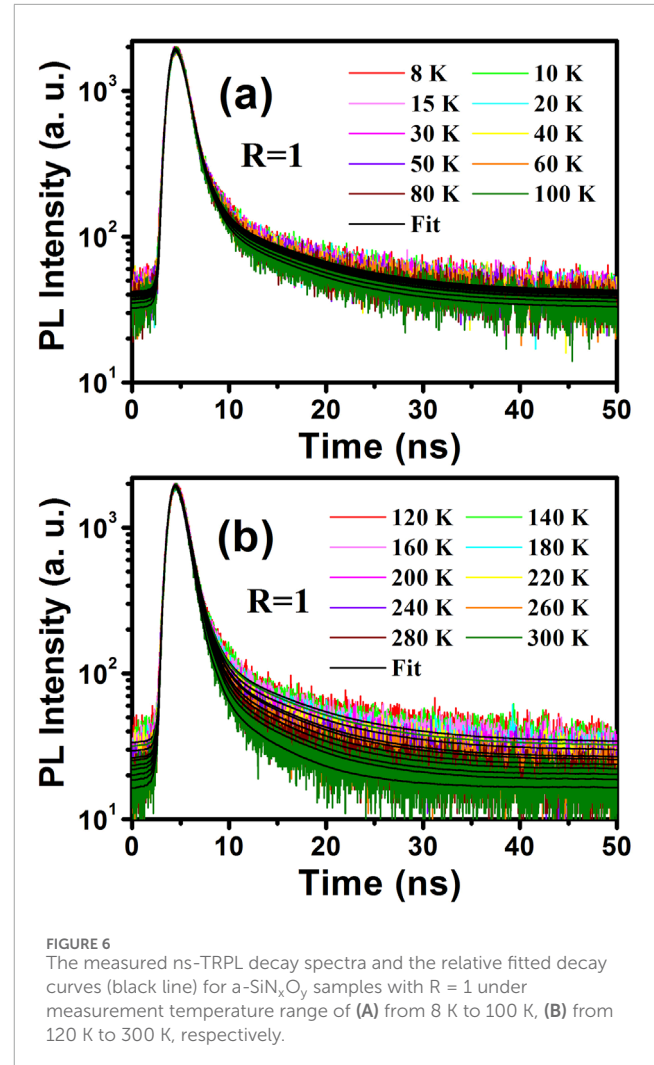


**FIGURE 5**  
The excitation signal (blue line), the measured ns-TR PL decay spectra and the relative fitted decay curves (black line) of both (A)  $a\text{-SiN}_x$  films ( $R = 1$ ) and (B) the controlled  $a\text{-SiN}_x\text{O}_y$  films detected at different emission wavelengths ( $\lambda_{\text{emi}}$ ). (C) The ns-PL lifetimes  $\tau_{\text{average}}$  vs  $\lambda_{\text{emi}}$  for  $a\text{-SiN}_x\text{O}_y$  samples ( $R = 1$ ) and the controlled  $a\text{-SiN}_x$  films at RT. Red and black lines show the error bars of the ns-PL lifetimes  $\tau_{\text{average}}$ .

fabrication, the samples were subsequently oxidized *in situ*, and then post-treated by combining thermal annealing with pulsed laser annealing.

## 2.2 Characterization of A-SiN<sub>x</sub>O<sub>y</sub> thin films

The structure of the  $a\text{-SiN}_x\text{O}_y$  films was investigated through XPS and FTIR measurements. To intensively investigate the atom scale structure defects of  $a\text{-SiN}_x\text{O}_y$  thin films, we measured the EPR spectra under different R conditions at room temperature with a Bruker EMXplus in the X-band (microwave frequency  $f \sim 9.85$  GHz, microwave power 20 mW). The temperature dependent time resolved PL (TD-TRPL) properties of  $a\text{-SiN}_x\text{O}_y$  films with different R were measured with a Fluorolo-3 system (Jobin Yvon) and a HP4284 LCR meter in a computer-controlled Delta 9,023 oven, using a FLS980 (Edinburgh Instrument) equipped with an



**FIGURE 6**  
The measured ns-TRPL decay spectra and the relative fitted decay curves (black line) for  $a\text{-SiN}_x\text{O}_y$  samples with  $R = 1$  under measurement temperature range of (A) from 8 K to 100 K, (B) from 120 K to 300 K, respectively.

EPL375 pulse diode laser (pulse width  $\sim 53$  ps, repetition rate = 20 MHz,  $\lambda_{\text{exc}} = 375$  nm, pumping fluence  $W_{\text{PF}} = 5$  mJ/cm<sup>2</sup>) as light sources. A time-correlated single photo counting (TCSPC) system (time resolution  $\sim 100$  ps) were used to record the characteristics of TD-TRPL decay properties. Here we consider that the initial decay of the PL intensity coincides with the excitation signal which is origin from the instrumental response (the instrumental response is about 100 ps). Thus, to deduct the impact of the initial excitation signal, we carefully deconvolved the measured ns-PL decay curves and modified the  $\tau_{\text{average}}$ .

## 2.3 Time-correlated single photo counting (TCSPC) measurement methods

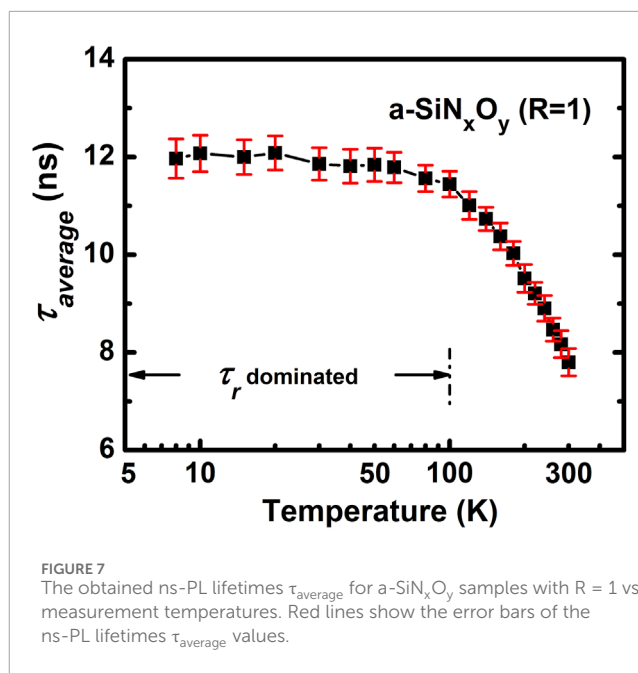
The principle of TCSPC is shown in Figure 1, where a sample is first excited with a narrow laser pulse, and the sample emits fluorescent photons after stimulus. It is assumed that the excitation laser pulse is weak enough so that the sample produces only a single fluorescent photon after each pulse. The time it takes for the first fluorescent photon emitted by the sample to reach the optical receiver (which can also be seen as the time  $t$  when a

single photon appears) is then measured. This time is proportionally converted into a corresponding voltage pulse by TAC, which is then fed into a multichannel analyzer via A/D conversion. Multiple counts are then performed, and in the multi-channel analyzer, these output pulses are sequentially fed into each channel for cumulative storage. Since the probability of a photon being detected in a certain time interval is proportional to the intensity of the fluorescence emission, repeated measurements can obtain a  $P(t)$  histogram of the probability distribution of fluorescent photons that is essentially the same as the original waveform. The histogram measured in this case is equivalent to the  $I(t)$  curve of the decay of fluorescence intensity over time after excitation has stopped. This is as if a beam of light (many photons) passing through a small hole creates the same diffraction pattern as a single photon passing through a small hole over a long period of time.

## 2.4 The PL lifetimes fitting methods of a-SiN<sub>x</sub>O<sub>y</sub> films

In general, the PL of solid films is a non-equilibrium radiation process, and the luminescence can continue for a period ( $>10^{-11}$  s) after the excitation stops. When the excitation stops, the PL intensity  $I(t)$  decays exponentially over time. The time required when  $I(t)$  drops to  $1/e$  of the maximum intensity at excitation is called PL lifetimes ( $\tau$ ) of the excited state, which indicates the average time that a particle exists in the excited state.  $\tau_{\text{average}}$  at a specific temperature can be generally obtained according to the formula  $I(t) = I_0 \exp(-t/\tau(T))$  [1]. The PL lifetimes of luminescent materials are related to their own structure, and this phenomenon mostly occurs from the nanosecond to the microsecond time range, which is in the time scale of molecular movement. Therefore, the property changes of the systems and the intermolecular interaction processes can be directly understood by the PL lifetimes determination. In particular, when fitting fast fluorescence lifetimes, two major types of fitting may be used: tail fitting and reconvolution fitting.

The stretched exponentials are used widely and accepted as good markers of light recombination in disordered systems [16, 18, 20]. For comparison, we firstly checked the recombination processes in the controlled a-SiN<sub>x</sub> films by using stretched exponential model and obtained nice fitting results. However, in the fitting processes of a-SiN<sub>x</sub>O<sub>y</sub> systems, we found that if we use stretched exponential model, the error is large and the fitting results are unstable. For band tail related a-SiN<sub>x</sub> films, the excited carriers relax to the deeper tail states then through the thermalization and radiative recombination to give luminescence. With the increasing excitation photon energy ( $E_{\text{exc}}$ ), the excited carriers occupied the higher states in the band tail [18]. In our a-SiN<sub>x</sub>O<sub>y</sub> systems, we have confirmed that the light emission is mainly originated from the N-Si-O-related defect centers in our previous work [21, 23]. The defect luminescence model has been confirmed by the Stokes Shift between Urbach edge ( $E_{\text{U Edge}}$ ) and PL energy ( $E_{\text{PL}}$ ) ( $\Delta E_{\text{stokes}} = E_{\text{U Edge}} - E_{\text{PL}}$ ) from PLE measurements. We found that the  $E_{\text{PL}}$  Stokes Shift showed a near constant value of about 0.75 eV, which were independent on the optical band gap. There are two steps in the PL recombination process of a-SiN<sub>x</sub>O<sub>y</sub> films. Firstly, the excited electronics are relaxed down to the band tail states meanwhile thermally ionized to the defect states in the band gap through non-radiative processes, then



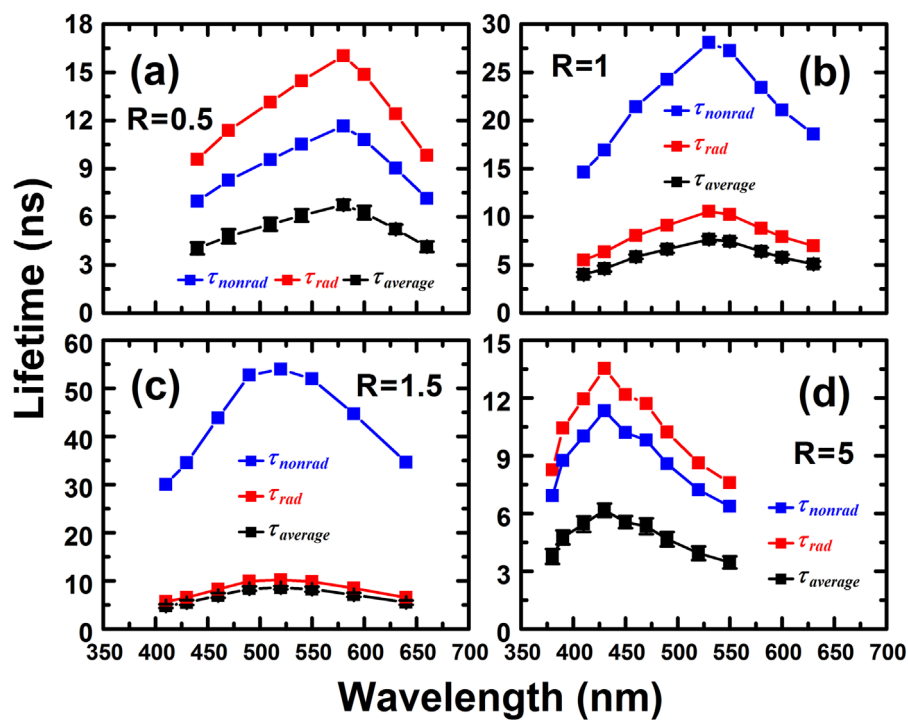
recombine via transition between the defect states and valence band tail states to give luminescence [21]. The recombination processes of a-SiN<sub>x</sub>O<sub>y</sub> films are different from band tail related a-SiN<sub>x</sub> films. Thus, here we choose the double exponential decays [11] instead of stretched exponentials to fit the PL lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> films.

## 3 Results and discussion

### 3.1 Chemical composition and bonding configurations

The presence of Si, N, and O is measured from the binding energies of the Si 2p, N 1s, and O 1s peaks in the XPS spectrum [23]. After the top layer (~60 nm) was removed by Ar ion beam, the O concentration changed slightly, and the average oxygen content in a-SiN<sub>x</sub>O<sub>y</sub> films for different R was about 3.5%. As the sputtering time increases, the O concentration tends to stabilize, which is direct evidence of the incorporation of O into a-SiN<sub>x</sub>. In order to further verify the N-Si-O bonding configuration, we measured the Fourier infrared absorption spectra (FTIR) of a-SiN<sub>x</sub>O<sub>y</sub> films and the corresponding a-SiN<sub>x</sub> films.

As shown in Figure 2, the vibration peaks of the Si-Si disordered structure ( $460 \text{ cm}^{-1}$ ), the Si-N stretching mode ( $840 \text{ cm}^{-1}$ ), the N-H rocking mode ( $1,170 \text{ cm}^{-1}$ ), the Si-H stretching mode ( $2,150 \text{ cm}^{-1}$ ), and the N-H stretching mode ( $3,350 \text{ cm}^{-1}$ ) are clearly visible in both of a-SiN<sub>x</sub>O<sub>y</sub> films and the controlled a-SiN<sub>x</sub> films. However, the Si-O stretch mode ( $1,070 \text{ cm}^{-1}$ ) was not seen in all FTIR spectra, suggesting that the oxygen atoms were incorporated only as trace impurities. It is worth noting that, from the vibration peaks of the Si-N stretching mode, we found that the Si-N stretching peaks of a-SiN<sub>x</sub>O<sub>y</sub> films are slightly shifted to the direction of higher wavenumbers than those of a-SiN<sub>x</sub>, and there is already an obvious shoulder peak (such as R = 1). This shoulder is clearly derived



**FIGURE 8** The ns-PL lifetimes  $\tau_{\text{average}}$ , and the calculated  $\tau_r$  and  $\tau_{nr}$ , vs  $\lambda_{\text{eml}}$  for a-SiN<sub>x</sub>O<sub>y</sub> with various R of (A) R = 0.5; (B) R = 1; (C) R = 1.5; (D) R = 2.5; under room temperature, respectively. Black lines show the error bars of the ns-PL lifetimes  $\tau_{\text{average}}$  values.

from the N-Si-O bonding configuration formed in a-SiN<sub>x</sub> by the incorporation of O.

### 3.2 N-Si-O related N<sub>x</sub> dangling bond defect states

Figure 3 shows the measurements of the EPR curves of a-SiN<sub>x</sub>O<sub>y</sub> films with different R. As can be seen from Figure 3, there is a strong resonance absorption peak near the x-axis with magnetic induction intensity of 3,515 G, indicating the presence of unpaired dangling bonds in a-SiN<sub>x</sub>O<sub>y</sub> films. Since the structure of a-SiN<sub>x</sub>O<sub>y</sub> films is regarded as an intermediate state with both a-SiN<sub>x</sub> and a-SiO<sub>x</sub>, it has been found that the suspensory bond defect states in the bandgap of a-SiN<sub>x</sub> and a-SiO<sub>x</sub> films may coexist in a-SiN<sub>x</sub>O<sub>y</sub> films. We calculated the value range of the zero-crossing g-factor under different R of a-SiN<sub>x</sub>O<sub>y</sub> films is 2.0025–2.0040, and the peak line width is 8.5–12.0 Gauss.

According to previous analysis [21], we selected the trivalent Si DBs and the N-Si-O configurations related N<sub>x</sub> defect states, and performed Lorentz function fitting on the experimental EPR curves. The fitting results show that the trivalent Si DBs and N<sub>x</sub> defect states coexist in the band gap of the a-SiN<sub>x</sub>O<sub>y</sub> film, and the relative dangling bond concentrations of the two defect centers are also obtained by fitting. Combined with the PL spectra of a-SiN<sub>x</sub>O<sub>y</sub> films of different R [23], we found that the PL integrated intensities ( $I_{\text{PL}}$ ) of a-SiN<sub>x</sub>O<sub>y</sub> films were proportional to the concentrations of N-Si-O related N<sub>x</sub> dangling bond defect states. At the same

time, we also found that the relative concentration of Si DBs in a-SiN<sub>x</sub>O<sub>y</sub> films was much higher than that in the N<sub>x</sub> defect states. However, due to the low PL efficiency of Si DBs defects in a-SiN<sub>x</sub>O<sub>y</sub> thin films [20], they can even be regarded as non-radiative recombination centers.

### 3.3 Fluorescence properties of a-SiN<sub>x</sub>O<sub>y</sub> films

We measured the PL spectra of a-SiN<sub>x</sub>O<sub>y</sub> films with different R ratios at 8 K under He-Cd continuous laser excitation at a wavelength of 325 nm. As shown in Figure 4, by adjusting the flow ratio R, we achieved a fluorescence emission of a-SiN<sub>x</sub>O<sub>y</sub> films with modulated luminescence wavelengths ( $\lambda_{\text{PL}}$ ) in the visible range. It is worth noting that as R increases from 0.3 to 5, the PL peak blue shifts from 590 nm to 425 nm as R gradually increases; the corresponding PL integrated intensity ( $I_{\text{PL}}$ ) first increases and reaches saturation (R = 1.5), and then gradually decreases.

### 3.4 TR PL decay properties of a-SiN<sub>x</sub>O<sub>y</sub> thin films

To further investigate the relationship between the PL properties of a-SiN<sub>x</sub>O<sub>y</sub> films and the defect states of N-Si-O-related N<sub>x</sub> dangling bonds, we systematically measured the ns-transient fluorescence PL characteristics of a-SiN<sub>x</sub>O<sub>y</sub> films (R = 1) at different

**TABLE 1** Summary of the calculated  $\tau_r, \tau_{nr}, k_r$  and  $k_{nr}$  by using the PL IQE ( $\eta$ ) and the obtained lifetimes  $\tau_{average}$  under room temperature for a-SiN<sub>x</sub>O<sub>y</sub> films with various R.

	R (R = NH <sub>3</sub> /SiH <sub>4</sub> ) ratios					
	5	2.5	1.5	1	0.5	0.3
$\eta$ (%)	45.6	56.9	84.1	72.7	42.1	34.5
$\tau_{average}$ (ns)	6.17	6.92	8.57	7.66	6.75	5.64
$\tau_r$ (ns)	13.52	12.16	10.19	10.54	16.03	16.35
$\tau_{nr}$ (ns)	11.33	16.05	53.92	28.08	10.16	8.61
$k_r$ (10 <sup>8</sup> s <sup>-1</sup> )	0.74	0.82	0.98	0.95	0.62	0.61
$k_{nr}$ (10 <sup>8</sup> s <sup>-1</sup> )	0.88	0.62	0.19	0.36	0.98	1.16

detection wavelengths. As a comparison reference, we also measured the related properties of a-SiN<sub>x</sub> films with the same flow ratio.

Figures 5A, B show the ns-TRPL decay spectra and the relative fitting decay curves for a-SiN<sub>x</sub> and a-SiN<sub>x</sub>O<sub>y</sub> thin films at R = 1, respectively. According to the formula  $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$  with  $\tau(T) = \sum_{i=1}^n \frac{A_i \tau_i^2}{A_i \tau_i}$  [11], we obtain the corresponding ns-PL lifetimes ( $\tau_{average}$ ) at different detection wavelengths, as shown in Figure 5C.

From Figure 5C, we can see that for a-SiN<sub>x</sub> films, the PL lifetimes of the samples continue to increase as the detection wavelength increases. This is a typical radiative recombination dynamics process of the band tail carrier transition, which is consistent with the previously reported results [18]. When the excitation photon energy ( $E_{exc}$ ) is less than the optical band gap ( $E_{opt}$ ) ( $E_{exc} < E_{opt}$ ), the absorption only occurs at the band tail, and with the decrease of  $E_{exc}$ , the luminescence peak  $E_{PL}$  gradually shifts to the deeper energy level of the band tail, that is, the  $E_{PL}$  red shift. At this time, the excited state carriers relax to the deeper energy level of the band tail, and emit light through thermal ionization inter-band recombination, resulting in a longer corresponding PL lifetime.

However, for a-SiN<sub>x</sub>O<sub>y</sub> films, with the increasing detection wavelength, the fluorescence lifetime of the sample first increases to saturation, and then gradually decreases, and its change trend is obviously different from that of a-SiN<sub>x</sub> films, but consistent with the change trend of defect density distribution, and the corresponding fluorescence lifetime value is proportional to the concentration of N<sub>x</sub> defect states. Therefore, we believe that the N<sub>x</sub> luminescence defect states related to the N-Si-O configuration dominate the radiation recombination process of a-SiN<sub>x</sub>O<sub>y</sub> films. The ns-TRPL properties of the a-SiN<sub>x</sub>O<sub>y</sub> films mentioned above verify that our high-efficiency light emission originates from the N-Si-O-related defect luminescence centers of the ns-order radiative recombination processes.

### 3.5 Temperature dependent ns-PL lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> films

Next, to gain a deeper understanding of the radiative and non-radiative recombination mechanisms of high-efficient light emission

from N-Si-O-related defect luminescence centers, we studied the PL kinetics of a-SiN<sub>x</sub>O<sub>y</sub> films at different test temperatures. Figure 6 shows the PL decay curve for the ns time range of a-SiN<sub>x</sub>O<sub>y</sub> thin films (R = 1) at a measured temperature range of 8 K–300 K. As shown in Figure 6A, the PL decay curve profiles remain unchanged at the test temperature range below 100 K, indicating that radiative recombination dominates the entire recombination process. When the test temperature is increased from 120 K to 300 K, it can be seen from the PL decay curve that the PL lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> films become shorter, and the non-radiative recombination effects become more and more obvious, as shown in Figure 6B.

At the same time, from the PL decay curve of a-SiN<sub>x</sub>O<sub>y</sub> films, we can further see two different ns fluorescence radiation recombination processes, which we call the fast ns-PL lifetimes and the slow ns-PL lifetimes, respectively. The PL decay curves of a-SiN<sub>x</sub>O<sub>y</sub> films were well fitted with a double exponential function, and the fitting results for all PL lifetimes are shown in Figure 7. The obtained ns-PL lifetimes  $\tau_{average}$  of the samples were reduced from 11.9 ns (less than 100 K) to 7.8 ns. As shown in Figure 7,  $\tau_{average}$  tends to be stable (about 11.9 ns) and does not change with temperature in the low temperature range (less than 100 K), indicating that the PL lifetimes are mainly due to the radiation recombination processes of the carriers. However, the non-radiative recombination increases with increasing temperature, resulting in a continuous decrease in  $\tau_{average}$ , which drops to 7.8 ns at 300 K. It is worth mentioning that, the variation trend of the PL lifetimes at a certain temperature  $\tau_{meas}$  (T) is consistent with the PL integration intensity of the steady-state temperature dependent PL spectra [23]. This phenomenon once again verifies the typical PL properties of luminescent N-Si-O-related defect states.

### 3.6 Radiative and non-radiative recombination lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> thin films

As Section 3.5 mentioned above, we use the ns-PL lifetimes  $\tau_{average}$  to determined the radiative and the non-radiative recombination lifetimes. Thus, the PL internal quantum efficiency at different temperatures ( $\eta(T)$ ) should be determined as [5]:

$$\eta(T) = \frac{k_r(T)}{k_r(T) + k_{nr}(T)} = \frac{\frac{1}{\tau_r(T)}}{\frac{1}{\tau_r(T)} + \frac{1}{\tau_{nr}(T)}} = \frac{\tau_{average}(T)}{\tau_r(T)}, \text{ with } \frac{1}{\tau_{average}(T)} = \frac{1}{\tau_r(T)} + \frac{1}{\tau_{nr}(T)}. \quad (1)$$

Here  $k_r(T)$  and  $k_{nr}(T)$  denote the radiative and the non-radiative recombination rates, and  $\tau_r(T)$  and  $\tau_{nr}(T)$  denote the radiative recombination lifetimes and the non-radiative recombination lifetimes.  $\tau_r(T)$  and  $\tau_{nr}(T)$  are expressed as [5]:

$$\tau_r(T) = \frac{\tau_{average}(T)}{\eta(T)}, \text{ and } \tau_{nr}(T) = \frac{\tau_{average}(T)}{1 - \eta(T)} \quad (2)$$

Based on our previous work [23], we obtained the PL IQE values from TD PL spectra and the directly measured PL QYs. Thus, by combining the resulting PL IQE values with the ns-PL lifetimes, we can further determine the radiative recombination lifetimes

and non-radiative recombination lifetimes of the sample according to Equation 2. Figure 8 shows the radiative recombination lifetimes and non-radiative recombination lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> films with different R at different detection wavelengths. The detailed of the calculated  $\tau_r$ ,  $\tau_{nr}$ ,  $k_r$  and  $k_{nr}$  by using the PL IQE ( $\eta$ ) and the obtained lifetimes  $\tau_{average}$  under room temperature for a-SiN<sub>x</sub>O<sub>y</sub> films with various R are listed in Table 1. We note that the trends of radiative recombination lifetimes are also consistent with the trend of the densities of the N<sub>x</sub> defect states. When  $\tau_{nr}(T)$  is much greater than  $\tau_r(T)$  (R = 1, 1.5, 2.5), the radiative recombination dominates the whole recombination process, and the PL IQE is higher (~70%). When  $\tau_{nr}(T)$  is less than  $\tau_r(T)$  (R = 0.3, 0.5, 5), the effect of non-radiative recombination is relatively obvious, resulting in a decrease in PL IQE (~40%).

Since the fluorescence lifetimes at low temperature are hardly affected by non-radiative recombination, we also can use that as the radiative recombination lifetimes ( $\eta \sim 1$ , and  $\tau_{average} \sim \tau_r$  in the low temperature range) to calculate the non-radiative recombination lifetimes at room temperature. We compared the radiative and non-radiative recombination lifetimes obtained by these two different calculation methods, and obtained the similar results at last. The average  $\tau_r$  is basically unchanged and tends to be stable at ~10 ns under different R conditions. These results show that the radiative recombinations of the luminescent N-Si-O defects remain in the order of  $10^8 \text{ s}^{-1}$  and keep unchanged throughout the whole recombination processes, which can be compared with those direct bandgap materials (e.g., typical cadmium selenide NCs,  $k_r \sim 10^8 \text{ s}^{-1}$ ).

## 4 Conclusion

In summary, we systematically studied the temperature dependent kinetic processes of radiative and non-radiative recombination in a-SiN<sub>x</sub>O<sub>y</sub> systems. We found that the PL lifetimes of a-SiN<sub>x</sub>O<sub>y</sub> films vary with the change of N-Si-O defect states concentrations, which is different from the typical luminescent kinetic characteristics of band tail related a-SiN<sub>x</sub> films. By combining PL IQE values with the ns-PL lifetimes, the radiative and non-radiative recombination lifetimes of our a-SiN<sub>x</sub>O<sub>y</sub> systems ranged from low temperatures (~8 K) to room temperature can be determined. The radiative recombination rates were also obtained ( $k_r \sim 10^8 \text{ s}^{-1}$ ), which can be compared to the results in the direct band gap.

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## Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

## Author contributions

PZ: Writing—original draft. XL: Methodology, Writing—review and editing. LZ: Methodology, Writing—review and editing. DW: Methodology, Writing—review and editing. KW: Writing—review and editing, Software. SW: Writing—review and editing.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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