



Radiative emission properties of a-SiN:H based nanometric multilayers for light emitting devices

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Abstract

Optical and photoluminescence characterizations were performed on nanometric multilayer structures based on amorphous silicon nitrogen alloys. Evidences are shown that the radiative efficiency of multilayers increases with respect to single-layer structures. This is ascribed to a strong electron–hole pair localization and a low heterointerfaces defect density. Time-resolved photoluminescence measurements yield fast recombination with an energy-dependent lifetime due to hopping processes. Finally, the performance of an electroluminescent device based on multilayers is presented. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of high radiative efficiency at room temperature of amorphous silicon-based alloys like a-Si_{1-x}C_x:H and a-Si_{1-x}N_x:H, many efforts were devoted to understand the nature of their radiative processes [1,2] and to apply such materials in electroluminescent devices [3,4]. Nanometric multilayers based on a-Si_{1-x}C_x:H and a-Si_{1-x}N_x:H, were investigated in the past with striking results concerning the high radiative efficiency [5]. In this work, optical and photo-

luminescence properties of a-Si_{0.4}N_{0.6}:H/a-Si₃N₄:H nanometric multilayers are presented and discussed. Taking into account the properties of a-Si_{1-x}N_x:H bulk samples, we show that the enhancement of the radiative recombination probability is due to the electron–hole localization induced by the quantum-well structure.

2. Experimental details

a-Si_{1-x}N_x:H films and multilayers were deposited by 13.56 MHz plasma enhanced chemical vapor deposition system with SiH₄ + NH₃ + H₂ gas mixtures. The deposition condition of both the homogeneous films and the multilayer structures have been carefully described elsewhere [5,6].

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Optical characterizations were performed by transmittance and reflectance measurements ($T-R$) and by photothermal deflection spectroscopy (PDS), from which the effective optical gap E_{04} (i.e., the energy at which the absorption coefficient $\alpha = 10^4 \text{ cm}^{-1}$) and the sub-band gap absorption were extracted.

Stationary photoluminescence measurements were performed using a $f/3.9$ grating monochromator, an Ar^+ laser line at 2.71 eV and a Si photodiode whose signal was processed by a DSP lock-in amplifier. Time-resolved photoluminescence measurements were performed using a mode-locked frequency-doubled Ti:Sapphire laser as pulsed excitation source (pulse duration 2 ps, line energy 3.2 eV, repetition frequency 4 MHz). A monochromator coupled to a streak-camera was used to have two-dimensional (time and wavelength) luminescence maps.

3. Results and discussion

The analyzed structures consist of a periodic repetition of understoichiometric $\text{a-Si}_{0.6}\text{N}_{0.4}:\text{H}$ with optical gap of 2.6 eV (well layer) and of stoichiometric $\text{a-Si}_3\text{N}_4:\text{H}$ with optical gap of 5 eV (barrier layer) with several thickness ranging from 5 to 100 Å.

Fig. 1 shows the room temperature stationary photoluminescence (CW PL) spectra of multilayers with 30 periods of $\text{a-Si}_{0.6}\text{N}_{0.4}:\text{H}/\text{a-Si}_3\text{N}_4:\text{H}$ layers, and of a reference bulk $\text{a-Si}_{0.6}\text{N}_{0.4}:\text{H}$ sample 7500 Å thick. The spectra are normalized for the sample absorptance at the excitation energy. The multilayer structures show a higher PL intensity with respect to the reference bulk specimen. In Fig. 1a, the comparison between multilayers with fixed barrier thickness ($d_b = 100 \text{ Å}$), and several well thickness ($d_w = 5\text{--}30 \text{ Å}$) yields a blue shift of the emission energy and an increase of the radiative efficiency as the well thickness decreases. Such a marked increase can be ascribed to a strong spatial localization of electron-hole pairs in the well layers, which augments by decreasing the well layer thickness. In addition, a reduction of the nonradiative recombinations occurs when d_w becomes small with respect to the average defects

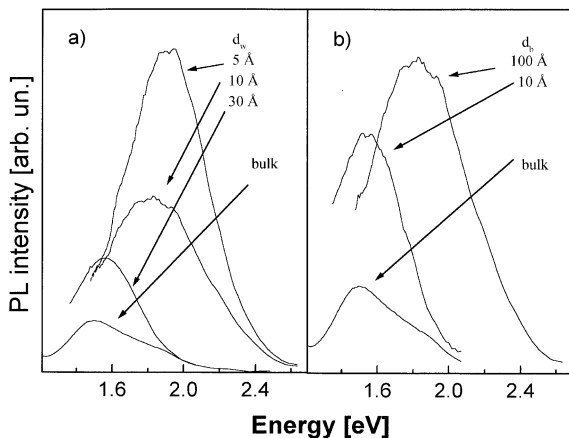


Fig. 1. Room temperature photoluminescence spectra of multi-layer samples whose parameters are: (a) fixed barrier thickness of 100 Å and different well thickness as indicated, (b) fixed well thickness of 10 Å and different barrier thickness as indicated. As a reference the spectra of an $\text{a-Si}_{0.6}\text{N}_{0.4}:\text{H}$ film is reported (indicated as bulk).

separation [7]. The observed blue shift is justified by the concurrent reduction of deep tail states. The spatial localization induced by the nanometric thickness of the well layers and by the presence of the barrier layers which prevent carrier diffusion, is confirmed by the spectra in Fig. 1b. The PL intensity diminishes as the barrier thickness decreases. For thin d_b , a tunneling between well layers through the barrier layers becomes possible, reducing the radiative recombinations. The observed decrease of the radiative efficiency for multilayer structures with lower barrier energy-gap [8] confirms the hypothesis of a strong localization forced by the multilayer structure.

In the past, a quenching of radiative efficiency was observed when the well layer thickness was reduced under a few tenths of Å [9]. This was attributed to a large density of nonradiative defect lying at the barrier-well heterointerfaces. In particular, Si dangling bonds and coupled pairs of positively charged threefold-coordinated silicon and negatively twofold-coordinated nitrogen have been revealed by optically detected magnetic resonance measurements [10].

In order to check the presence of heterointerface defects in our samples, PDS measurements were

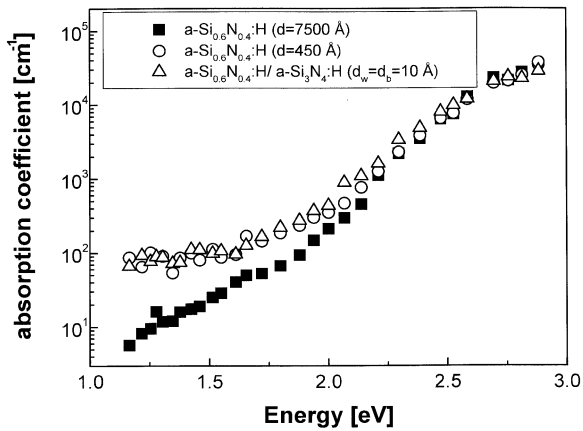


Fig. 2. Absorption coefficient for a-Si_{0.6}N_{0.4} films of different thickness and a multilayer sample with 25 periods of 10 Å wide barrier and well layers.

performed on single layer samples with different thicknesses (7500 and 450 Å, respectively) and on a multilayer structure with 50 periods ($d_w = d_b = 10$ Å) whose total thickness of absorbent layers is 500 Å (see Fig. 2). The thick specimen is dominated by bulk defects, the 450 Å thick one by interface defect. A comparison of the absorption spectra of these samples with that of the multilayer sample should reveal the importance of the heterointerfaces. In the low-energy region, where defect absorption predominates, the thick specimen presents an absorption one order of magnitude lower than the thinner one. On the other, the thin single-layer sample and the multilayer sample show an almost similar absorption. Thus, it can be argued that no noticeable amount of optical active barrier-well heterointerface defects has been introduced by the multilayer structuring.

Time-resolved photoluminescence measurements (TRL) were performed both on a-Si_{1-x}N_x:H alloys and on multilayer structures. A geminate recombination has been checked experimentally by verifying that no dependence of the decay line shape on the excitation intensities is observed, and that there is a linear dependence of the PL intensity on the excitation intensity. Fig. 3 shows the PL decays for a reference bulk a-Si_{0.4}N_{0.6}:H (Fig. 3a) and for a 30 period a-Si_{0.6}N_{0.4}/a-Si₃N₄ multilayer structure (Fig. 3b) at several emission energies (E).

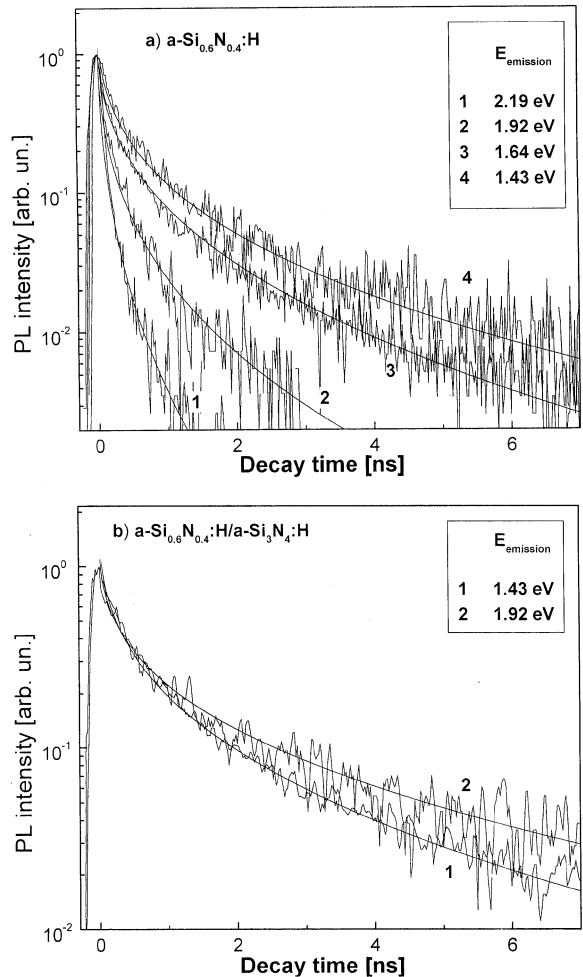


Fig. 3. Time-resolved photoluminescence at room temperature for (a): a-Si_{0.6}N_{0.4}:H film, (b): a-Si_{0.6}N_{0.4}:H/a-Si₃N₄:H multilayer ($d_w = 10$ Å, $d_b = 100$ Å). The spectra at several emission energies are reported. The smooth curves show the results of the best fit using the stretched-exponential function.

As the detection energy increases the decay time shortens. This occurs more for a-Si_{0.4}N_{0.6}:H sample than for the multilayer sample. All the samples show a nonexponential decay which is fitted with a stretched exponential law $I(t) = I_0 \exp[-(t/\tau)^\beta]$, where τ is the lifetime and β a dispersion exponent. Small $\beta \approx 0.3 - 0.4$ are deduced by least-squares fits of the decay data. To discuss the experimental data, we calculated the average decay time $\bar{\tau}$ as K Suzuki et al. [11].

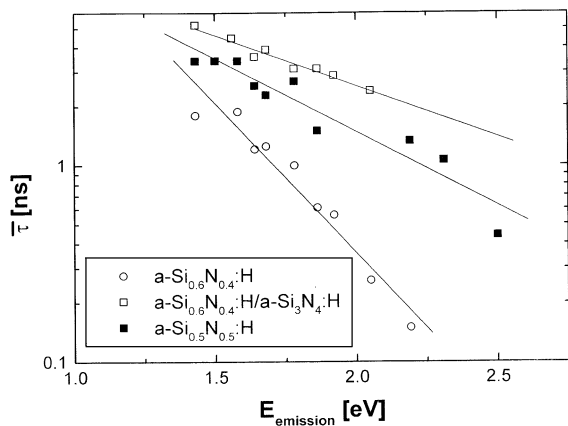


Fig. 4. Average decay time versus detection energy for a-Si_{0.6}N_{0.4}:H and a-Si_{0.5}N_{0.5}:H films and for a-Si_{0.6}N_{0.4}:H/a-Si₃N₄:H multilayer ($d_w = 10 \text{ \AA}$, $d_b = 100 \text{ \AA}$).

In Fig. 4, $\bar{\tau}$ is plotted versus E for a multilayer structure (30 periods of a-Si_{0.6}N_{0.4}:H/a-Si₃N₄:H, $d_w = 10 \text{ \AA}$, $d_b = 100 \text{ \AA}$) and two homogeneous a-Si_{1-x}N_x:H alloys (a-Si_{0.6}N_{0.4}:H and a-SiN:H sample with an emission band at the same energy as the multilayer). Smaller $\bar{\tau}$ values are measured for alloys than for multilayers. An exponential dependence $\bar{\tau} \propto \exp(-E/\gamma)$ fits the experimental data with higher γ for a-Si_{1-x}N_x:H alloys with high x .

Such a dependence could be accounted by a dominant phonon-assisted hopping process through which photogenerated carriers thermalize in lower-energy tail states. Hopping opens an escape mechanism which acts to reduce the recombination lifetime. The hopping rate is proportional to the density of localized states which are involved in the thermalization [12]. Moreover, due to the static disorder, a-SiN:H alloys are characterized by a density of states (DOS) which shows exponential band tails at the band edges. γ depends on the slope of the exponential DOS: sharper is the DOS onset and lower is γ . In a-SiN:H the exponential slope of the DOS is a decreasing function of N content and the DOS extent is larger for N-rich alloys [2]. These facts help to understand the N content and energy dependencies of $\bar{\tau}$. When the same energy interval is observed for the emission of a-SiN:H alloys, by increasing the N content one expects and,

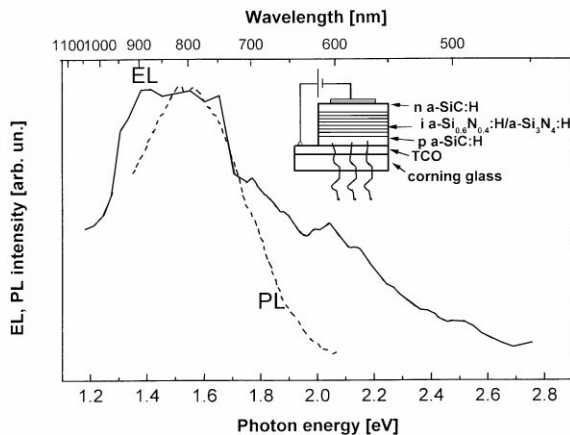


Fig. 5. Electroluminescence spectrum of a LED (whose structure is reported in the inset) under 15 V forward bias and 20 mA/cm² current injection. The PL spectrum of the multilayer inserted in the device is reported for a comparison.

indeed, measures (i) a larger $\bar{\tau}$ due to the lower tail DOS, and (ii) a higher γ due to a lower slope of the exponential DOS. The high decay times and the weak energy dependence of $\bar{\tau}$ for multilayer, compared to alloys, can be explained by the same arguments taking into account a widening of tail states in the well layers due to static disorder and/or to a decrease of edge states [13].

Finally, to evidence the potentiality of the a-SiN:H multilayers in electroluminescent devices, the performance of a light-emitting device (LED) is presented. The LED is based on a p-i-n diode where the intrinsic region is an a-Si_{0.6}N_{0.4}:H/a-Si₃N₄:H multilayer ($d_w = d_b = 10 \text{ \AA}$, 25 barrier layers and 26 well layers) embedded in two a-Si_{1-x}C_x:H-doped layers. Fig. 5 shows the electroluminescence spectrum (EL) of the device, compared with the PL spectrum of the active multilayer. PL and EL occurs at the same energy with a slightly broader EL emission band. It should be emphasized that EL is due to double injection of electrons and holes in the multilayer structure, respectively, by n and p layer, so the spectrum is the result of the non-geminate radiative recombination in the tail and defect states of the well layers, while the recombination due to photoexcitation is mono-molecular.

4. Conclusions

In summary, photoluminescence and optical investigations were performed on $a\text{-Si}_{1-x}\text{N}_x\text{:H}$ alloys and on nanometric multilayer structures based on them. A dependence of the emission band and of the radiative efficiency on the well and barrier thickness is observed. The luminescence properties of the multilayers sample are superior to those of the corresponding alloys. Such features are ascribed to the strong carrier localization caused by the multilayer potential and to the low concentration of heterointerface defects. Time-resolved luminescence measurements yield fast mono-molecular recombination (a few ns) with an energy exponential dependence of the lifetime, whose slope is weaker for the multilayer structures than for alloys. An electroluminescent device based on multilayers has been demonstrated.

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