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Optical properties of Er and Er + Yb doped hydrogenated amorphous silicon films

V I de Oliveira[1], **F L Freire Jr**[2] **and A R Zanatta**[1]

[1] Instituto de Física de São Carlos—USP, São Carlos 13560-250, SP, Brazil
[2] Departamento de Física—PUC, Rio de Janeiro 22452-970, RJ, Brazil

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Abstract
Hydrogenated amorphous silicon (a-Si:H) films were prepared by sputtering a Si target in an atmosphere of $Ar + H_2$. The Er (and Er + Yb) doping of the films was achieved by partially covering the Si target with small pieces of Er (Er + Yb) metal. After deposition the films were annealed up to 700 °C in an inert atmosphere. Ion beam analyses, Raman spectroscopy, optical transmission and photoluminescence measurements were employed for characterization purposes. According to the experimental results, thermal treatments up to ∼300 °C do not significantly alter the composition, atomic structure or optical bandgap of the present a-Si:H films. On the contrary, the Er-related photoluminescence intensity at 1540 nm increases and reaches its maximum at about 400 °C. Treatments at temperatures higher than ∼400 °C reduce both the Er-related light emission and the optical bandgap of the films due to the out-diffusion of hydrogen atoms. Furthermore, the relatively small optical bandgap and the presence of tail states prevent any optical activity of Yb^{3+} ions in the measured a-Si:H films. At the present doping levels and sample characteristics, ytterbium only increases the incidence of non-radiative processes.

1. Introduction

For a long time, rare-earth (RE) species have been considered for technological applications such as phosphor materials and active media for solid-state lasers [1]. More recently, and taking into account the possibility of combining some of the unique optical characteristics of RE^{3+} ions with the electrical properties of semiconductor hosts, the interest in RE-doped compounds has been renewed [2]. RE-doped silicon-based materials, in particular, are expected to revolutionize our actual (tele-) communications system through the development of hybrid Si photonic devices. With that aim in mind, Er^{3+} is one of the most interesting RE^{3+} ions since its ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition takes place at about 1540 nm, the wavelength at which the transmission loss of the actual silica-based optical fibres is a minimum. The luminescence

intensity at ∼1540 nm, however, is highly influenced by both the low absorption cross section of the Er^{3+} ions [2] and the optical bandgap of the host compound [3]. In principle, some of these shortcomings can be circumvented by inserting relatively high Er concentrations in amorphous networks and/or by using wide bandgap matrices. Despite that, a high Er concentration is known to promote substantial losses through the advent of detrimental cooperative interactions like self-quenching, up-conversion, etc. In the same way, wide bandgap materials cannot be a reasonable choice for electron injection purposes. An alternative approach to improving the Er-related emission efficiency could be the sensitization of Er^{3+} with, for example, Yb^{3+} ions [4], silicon nano-clusters [5], silver nano-particles [6], organic ligands [7], etc. Actually, the effectiveness of ErYb co-doping has been demonstrated in various materials (mainly glasses), and it has been established that [1, 8]: (a) the only excited Yb^{3+} energy state ($^2F_{5/2}$) aligns almost perfectly with the $^4I_{11/2}$ level of Er^{3+} at about 980 nm, (b) Yb^{3+} ions significantly increase the optical absorption at ∼980 nm of compounds containing both Er and Yb species, and (c) the energy transfer generally occurs from the Yb^{3+} to the Er^{3+} ions. It is also noteworthy that much of the experimental research involving ErYb-doped Si-based systems refers to SiO_2 [9] or to porous silicon [10] structures.

Based on these facts, and looking for additional information regarding Er-doped Si-based compounds, this paper reports on the optical properties of Er- and ErYb-doped a-Si:H films with relatively small optical bandgaps (in the ∼1.5–2 eV range). The samples considered in this study were deposited by co-sputtering and investigated by means of different spectroscopic techniques. Our main conclusions take into account the effect of different thermal treatments as well as the composition of the samples.

2. Experimental details

The a-Si:H films were prepared by radio frequency (13.56 MHz) sputtering a 5-inch diameter Si target (99.999% pure) partially covered at random with Er or Er + Yb platelets (99.9% pure). During deposition a total pressure of 5×10^{-2} Torr (corresponding to a mixture of Ar + H_2 ultra-high-purity gases) and a power density of ∼0.85 W cm^{-2} were employed. The films, typically 1 μm thick, were prepared at 125 °C on both polished crystalline (c-) Si and soda-lime glass substrates in the same deposition run. After deposition, the films were submitted to cumulative thermal annealing treatments up to 700 °C under a continuous flow of dry Ar. Each thermal treatment took place at a pre-defined temperature ($T_a \pm 10$ °C) and was 15 min long. Films deposited onto glass substrates were investigated by optical transmission in the near-infrared–visible (NIR–Vis) range, Raman scattering (RS), Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) analysis. Energy dispersive x-ray (EDX) and photoluminescence (PL) experiments were carried out on films deposited on c-Si substrates.

The optical transmission measurements were performed in the ∼400–900 nm wavelength range and, after appropriate data processing [11], provided the thickness and optical bandgap of the films. Room temperature RS measurements were obtained from a Raman micro-probe system and used the 632.8 nm line of a HeNe laser (average power density of ∼200 μW μm^{-2}). A 4 MV van de Graaff accelerator supplied the incident particle beam for the RBS (3.0 MeV He^+) and ERD (2.2 MeV He^+) analyses. The concentration of Si, Er and Yb was achieved from both RBS and EDX (20 kV incident electron beam) measurements. The hydrogen content was obtained from ERD. PL spectroscopy was performed mainly at 10 K with the samples being excited with the 488.0 nm line of an Ar^+ laser (∼15 mW). The PL emitting radiation was dispersed by a 500 mm Czerny–Turner type monochromator and detected with a liquid nitrogen cooled p–i–n cooled Ge detector using standard in-phase techniques.

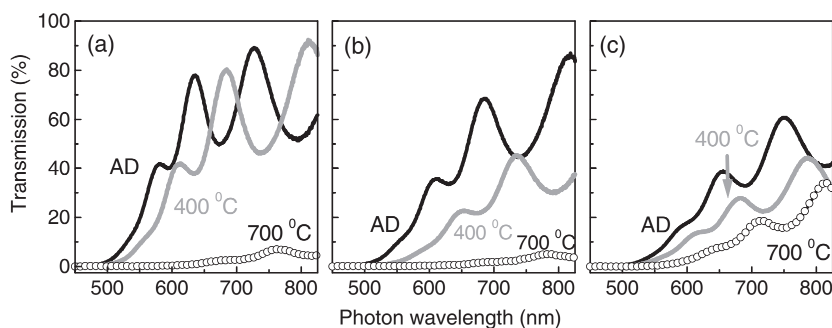

Figure 1. Optical transmission spectra of some a-Si:H films: (a) undoped, (b) doped with Er and (c) doped with Er + Yb. As indicated in the figure, the spectra correspond to a-Si:H films as-deposited (AD) and after thermal annealing at 400 and 700 °C.

Table 1. Atomic concentration of some of the a-Si:H films considered in this study. The data, corresponding to as-deposited samples, were obtained from Rutherford backscattering (RBS), energy dispersive x-ray (EDX) and elastic recoil detection (ERD) analyses. The relative impurity-to-Si target areas A_{Er} and A_{Yb}, considering a total area of 126.6 cm^2, are also indicated for each sample. NA stands for not available.

Sample	A_{Er} (cm^2)	A_{Yb} (cm^2)	$[Er]_{RBS}$ (at.%)	$[Er + Yb]_{RBS}$ (at.%)	$[Er]_{EDX}$ (at.%)	$[Yb]_{EDX}$ (at.%)	$[H]_{ERD}$ (at.%)
Si1 (a-Si:H)	0	0	<0.3	—	<0.1	<0.1	16
Si2 (Er)	8	0	0.8	—	0.6	<0.1	12
Si3 (Er + Yb)	8	5	—	NA	0.6	0.4	20
Si4 (Er + Yb)	4	4	—	1.0[a]	0.4	0.5	NA

[a] Due to the proximity between the atomic masses of Er (167.26 amu) and Yb (173.04 amu) it was not possible to determine, from the RBS measurements, the individual contribution of each atom.

3. Experimental results

It is well established that the optoelectronic properties of amorphous semiconductors depend not only on their atomic composition and structure but also on their method (and conditions) of deposition [12, 13]. When applicable, post-deposition sample processing should also be considered in detail. Accordingly, the study of amorphous semiconductors requires a systematic examination by means of different characterization techniques.

For the convenience of readers our main experimental findings will be considered separately.

The atomic composition of some of the films under investigation, as obtained from RBS, EDX and ERD, is presented in table 1. The experimental data of table 1 refer to as-deposited films, and the relative impurity-to-Si target area is also indicated. The concentrations of Er and Yb of some films after thermal annealing treatment were also investigated and, except for the hydrogen content, they remained almost unchanged.

The optical transmission spectra of one undoped a-Si:H film (sample Si1), as-deposited and after thermal annealing at 400 and 700 °C, are illustrated in figure 1(a). For comparison purposes, the spectra of a-Si:H films doped with Er (sample Si2) and Er + Yb (sample Si3) are also shown in figures 1(b) and (c), respectively. It is clear from the results of figure 1 that both the doping and the thermal annealing procedures exert considerable influence on the optical transmission characteristics of the present a-Si:H films. The very small concentration of REs

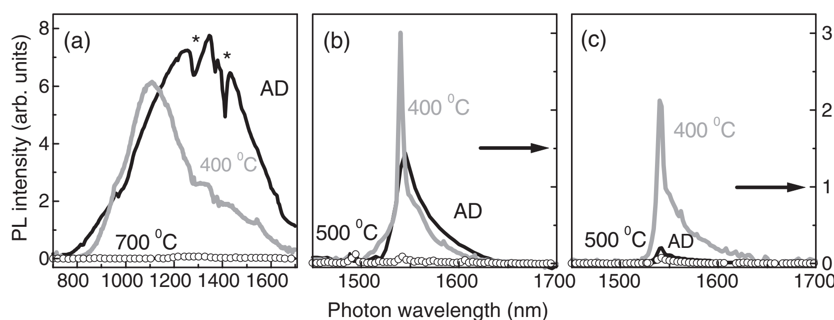

Figure 2. Photoluminescence spectra of some a-Si:H films: (a) undoped, (b) doped with Er and (c) doped with Er + Yb. The spectra were obtained at 10 K by exciting with 488.0 nm photons. The temperatures at which the samples were annealed are indicated in the figure. Notice the different PL intensity scales corresponding to undoped (left-hand side) and doped (right-hand side) samples. The stars in (a) indicate experimental artefacts (grating blaze and atmospheric absorption).

as well as the typical thickness of the a-Si:H films prevent any absorption feature at ~980 nm (due to Yb^{3+} ions) and at ~1540 nm (due to Er^{3+} ions).

Similarly, the light emission of the present a-Si:H films is highly susceptible to their composition and annealing history. Figure 2 shows the PL spectra of some a-Si:H films (both undoped and doped) after different annealing temperatures. Our main PL results can be summarized as:

(1) Undoped a-Si:H (figure 2(a))—light emission from the as deposited film is characterized by a relatively intense and broad PL signal corresponding to contributions due to defect-related transitions at ~1300–1400 nm, and involving tail states at ~1100 nm. After annealing at 400 °C, most of the PL signal originates from tail-to-tail transitions [12], which almost disappears at increasing annealing temperatures.

(2) Er- and ErYb-doped a-Si:H (figures 2(b) and (c))—both the Er- and ErYb-doped a-Si:H films only present light emission at about 1540 nm due to the $^4I_{13/2} \rightarrow {^4I_{15/2}}$ transition of Er^{3+} ions. Thermal treatment of these films considerably improves the 1540 nm light emission, which is maximum at ~400 °C. Further annealing decreases the PL intensity at 1540 nm. Light emission from the a-Si:H host is completely absent for all annealing steps considered in this study.

(3) In the ErYb-doped a-Si:H films, no PL signal was detected at about 980 nm, corresponding to the $^2F_{5/2} \rightarrow {^2F_{7/2}}$ optical transition of Yb^{3+} ions. Actually, even for a-Si:H films doped only with Yb at different concentrations, optical activity of the Yb^{3+} ions could not be observed.

The effect of thermal annealing and of the insertion of impurities into the atomic structure of the present a-Si:H films have been probed by Raman scattering spectroscopy. It is well established that the transverse-optical (TO) phonon mode of a-Si(:H) films at ~475 cm^{-1} is a sensitive probe for detecting variations of the dihedral bond angle between neighbouring Si atoms [12, 13]. Accordingly, the line width of the TO-like signal ($\Delta\omega$) provides a good qualitative indication of the degree of structural (dis)order of the a-Si films: higher $\Delta\omega$ values correspond to more disordered Si networks. Since the $\Delta\omega$ line width of all samples investigated (undoped and doped, as-deposited and thermally annealed) exhibits almost the same value (~70–80 cm^{-1}) we can conclude that within the temperature range 200–700 °C and impurity concentrations (~0.5–1 at.%) considered, no significant structural modification was verified for the a-Si:H films.

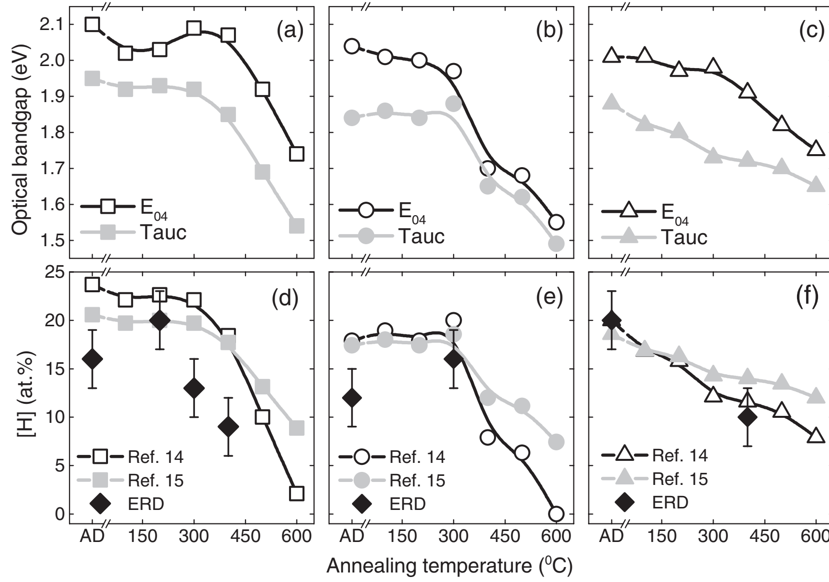

Figure 3. E_{Tauc} and E_{04} optical bandgaps of a-Si:H as a function of the annealing temperature. The hydrogen concentration, as obtained experimentally (by ERD) and as estimated from the relationships of [14, 15], are also displayed. All lines are guides to the eye. The following apply: (a) and (d), undoped a-Si:H (sample Si1), (b) and (e) Er-doped a-Si:H (sample Si2), and (c) and (f) ErYb-doped a-Si:H (sample Si3).

4. Discussion

As stated before, the present a-Si:H films were prepared by radio frequency sputtering. According to this deposition method, insertion of the Er (or Er + Yb) impurity into the a-Si:H network was achieved during sample preparation by partially covering the Si target with small pieces of metallic Er (or Er + Yb). Contrary to other preparation methods, sputtering allows accurate control of the impurity content by simply varying the relative impurity-to-Si target areas. The same applies to the hydrogen concentration, which can be changed depending on the hydrogen partial pressure during deposition. Alternatively, the hydrogen present in the a-Si:H films can be rearranged (or even removed) by thermal treatments at increasing temperatures. In this respect not only the RE^{3+} ions but also the presence of hydrogen determine most of the optoelectronic properties (optical transmission, optical bandgap, carrier recombination, etc) of the a-Si:H samples. In amorphous semiconductors, for example, hydrogen passivates dangling bonds and induces the breaking of weak bonds. Additionally, and as a consequence of the recession of the top of the valence band, the optical bandgap widens with hydrogenation. As a result, the hydrogen content and optical bandgap are closely connected in a-Si:H.

The optical bandgaps of all films considered in this study were obtained from the optical transmission curves [11] and are indicated in figure 3. Usually, the optical bandgap of amorphous semiconductors is denoted by the Tauc gap (E_{Tauc}) or by the energy at which the absorption coefficient reaches 10^4 cm^{-1} (E_{04}) [12, 13]. The hydrogen concentration [H] of each sample is also indicated in figure 3. The values of [H] presented in figure 3 were obtained following two different approaches: experimentally (by ERD) and by estimation from the linear relationship between E_{04} and [H] of similar a-Si:H samples [14, 15].

Based on the experimental results of figure 3, it is interesting to notice that, except for the ErYb-doped a-Si:H film, thermal treatments up to ~300 °C do not significantly alter the optical

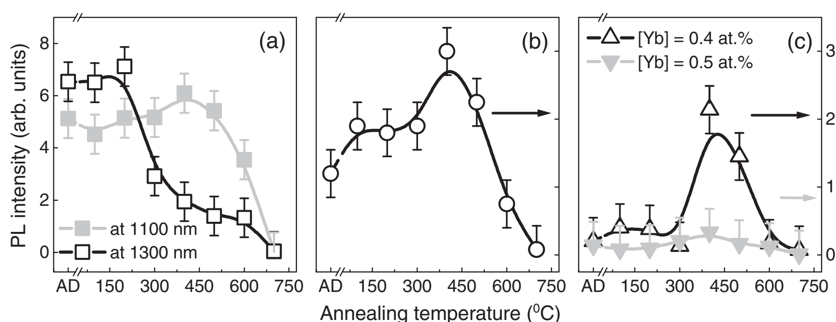

Figure 4. Photoluminescence intensity as a function of the annealing temperature of the following a-Si:H samples: (a) undoped, (b) Er-doped and (c) ErYb-doped at two different concentrations. The data refer to spectra taken at 10 K under 488.0 nm photon excitation. Notice the different PL intensity scales corresponding to undoped (left-hand side) and doped (right-hand side) samples. The lines are just guides to the eye.

bandgap (and, consequently, [H]) of the present samples. As will be shown in conjunction with the PL results, within this temperature range, thermal annealing only promotes some structural re-ordering (and/or hydrogen diffusion) [16]. Increasing annealing temperatures reduce the optical bandgap of the samples as a result of a considerable out-diffusion of hydrogen [16]. The ErYb-doped films, on the contrary, seem to depend on the annealing temperature in a different (monotonic) way. We believe that this behaviour can be associated with an increased density of defects (mainly band tail states), either because of the impurity concentration (almost twice that adopted in the Er-doped film—see table 1) or because of the expected energy position of the Yb^{3+} ions within the bandgap of a-Si:H (around 980 nm or approx. 1.25 eV). In other words, in the ErYb-doped films the optical transitions will be greatly influenced by an augmented density of conduction band tail states.

Most of the above discussion is supported by the PL experiments. PL is the radiation emitted by the process of photo-excited carrier recombination and, consequently, is a direct measure of the radiative transitions. In amorphous semiconductors, PL measurements are usually made at low temperature because the competing non-radiative transitions are dominant at elevated temperatures. In fact, at room temperature the luminescence intensity is low and almost undetectable in poor quality a-Si:H films. Even at very low temperature, as illustrated in figure 2, the PL spectrum is featureless and broad. It is generally accepted that most of the PL signal originates from transitions between the conduction and valence band tail states giving rise to light emission at about 1100 nm [12]. Moreover, the PL intensity in doped a-Si:H is strongly quenched by the defects (either tail states or dangling bonds) induced by doping. The emission due to these defect-related transitions typically takes place at ∼1300 nm.

In the present study, only the undoped a-Si:H samples exhibit light emission with the above characteristics. The presence of either Er or Er + Yb completely inhibits the PL signal from the amorphous host and light emission is verified only at ∼1540 nm. This is consistent with the fact that Er^{3+} ions are highly efficient recombination centres that effectively compete with other (non-)radiative processes taking place in the amorphous host [17].

The effect of thermal treatments onto the PL intensity of the present samples is displayed in figure 4. In order to minimize non-radiative processes most of the PL measurements were carried out at 10 K. However, it is important to mention that, at room temperature, the PL signal from the optimized samples (usually after annealing at 400 °C) is still detectable with an intensity that is 10–20% of that measured at 10 K.

The data of figure 4(a), corresponding to undoped a-Si:H films, clearly discriminate the PL contribution due to tail-to-tail (at ∼1100 nm) and defect-related (at ∼1300 nm) transitions. According to figure 4(a), annealing at increasing temperatures improves the tail-to-tail transitions in detriment to those associated with defects. After annealing at 700 °C, and because of the very low hydrogen content (figure 3(d)), no light emission occurs. In fact, the PL behaviour exhibited by the three classes of samples (undoped, Er-doped and ErYb-doped) seems to depend on the thermal treatments in the following similar way. (a) Before the attainment of the maximum PL intensity (at about 400 °C), thermal annealing induces either the diffusion of hydrogen atoms or some structural rearrangement of the a-Si network. In both cases, thermal annealing acts to minimize non-radiative losses, characteristic of doped amorphous semiconductors and/or those with a high density of defects. Specifically for the RE-doped samples, thermal annealing (and consequent bandgap shrinkage (figures 3(b) and (c))) can also improve the energy transfer mechanism from the a-Si host to the RE^{3+} ions. (b) After the maximum PL intensity is reached, annealing at increasing temperatures promotes the out-diffusion of hydrogen and the consequent development of non-radiative centres.

The effect of different RE concentrations on the PL of the ErYb-doped a-Si:H films is also illustrated in figure 4(c). According to figures 4(b) and (c), and taking into account the RE concentration of the films (Si2, Si3 and Si4 in table 1), it is reasonable to suggest that the observed decrease in the PL intensity at ∼1540 nm is not only a result of the lower [Er]. The presence of Yb species seems to play an important role in increasing the density of tail states, and consequently the number of non-radiative transitions. Such a proposition is also supported by the optical data, from which is apparent the effect of the tail states through a lower optical transmission (figure 1(c)) and a relatively weak dependence of the optical bandgap with the annealing temperature (figure 3(c)).

The photoluminescence of all a-Si:H films annealed at 400 °C was also investigated following different excitation wavelengths: 457.9, 476.5, 488.0, 501.7 and 514.5 nm (from an Ar^+ laser), 632.8 nm (HeNe laser) and ∼800 nm (diode laser). The measurements were carried out at 10 K, under very low power excitation (∼10 mW), and in the same experimental setup. According to the experimental results, photon energies around ∼2 eV (or 600 nm) seem to be the most effective in producing light emission in the present a-Si:H (either undoped or RE-doped) films. At this wavelength, photo-carriers are generated along the whole thickness of the film (∼1 μm), rendering the most intense PL signal. Considering the ensemble of optical data achieved so far it is evident that the RE^{3+} ions are excited via the amorphous host. It is also apparent that the band tail states (and/or the relatively small optical bandgaps) of the present a-Si:H films are behind the absence of any optical activity of Yb^{3+}. At the present doping levels and sample characteristics, ytterbium does not act as a sensitizer to the Er^{3+} ions, but only increases the incidence of non-radiative processes.

5. Concluding remarks

The present work reports on the optical properties of a-Si:H thin films doped with Er and with Er + Yb. The films were prepared by co-sputtering and systematically annealed up to 700 °C. An accurate analysis of the present experimental data allowed us to conclude that: (1) thermal treatments up to ∼300 °C do not significantly alter the composition, atomic structure or optical bandgap of the a-Si:H films (either undoped or RE-doped); (2) within this range of annealing temperatures, however, changes can be observed in the light emission of the films; (3) the Er- and ErYb-doped films exhibit light emission only at ∼1540 nm, corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition due to Er^{3+} ions; (4) depending on the annealing temperature, PL from the undoped a-Si:H film clearly presents band tail- and defect-related transitions at

~1100 and 1300 nm, respectively; (5) the maximum PL intensity achieved in both RE-doped and undoped a-Si:H takes place after thermal annealing at ~400 °C and is associated with some ideal diffusion of hydrogen atoms and structural reordering; (6) thermal treatments at temperatures higher than ~400 °C reduce both the Er-related light emission and the optical bandgap of the films due to the out-diffusion of hydrogen atoms; and (7) the relatively small optical bandgap and the presence of tail states prevent any optical activity of Yb^{3+} ions in the measured a-Si:H films.

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