Optical properties of Er-doped Si-based media
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Amorphous silicon (a-Si) has been thoroughly investigated in the last 20 years. The disordered nature of this material enhances some of the optical properties with respect to crystalline silicon. a-Si is, in fact, a really interesting material because of its properties and perspectives for practical applications, such as multijunction solar cells, liquid crystal displays, image sensors and detectors \[102,103,104\].

Amorphous silicon is disordered on the nanometer scale but it has the same chemical bond as in the crystalline form. In fact, silicon atoms are 4-fold coordinated in a tetrahedral bonding system, although the bond orientations and lengths have a not negligible distribution. The electronic structure presents valence and conduction band separated by a band gap, close to the one of c-Si, but with bandtails and localized states extending into the bandgap \[105,106,107,108\].

Bandgap of a-Si, because of both weakly and strongly localized states between valence and conduction band, is not a well defined parameter. Therefore, various definitions of the bandgap have been proposed \[109,110,111,112\]. A simple one states that \(E_g\) is the energy that corresponds to an absorption coefficient \(\alpha\) of \(10^3\) cm\(^{-1}\) or \(10^4\) cm\(^{-1}\), respectively called iso-absorption gaps \(E_{03}\) and \(E_{04}\). Another approach is given by the extrapolation of the absorption coefficient to zero absorption in the following empirical law:

\[
(h\nu\alpha)^{1/2} = B^{1/2}(h\nu - E_{Tauc}),
\]  

(6.1)
Defect luminescence from hydrogenated amorphous silicon

Figure 6.1: DOS of a-Si in case of n- and p- type, and undoped material.

where \( \alpha \) is on the order of \( 10^4 \) cm\(^{-1} \) and \( B^{1/2} \) is a factor including information on the convolution of the VB and CB states, and on the matrix elements of optical transitions.

Electronic density of states (DOS) of a-Si has been computed; on Fig. 6.1 electronic DOS of p-, n- and undoped a-Si are shown. Besides the bandtails, localized states for the different condition of doping are present [113,114]. In a-Si, three different kinds of absorption bands are present due to transitions between different electronic states [115,111]:

1. The high energy region, caused by transitions between delocalized states, analogous to the extended states in c-Si. Absorption coefficient \( \alpha \) for this region is larger than \( 10^4 \) cm\(^{-1} \) and has a parabolic dependence on the energy.

2. The Urbach region, due to transitions between localized states in one band tail and extended states in the other band. For such transitions, \( \alpha \) extends over several orders of magnitude below the value of \( 10^3 \) cm\(^{-1} \) and shows an exponential dependence on the energy.

3. The defect region with an absorption coefficient lower than the Urbach one, characterized by transitions involving deep states in the band gap.
States in the band tails come from the structural disorder given by the random (within certain limits) distribution of the lengths and angles of the Si-Si bonds. Since those represent only minor distortions to the crystalline structure, they introduce states in the ideal crystalline band gap that are energetically close to the valence and conduction bands. Deep states are instead produced by the presence of threefold coordinated silicon and, consequently, of broken or dangling bonds. They introduce states close to the center of the band gap and their number increases with the concentration of defects.

6.1 Samples and experiments

The investigated sample is an Er-doped hydrogenated amorphous Si sample, as described in the Sec. 1.1.4.

The samples were excited using an Millennia laser at 532 nm for cw measurements or a tunable Optical Parametric Oscillator (OPO) producing pulses of 5 ns duration at 20 Hz repetition rate. The luminescence was resolved with a 1 m F/8 monochromator (Jobin-Yvon THR-1000) equipped with a 900 grooves/mm grating blazed at 1.5 µm and detected by an infrared photomultiplier with a 30 µs response time. A flow cryostat permits to perform measurements at different environmental temperatures.

More details about experimental setup are given in Chapter 1.

6.2 Experimental results and discussion

Characterization of Er-doped a-Si:H samples started with recording PL spectra in a large range of emission energies at different excitation fluxes. In Fig. 6.2 four spectra of PL at a different excitation flux are shown. It is evident that at low pumping flux the spectrum is characterized only by the Er-related emission around 0.8 eV. Increase of the excitation flux causes the appearing of a luminescence band extended in a wide range of energies, namely from 0.7 to 1.2 eV.

If now we fix the detection at two distinct energies, the maximum of Er-related emission and away from the Er-related region, respectively at 0.8 and 0.92 eV, and record the PL in function of excitation flux, we get the curves in Fig. 6.3. PL at 0.8 eV shows an initial increasing with saturation at high fluxes until a certain value at which PL rises again with an exponential behavior. Emission at 0.92 eV, instead, has null intensity until the flux reaches a threshold value that corresponds to the one at which the exponential increase of PL at 0.8 eV sets in. Grey curve shows subtraction of the two flux dependencies of PL at 0.8 and 0.92 eV; once the exponential increase at high flux is
cancelled out only a saturated curve remains. Interpretation of the picture is unequivocal: at low excitation flux, Er$^{3+}$ ions are excited and start to emit, and their PL increases and eventually reaches a saturation value, as usual for Er-doped Si systems. When excitation flux comes to the “threshold” value afore mentioned, a new broad luminescence appears with a non-linear flux dependence. This new luminescence is due to transitions in the amorphous matrix as described earlier in this chapter, and not to Er.

Luminescence spectra in Fig. 6.4 recorded at high excitation power, show clearly the occurrence of two PL regions, generated from transitions between different electronic states. Recombination from the conduction to valence band, analogous to electron-hole recombination in c-Si, gives rise to the high
6.2 Experimental results and discussion

Figure 6.3: Er-related PL at 1350 nm, associated with recombination through defect states, is absent until the excitation flux reaches a threshold value, after which its intensity increases exponentially. Er-related PL at 1540 nm increases at low excitation flux until saturation and then rises exponentially at the same flux value as for the PL recorded at 1350 nm.

Energy band PL (1.5 - 2 eV). The region extending from 0.8 to 1.5 eV is instead due to the presence of defect states within the band gap of a-Si:H. The intense emission at 0.8 eV is, as before mentioned, to be attributed to Er$^{3+}$ ions, although at high excitation flux it saturates and the defect PL occurring also at this energy dominates. Further spectra have been recorded at different moments with unchanged configuration. We note that while the defect luminescence band changes due to rearrangements and degradation of the system, the band-to-band PL remains unperturbed. This is consistent with an interpretation that this luminescence comes from transitions between extended states in the crystal that are not affected by collateral effects such as thermal or diffusive phenomena. The second band at low emission energy is attributed to recombination between the tails of the two bands (or from one tail to the other band) and to recombination through the defect states in the band gap. The overlap between the two PL sub-bands is due to the fact that the defect states, created by the dangling bonds, are extended in the entire
band gap. In fact simulations have been performed [105] to reconstruct the electronic DOS of a-Si and they show that for large system (> 4000 atoms) the introduction of dangling bonds produces a featureless increase of the density of states in the gap, rather than localized states in the vicinity of the Fermi level.

We postulate that superlinear rise of PL originates from the increase of density of defects in the material. In fact, PL is directly proportional to the density of defects present in the material. These defects, mainly dangling bonds, can be formed by light-induced Stabler-Wronski effect (SWE) [116,117] or thermally [118].

The mechanism of the SWE involves the trapping of a hole at a weak Si-Si bond followed by recombination of an electron-hole pair that provokes the breaking of the bond [119,120]. In case that the Si-Si bond is adjacent to a Si-H bond, the recombination of e-h pair and breaking of the Si-Si bond causes the flipping of the Si-H bond towards the Si-Si one, leaving a dangling bond behind. The result is the formation of two dangling bonds of different
kind, a normal and a hydrogen related one. The density of dangling bonds $N_D$ depends on illumination time $t$ and on e-h pair generation rate $G$ (directly proportional to the excitation flux) with the following relation:

$$N_D \propto t^{1/3}G^{2/3} \quad \text{(6.2)}$$

The sublinear dependence of PL on defect generation rate is not in accordance with our experimental finding, in which an exponential rise is observed instead. This obvious experimental fact rules out the SWE as a possible cause of the increase of defects density and consequently PL.

As mentioned before the increase of density of defects can be caused by the rise of temperature under laser illumination. Assuming that the temperature depends on the laser flux $\Phi$ in a linear way:

$$T(\Phi) = k \times \Phi + 300K \quad \text{(6.3)}$$

with $k$ being a constant, the density of defects reaches a thermodynamical equilibrium at the given temperature according to the following expression:

$$N_D = N_{Si-Si} \exp\left(-\frac{U_D}{kT}\right), \quad \text{(6.4)}$$

where $N_{Si-Si}$ and $U_D$ are, respectively, the density of weak Si-Si bonds and the energy of dangling bond formation (that is taken as uniform for all Si-Si bonds, for sake of simplicity). Due to the linear dependence of the sample temperature on laser excitation flux, the density of defects in Eq. 6.4 has the same exponential behavior also in function of the laser flux.

Emission regions (related to the afore mentioned absorption bands) show different behaviors in function of the temperature of the sample (temperature of the sample is controlled by a cryostat). PL spectra change dramatically their shape when temperature of the sample is varied (Fig. 6.5). In particular, at low temperatures, a PL band with a maximum around 1.35 eV is the main emission. Increasing the temperature, this luminescence decreases and a second band centered at 1 eV starts to appear and eventually dominates the emission of the sample. Fig. 6.5 gives a further confirmation of the role of temperature in formation of dangling bonds. In fact, spectra shift towards lower energies when temperature is risen, in agreement with the fact that it is easier to create dangling bonds at higher temperatures. At the same time, as shown in he inset, threshold of the inset of exponential intensity increase of defect PL moves to higher excitation flux when temperature is lowered; laser, in fact, has to supply now more energy to reach the temperature at which dangling bonds start to form.
If we look at the decay kinetic of PL at $E = 0.8$ eV at different excitation flux, we can determine lifetime of related PL defect states and distinguish it from that of Er since at low flux only Er-related PL is present and at high flux defect PL prevails. Photon counting setup allows to have information of the decay lifetime in the two “states” simultaneously. Grey and black curves in Fig. 6.6 refer, respectively, to low and high excitation photon flux. The grey curve can be fitted with a double exponential function (solid grey line) and the two components have values of hundreds of ns and few µs, as reported elsewhere [121]. A longer component of hundreds of µs has been also reported [121], but is not visible here due to the smaller time window (since only fast processes are investigated in this study). At high excitation flux, besides the two components detected at weak excitation conditions, a new fast component with the value of $\sim 15$ ns appears.

### 6.2.1 Optical hysteresis

Among the many peculiar optical characteristics of the investigated a-Si:H<Er> sample, one revealed itself to be particularly interesting. In this
Figure 6.6: *PL decay dynamics as recorded in a photon-counting measurement. The two curves are recorded for the maximum of PL occurring at the emission energy of 0.8 eV for low (grey symbols) and high (black symbols) excitation flux.*

In this case, PL has been recorded in function of the excitation flux, in the increasing and decreasing mode, i.e. going from low to high excitation flux and then returning to low excitation reversing the process. This has been done for several cycles in order to investigate whether a hysteresis effect was present. Fig. 6.7 shows a set of measurements of such type.

The labels of the curves refer to the path followed to record them, namely “up” for excitation flux going from low to high and “down” for the reversed process. The number indicate the temporal position in the cycle. It has to be mentioned that the curves have been taken without time delay between them, for instance once arrived at the maximum of curve “up1” the reversed measurement “down1” has been performed, and so forth.

As can be seen from Fig. 6.7 hypersthesis effect is indeed present. Luminiscence grows with its typical exponential trend in function of the flux. At a certain point in the high flux regime, the path is reversed. The intensity of PL recorded at the excitation flux immediately before the maximum has now a lower value with respect to the corresponding point in the “up” curve.
Approaching the low excitation from this reversed perspective, a new curve is drawn, lower than the one obtained going from low to high flux. Once the zero excitation is reached, a new cycle begins. The recorded curve (again “up”) overlaps with the previous one.

Hysteresis, in the present case, can be explained with the help of an additional measurement. PL, in fact, has a peculiar temporal behavior; when excitation is switched on and instantaneous PL is detected with a certain intensity, after some time, leaving the excitation on and unchanged, luminescence starts to decrease slowly towards a certain constant value. This fact is unequivocally displayed in Fig. 6.8. In particular, the left panel shows that the effect is independent of the emission energy and the intensity of PL reaches its constant equilibrium value in about 20 s. Right panel, in which PL at 0.81 eV and for a large time range is drawn, confirms that once the steady state is approached PL stays at this level without further decrease.

The experiment is in some way analogous to the one revealing the “hysteresis”. In fact, in that experiment excitation is increased until a maximum at which the PL has a certain intensity. Since PL is steadily decreasing, as shown...
in Fig. 6.8 the next recorded point ("down" curve) at a smaller excitation flux has a value lower than the corresponding one on the "up" curve. PL intensity follows the descending curve until excitation goes to zero. At this point, since excitation flux is null, experiment is "restored" to the original conditions and PL follows the same trend as in the previous "up" trajectory and the whole cycle starts again. The two experimental facts, that seem to refer to the same effect, tend to confirm that light illumination causes the formation of dangling bonds which give rise to additional PL. However, the decrease of luminescence under constant light illumination suggests also presence of another process which competes with the formation of dangling bonds. This could be, for instance, hydrogen atoms diffusing in the system after being excited by the laser and consequently saturating the dangling bonds and passivating them (as proposed also by Ref. [119]).

Further investigations will be necessary in order to corroborate that hypothesis and to draw a complete picture of the defect formation and annihilation in this complicated system.
6.3 Conclusions

In this chapter defect luminescence in hydrogenated a-Si has been characterized and related to the background information available on that material. Beside the Er related PL, a different more intense PL band appears. It is attributed to dangling bonds, whose number is strongly enhanced under laser illumination. We postulate that the increase of density of dangling bonds is due to the increase of temperature of the sample, produced by the laser excitation. We argue that such an increase in the density should follow exponential behavior in function of photon flux, consistent with experimental data. Future studies will further investigate this promising but also very complex optical system.