PHOTO- AND ELECTROLUMINESCENCE STUDY OF EXCITATION MECHANISM OF Er LUMINESCENCE IN a-Si:H(Er)

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ABSTRACT

Photo- and electroluminescence were studied in erbium-doped amorphous hydrogenated silicon films. A mechanism of excitation of erbium ions by defect-related Auger process is proposed which permits to explain consistently the whole set of our experimental results.

INTRODUCTION

The idea to fabricate LEDs integrable into silicon electronics and emitting at the wavelength of 1.5 µm corresponding to the absorption minimum of optical fibers attracted much attention to the luminescent properties of erbium-doped silicon [1]. Experiments showed that crystalline erbium-doped silicon (c-Si(Er)) suffers as an optical active medium from several drawbacks: the main are strong temperature quenching and a long radiative lifetime of erbium ions [2].

Recently we have demonstrated that the films of erbium-doped amorphous hydrogenated silicon (a-Si:H(Er)) prepared by cosputtering exhibit strong room-temperature photoluminescence and the lifetime of erbium ions in this material is considerably shortened by the effect of amorphous-matrix disorder [3].

Here we present results of more detailed studies of photoluminescence (PL) and the first observation of electroluminescence (EL) of a-Si:H(Er). The results of these studies gave a key to understanding of the excitation mechanism of erbium luminescence in amorphous matrix.

EXPERIMENT

Erbium-doped amorphous silicon films were prepared by cosputtering applying magnetron-assisted silane decomposition (MASD) technique [4]. The concentration of erbium introduced was measured by Rutherford back scattering method and reached up to 1×10^{20} cm^{-3}. For electroluminescent structures films of 0.5 µm thickness were deposited on n-silicon substrates with concentration of donors of 5×10^{17} cm^{-3}. Aluminium contacts were made to the amorphous film and to the n-type substrate. I-V characteristics of the EL structures had conventional diode type.

PL and EL spectra were analysed with a double grating spectrometer and detected by a nitrogen-cooled germanium photodetector. Excitation of PL was done by argon cw laser with the pumping power up to 100 mW. For EL studies excitation current pulses at 25 Hz were passed through the EL structure either in forward (plus on the amorphous film, minus on the substrate) or in reverse direction. PL was measured in the temperature range 77-300K while EL at room temperature.

RESULTS

PL-spectra of a-Si:H(Er) measured at 77K exhibit emission from both the Er^{3+} centers and the amorphous Si-matrix (Fig. 1). The latter is seen as a broad band at 0.9 - 1.3 eV, which is believed to arise from radiative tunneling between localized band-tail states. The intrinsic emission is low and the band width is much larger than in a typical a-Si:H of good quality. The spectrum in Fig. 1 is dominated by strong Er- induced emission at 0.8 eV. There is no indication of defect-related emission which can be usually observed in a-Si:H of low quality at 0.8 - 0.9 eV. In our previous study where the amorphous film had been of minor quality this emission formed a broad background of the Er - photoluminescence [3]. At 300K the emission from the a-Si:H matrix is suppressed by temperature quenching and the remaining signal is entirely due to Er^{3+} ions (cf. the inset in Fig.1). Er- induced emission consists of two narrow lines at 0.806 eV and 0.798 eV which can be attributed to crystal field splitting of the ground state of the Er ions.The lines are broadened in comparison with the lines observed in erbium-implanted crystalline silicon pointing to an important role of disorder in amorphous matrix.

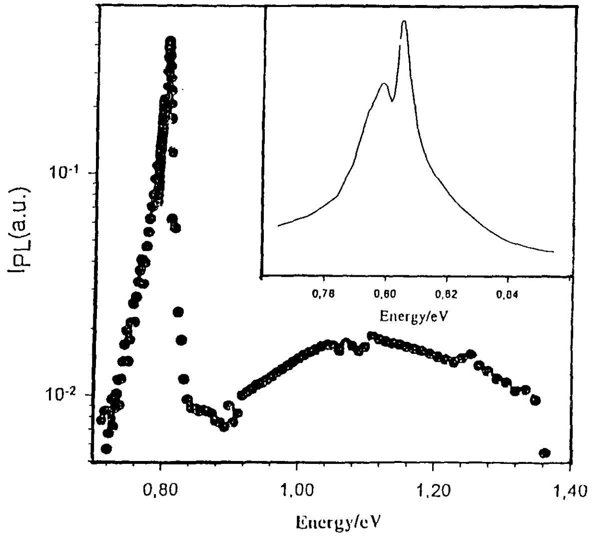

Fig.1
Photoluminescence of
a-Si:H(Er) at 77K

Our measurements of absorption in a-Si:H(Er) films show that significant absorption occurs at energies below 1.5 eV, where the absorption from deep defect states prevails. From the subgap absorption we inferred defect densities in the range 5×10^{17} to 10^{18} cm^{-3}.

Temperature dependences of intensity of PL for different optical transitions are displayed in Fig.2 (curve a - PL of erbium ions in a-Si:H(Er), curve b - PL of intrinsic emission of amorphous silicon in a-Si:H(Er), curve c - PL of erbium ions in erbium-doped crystalline silicon (c-Si(Er)).

In order to achieve high emission intensity in crystalline silicon the samples should be coimplanted with erbium and oxygen and optimization need extended high-temperature annealing [1]. In the case of a-Si:H the preparation is much simpler since high emission intensity does not require additional treatment of the films and high concentration of Er can be incorporated using the cosputtering technique. At low temperature ($T < 100K$) the Er-induced emission is larger by 1.5 - 2 order of magnitude than that in optimized c-Si(Er,O). The Er concentration amounted to 10^{20} cm^{-3} and 10^{17} cm^{-3} in a-Si:H(Er) and c-Si(Er,O), respectively. The oxygen content in the c-Si(Er) sample was about 10^{18} cm^{-3} . Note that in crystalline silicon, the maximum of Er-luminescence intensity was realized with oxygen content larger by one order of magnitude than erbium concentration. In a-Si:H(Er) oxygen was not introduced deliberately but it is well known that such films contain oxygen on the order of 10^{19} cm^{-3} due to contamination.

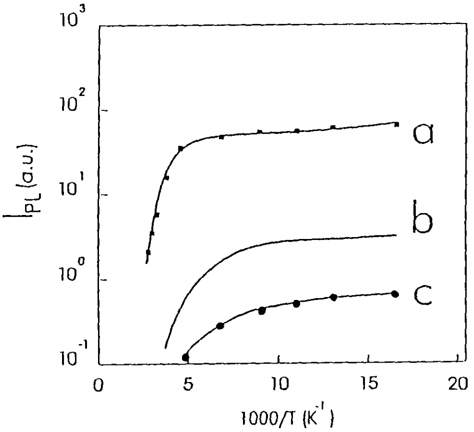

Fig. 2 Temperature dependence of PL of Er ions (curve a) and intrinsic band (curve b) for a-Si:H(Er) and Er ions for c-Si(Er) (curve c)

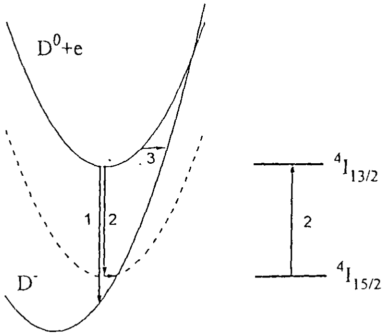

Fig.3 Configuration-coordinate diagram for $e + D^0 \rightarrow D^-$ transition

The results presented in Figs.1,2 have been obtained in linear regime of pumping .It should be stressed that at sufficiently high pumping power PL of erbium ions is saturated which is well known for c-Si(Er) and was demonstrated by us for a-Si:H(Er). The saturation of Er-emission in a-Si:H(Er) samples takes place at much higher pumping level than in c-Si(Er,O) [3]. Saturation of erbium-ions luminescence is traditionally ascribed to a finite number of optical centers and comparatively long lifetime of the Er^{+3} ion in the $^4I_{13/2}$ excited state.

In saturation regime, there is no temperature dependence of I_{PL} in the region 77 - 300K. This fact indicates that the number of optically activated Er-centers and the radiative life time of the excited $^4I_{13/2}$ - state are independent of temperature. It is of great interest that the defect luminescence band has been distinctly detected in the saturation regime even at room temperature.

In the linear regime I_{PL} decreases only slightly at low temperature but is strongly quenched above about 200K. The slope of the temperature dependence suggests an activation energy of about 250 meV (curve a). This behavior is different from that of the optimized c-Si(Er,O) sample (curve c). In that case I_{PL} starts from a much lower level as outlined above and exhibits pronounced temperature quenching with the characteristic energy of 20 meV at low temperature and the energy of 150 meV at higher temperatures. Here I_{PL} at room temperature is smaller by two orders of magnitude than that in the amorphous specimen. This behavior of c-Si(Er,O) is quite familiar and typical for an oxygen doped sample [1].

It is well known that the intrinsic band (curve b) is quenched strongly above about 60K when the carriers in the tail states become mobile due to thermally activated tunneling or are excited to the mobility edge which enhances non-radiative recombination through defect states.

Now we should like to discuss possible mechanisms of excitation of erbium ions in an amorphous matrix.

The energy transfer from electron states of the conduction band or electron states corresponding to localized levels in the forbidden gap to the strongly localized *f*-electron multiple states is produced by the Coulomb interaction. In amorphous matrix there are three possible ways of electronic excitation: impact ionization by mobile carriers, Auger-excitation in the recombination process of band electron-hole pairs, and Auger-process in which electron (or hole) is captured in a localized state in the forbidden gap.

The impact excitation need a great number of mobile carriers with high energy and therefore is usually not efficient in the amorphous matrix.

In amorphous silicon there are long tails of band states with energies lower than the mobility threshold. Here the intrinsic luminescence is observed as a broad band with the center near 1.3 eV. Thus, one may suppose that the excitation of Er^{3+} ion to the second excitation state $^4I_{11/2}$ from the ground state $^4I_{15/2}$ (the transition energy is equal to 1.24 eV) could be induced by the Coulomb interaction in the process of recombination of electron-hole pairs located in the band tails. The process can be designated as the resonance band Auger excitation. If this process played an important role in amorphous silicon, we should observe similar temperature quenching for both Er^{3+} ion and intrinsic luminescence bands since both bands are produced by mobile thermalized electron-hole pairs. However, one can see that the temperature quenching of Er-luminescence starts only at $T \geq 200K$, when the intrinsic luminescence is already absent (see Fig.2).

Our experimental results have demonstrated that there is a great number of defect states in a-Si:H(Er) which is typical for a-Si:H. In a-Si:H(Er), the defect absorption band is observed in the range 1.0 - 1.1 eV. It is the energy range where defect absorption band is usually observed in a-Si:H doped by various impurities or in films of minor quality. The defect absorption band is traditionally associated with dangling bond D-defects. The band is connected with the optical transition from donor D^0 states to the conduction band. It is accepted that in amorphous silicon there exist also D^- states originating from the ability of D^0 defects to capture the second electron. The splitting between these states is of the order of 0.1-0.2 eV. The defect luminescence band is observed in the region 0.8 - 0.9 eV and is ascribed to the radiative transition $e + D^0 \rightarrow D^-$. D- defects are also effective centers of nonradiative multiphonon recombination in a-Si:H due to strong electron-phonon coupling for electrons located in D^0 and D^- states.

The energy that should be taken away in the transition $e + D^0 \rightarrow D^-$ is close to the energy of transition $^4I_{15/2} \rightarrow {}^4I_{13/2}$ in the system of Er-ion *f*-electrons. As stated above, the introduction of erbium ions into the amorphous matrix is accompanied by formation of a great number of dangling bond defects with concentration ~ 10^{18} cm^{-3}. Therefore, we can deduce that in a-Si:H(Er), practically all the defects should be associated with Er^{3+} ions. Thus, effective resonance excitation of the *f*-electrons may take place in the process of electron capture in D^0 -state due to an Auger process. The absence of defect luminescence in a-Si:H(Er) in linear regime confirms the efficiency of this resonant defect-related Auger-excitation (DRAE) process. In saturation regime, when all Er^{3+} ions occur in the excited $^4I_{13/2}$ state and, therefore, the Auger process is blocked, the defect luminescence appears and can be observed even at room temperature. This fact supports our Auger excitation model. It is not necessary to have the precise resonance since the excess energy on the order of the Franck-Condon shift (which is about 0,1 eV in a-Si:H) can be easily transformed to the system of local vibrations due to electron-phonon coupling.

The transitions involved are shown in the configuration-coordinate diagram of Fig.3. Besides radiative transition from e + D^0 to D^- -state (transition 1), defect-related Auger-excitation (DRAE) (transition 2) and multiphonon (transition 3) nonradiative processes are presented in this diagram.

In the framework of our model of excitation it is easy to understand the difference in the temperature behavior of the Er-emission and the intrinsic emission of a-Si:H. It should be noted that in a-Si:H(Er) the basic channel of recombination is the nonradiative (multiphonon) recombination via D- defects because the quantum yield of radiation is only about 2%. Since the carrier mobility is low in amorphous matrix, the recombination should be controlled by spatial diffusion of excess carriers. Thus, we deal here with so-called Langevin mechanism of nonradiative recombination in which the carrier transport in the vicinity of the defect is a "bottleneck" of the capture processes because the time of spatial redistribution of excess carriers is longer than the time of energy losses. In amorphous silicon with a great number of defects the mobility of holes is much lower than the mobility of electrons. So, we can think that electron-hole recombination is controlled by the rate of the hole capture by defects in D^0 and/or D^- - states.

Strong room-temperature erbium-ion electroluminescence was observed by us in erbium-doped amorphous silicon films. Erbium luminescence corresponding to a narrow line at 1.54 μm (the energy of 805 meV) is observed only for the reverse bias when the excitation current through the structure exceeds the threshold value of ~ 5 mA (the applied voltage is ~15 V). Spectra measured for two values of the excitation current at reverse bias are shown in Fig.4. Besides the narrow line corresponding to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in the f-shell of erbium ion a broad band at 0.8-0.9 eV can be seen. This broad band corresponds to defect-related luminescence of a-Si:H matrix as discussed above. Similar to the case of PL erbium luminescence exhibits a trend to saturation with the current increase.

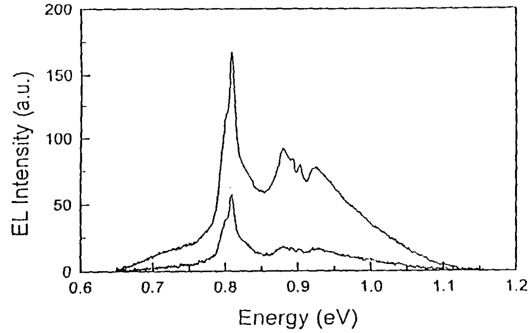

Fig. 4 EL spectra of a-Si:H(Er) with a reverse bias

In the case of forward bias no luminescence from erbium ions or defects is observed, but we detected free exciton line from crystalline silicon substrate (Fig.5). This fact demonstrates undoubtedly that free holes are injected into n-silicon substrate, i.e. the current through the amorphous layer is carried by holes in this case. What is more remarkable, the holes moving through amorphous material excite neither erbium nor defect luminescence.

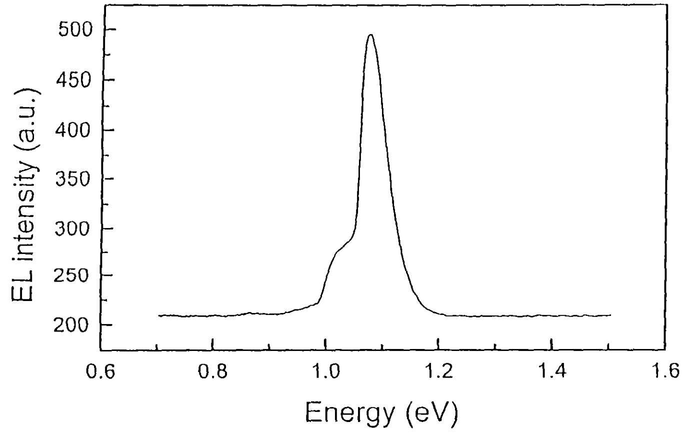

Fig.5 EL spectrum of photodiode structure with a forward bias

The aluminium contact to amorphous silicon operates usually as a holes injector. The Fermi level in the aluminium contact is situated below the defect level being in the middle of the forbidden gap of amorphous silicon. Due to high resistance of the amorphous film the potential drop is concentrated on the film itself. For the forward bias holes are injected from the contact due to thermostimulated tunneling and travel via amorphous layer until they arrive in the n-type crystalline silicon substrate and produce here luminescence caused by formation of free excitons in the crystalline material.

In the case of sufficiently high reverse bias electrons are injected by aluminium contact into the amorphous layer due to thermally activated tunneling. While moving in the amorphous layer the electrons excite erbium and defect-related luminescence. According to our dark-conductivity measurements the Fermi level in erbium-doped amorphous silicon at room temperature is slightly displaced upward from the middle of the gap, i.e. amorphous silicon doped by erbium is slightly n-type. In this case defects connected with the dangling bonds occur in D^0 or D^- states. Since we have not observed defect-related luminescence at forward bias, we can deduce that no radiative capture of holes occurs to D^0 or D^- centers. On the contrary, this emission band is observed when electrons are injected into amorphous silicon. Thus, our observations support traditional point of view that the broad emission band at 0.8-0.9 eV corresponds to processes of radiative capture of electrons from conduction band by neutral dangling bonds being described by a transition $e + D^0 \rightarrow D^-$.

. The reverse transition $D^- \rightarrow e + D^0$ which is necessary for continuous operation of LED is achieved due to thermal ionization enhanced by tunneling in high electric field (~ 10^5 V/cm) existing in the amorphous layer.

Recently room temperature PL in a-Si:H(Er) was observed also in the work [5]. PL [6] and EL [7] of Er^{3+} ions at room temperature were also studied in Er-doped SIPOS, material closely related to amorphous silicon.

CONCLUSIONS

In conclusion, we have studied photo- and electroluminescence of erbium ions in erbium-doped amorphous silicon films. A mechanism of electronic excitation of erbium ions based on defect-related Auger excitation process is proposed and supported by experimental studies. Erbium-doped amorphous silicon can be regarded as a promising material for fabrication of LEDs compatible with the silicon electronics.

ACKNOWLEDGEMENTS

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