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Wide Gap Hydrogenated Amorphous Silicon for Visible Light Emission

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Abstract. A series of samples of hydrogenated amorphous silicon (a-Si:H) was prepared from silane diluted highly with He by the microwave electron-cyclotron-resonance PE CVD. Such a wide gap ($E_g \geq 2.0$ eV) a-Si:H emits room temperature photoluminescence (PL) in the visible region. We attempt to reveal the microscopic origin of this PL by monitoring variations of PL intensity vs frequency of infrared vibrations in the vicinity of 2100 cm^{-1}. We find that oligosilanes -$(SiH_2)_n$- act as one type of possible luminescence centres. We report also on room temperature electroluminescence (EL) from p-i-n junctions. Surprisingly, and unlike p-i-n structures from standard a-Si:H, weak EL radiation with external quantum efficiency of the order of 10^{-5}% is emitted under reverse bias only. EL and PL emission spectra resemble strongly each other, except high energy wing of the EL spectrum. This high energy widening indicates the participation of hot electrons in the EL excitation mechanism.

Keywords: wide gap amorphous silicon, photoluminescence, electroluminescence

I. Introduction

Porous silicon has opened a surge of interest in the research of a novel type of Si-based optoelectronic light sources [1]. At present, however, certain difficulties in the straightforward progress from the basic research towards porous Si electroluminescence (EL) devices (short device lifetime and/or still not high enough brightness) has motivated a renewed interest in other forms of luminescent Si, like e.g. silicon suboxides [2], Si^{+}-implanted SiO_2 films [3], and also wide gap hydrogenated amorphous silicon (a-Si:H). Wide gap a-Si:H is in fact a binary alloy with hydrogen content higher than ∼10 at. % H. The increase in H content causes band gap widening, shifting thereby light emission in a-Si:H from the infrared (IR) to the visible region. Even though visible room temperature photoluminescence (PL) of wide gap a-Si:H has been known for a long time [4], only a recently reported discovery that wide gap a-Si:H can be prepared effectively from He-diluted silane (SiH_4) [5] allowed a more systematic investigation of this material [6, 7]. In this contribution we speculate about the origin of PL and we report on basic EL properties of p-i-n junctions prepared from wide gap a-Si:H.

II. Experimental Results

Thin films of wide gap a-Si:H were prepared from SiH_4 diluted with He by microwave electron-cyclotron-resonance plasma enhanced chemical vapor deposition (MW ECR PECVD). Typical microwave power was 200 W, typical ratio of silane to He flow rates was 1 : 35 and the substrate (Corning glass 7059) temperature varied in the range 95–200°C. The PL properties of the films were driven to a large extent by a negative floating potential of the substrate. For the EL study, samples in the form of p-i-n structures were prepared (*p* and *n* layers were deposited from B_2H_6/SiH_4/He and PH_3/SiH_4/He mixtures, respectively).

The hydrogen content was determined by thermal desorption spectroscopy and varied between 13 and 51 at. % H. IR absorption data were acquired with a FT-IR spectrometer. PL spectra were measured under excitation with the 488 nm line of an Ar-ion laser (∼30 mW cm^{-2}). EL was excited with a Keithley 237 power source. PL and EL were detected with a cooled S1- type photomultiplier. The emission spectra have been corrected for the spectral sensitivity of the detection channel. All measurements were performed at room temperature.

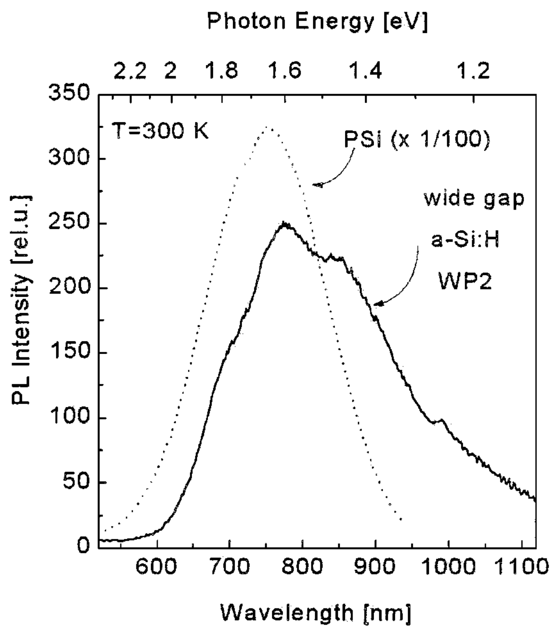

Figure 1. Comparison between PL spectra of wide gap a-Si:H (solid line) and a typical porous Si sample (dotted line).

Figure 1 shows PL spectra of wide gap a-Si:H #WP2 (solid line) and of a typical sample of strongly red luminescing nanoporous Si (dotted line). The comparison demonstrates that PL from our wide gap a-Si:H is about two orders of magnitude weaker than that of porous Si. For each sample, an IR absorption spectrum has been measured and the frequencies of the absorption peaks have been evaluated carefully. In Fig. 2 the PL intensity is plotted against the frequency of the IR vibration modes between 2000–2115 cm^{-1} for the whole set of the investigated samples. It can be seen that the samples with the IR peak located in the close neighbourhood of 2100 cm^{-1} exhibit the strongest PL.

Electrical and EL properties of wide gap a-Si:H were studied on the p-i-n junctions. The current-voltage curves exhibit a rather low rectification ratio (<10). This behavior differs markedly from usual good rectification properties of "device grade" p-i-n junctions fabricated from standard (low hydrogen content) a-Si:H. The second unexpected and unwelcome difference with respect to standard p-i-n devices is the absence of any EL emission under forward bias: Weak EL (with the external quantum efficiency of ∼10^{-5}%) is observed, after an intial formation, under reverse bias only. The EL emission spectrum of the p-i-n junction is displayed in Fig. 3 (solid curve) together with PL emission spectrum of the *i*-layer alone (dotted curve). The EL integral

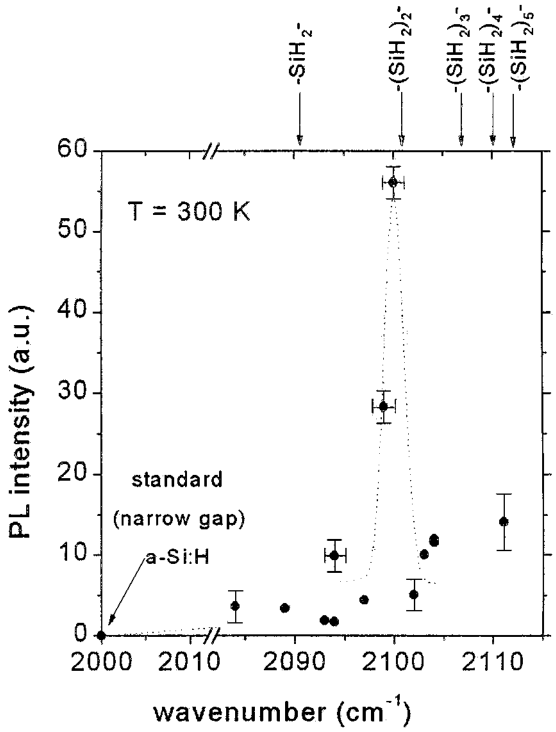

Figure 2. Integral PL intensity as a function of the frequency of the IR vibration mode in the vicinity of 2100 cm^{-1} for the set of investigated samples. The dotted line is a guide for the eye.

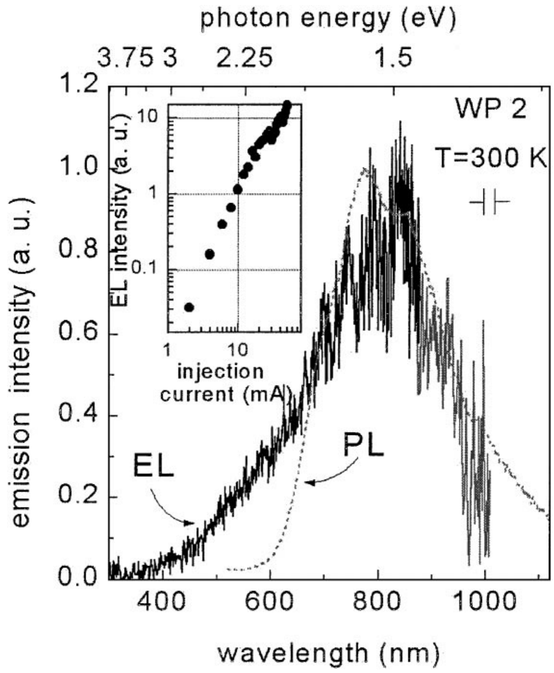

Figure 3. Comparison of the p-i-n EL emission spectrum (reverse bias 11 V, 40 mA—solid curve) with the PL emission spectrum of a relevant i-layer (dotted curve). Inset shows integral EL intensity as a function of the injection current.

intensity is plotted against the injection current in the inset of Fig. 3.

III. Discussion

Let us speculate about the conceivable microscopic origin of PL in wide gap a-Si:H. Figure 2 shows the PL intensity as a function of the frequency of the IR vibration modes in the range 2000–2115 cm^{-1}. The vibration frequencies 2090–2117 cm^{-1} have been ascribed to stretching vibration modes of oligosilanes -$(SiH_2)_n$- embedded in voids in the a-Si:H network. An increasing number n (=1, 2, ..., 12) of -SiH_2- units in the chain leads to a higher characteristic vibration frequency [8], as indicated at the top of Fig. 2 for $n = 1, 2, \ldots, 5$. The data in Fig. 2 therefore point to the important role of the oligosilanes in wide gap luminescent a-Si:H and, moreover, they suggest that -$(SiH_2)_2$- units probably form the most efficient luminescence centers. It is worth noting that the oligosilane “bridges” were also suggested to be responsible for red PL of porous Si [9].

On the other hand, the well established mechanism of radiative recombination in a-Si:H is tunneling of carriers in the localized (tail) states [10] and one should not rule it out a priori. Accordingly, two parallel radiative channels are likely present in wide gap a-Si:H: (i) recombination in tail states and (ii) the oligosilanes. Their relative weights may be different in different samples.

We should note that we have several additional experimental observations, though indirect, supporting the existence of two luminescence centres. Thermal desorption spectra of wide gap a-Si:H display, unlike standard a-Si:H, two distinct peaks (see Fig. 4). This means that hydrogen is incorporated in the samples in two basically different ways. Moreover, PL temperature dependence as well as the PL excitation spectrum exhibit features which cannot be simply explained by invoking only one way of radiative deexcitation [6].

In light of the above considerations, the general EL behaviour can be understood as follows: Under forward bias, the energy of injected electron-hole (e-h) pairs ($\approx$ energy gap $\approx$ 2.1 eV) is not high enough to excite the oligosilane units. Radiative recombination in tail states in this case is probably inefficient (distant-pair recombination). In the strong electric field of the i-layer under reverse bias, “hot” e-h pairs can have

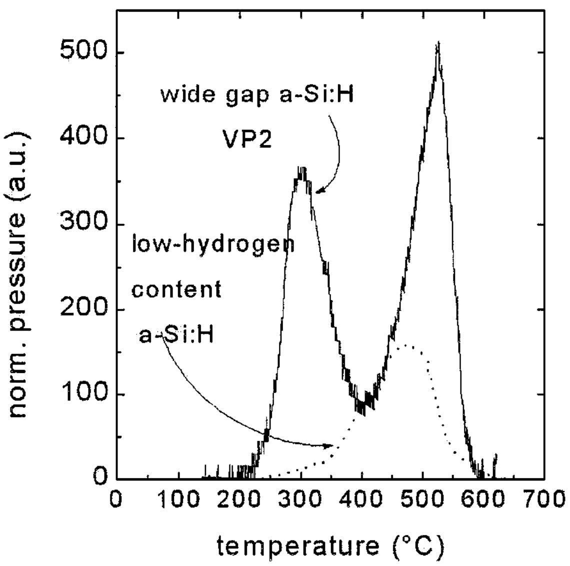

Figure 4. Comparison of a typical thermal desorption curve (normalized hydrogen pressure) of wide gap a-Si:H (solid line) with that of a-Si:H with low hydrogen content (dotted line).

sufficient energy and can transfer it into the embedded oligosilanes. Moreover, the "surplus" high energy part of the EL spectrum (with respect to the PL spectrum—see Fig. 3) suggests that under high reverse bias the hot electrons can achieve sufficient energy to realize also direct impact excitation of the oligosilane units.

IV. Conclusions

Wide gap a-Si:H prepared by MW ECR PECVD shows room temperature PL in the visible region. Further increase in PL intensity is probably achievable by means of proper variations of the technological parameters like the microwave power, substrate potential, substrate temperature etc. Further research is needed to better understand the PL and EL mechanisms and to answer the crucial question: Is a forward bias EL attainable?

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References

1. e.g. *Optoelectronic Properties of Semiconductors and Superlattices*, series editor M.O. Manasreh, *Vol. 5, Stuctural and Optical Properties of Porous Silicon Nanostructures*, edited by G. Amato, C. Delerue and H.-J. von Bardeleben (Gordon and Breach Science Publishers, Amsterdam, The Netherlands, 1997).
2. R. Janssen, U. Karrer, D. Dimova-Malinovska, and M. Stutzmann, 17th ICAMS, Budapest 1997, J. Non-Cryst. Solids **227–230**, 1151 (1998).
3. L. Rebohle, J. von Borany, R.A. Yankov, W. Skorupa, I.E. Tyschenko, H. Fröb, and K. Leo, Appl. Phys. Letters **71**, 2809 (1997).
4. D.J. Wolford, J.A. Reimer, and B.A. Scott, Appl. Phys. Letters **42**, 369 (1983).
5. K. Akiyama, A. Ogiwara, and H. Ogawa, Jpn. J. Appl. Phys. **33**, 5793 (1994).
6. I. Pelant, K. Luterová, P. Knápek, J. Kočka, J. Stuchlik, A. Poruba, S. Surendran, J. Valenta, J. Dian, and B. Hönerlage, Phys. Stat. Sol. **165**, 25 (1998).
7. J. Kudrna, I. Pelant, S. Surendan, J. Stuchlík, A. Poruba, and P. Malý, J. Non-Cryst. Solids **238**, 57 (1998).
8. S. Furukawa and N. Matsumoto, Phys. Rev. **B 31**, 2114 (1985).
9. Y. Takeda, S. Hyodo, N. Suzuki, T. Motohiro, T. Hioki, and S. Noda, J. Appl. Phys. **73**, 1924 (1993).
10. R.A. Street, in *Semiconductor and Semimetals*, Vol. 21, Part B, edited by J.I. Pankove (Academic Press, London/New York, 1984), p. 197.