HIGHLIGHT OF THE MONTH

Comment on:

Porous Silicon

by O.Bisi

University of Trento, Italy

1 Introduction

The rise of the communication high-way, the increased speed of computers, the diffusion of multimedia systems and the use of intelligent control systems are a few examples where a need for photonic applications has emerged. In this field the III-V and II-VI semiconductor compounds have been the materials to develop photonic applications up to now. Silicon has not been considered until the early nineties when Canham demonstrated that a Si based material was able to emit visible light at room temperature with quantum efficiencies approaching 10% [1, 2]. This material is porous Si (p-Si) which is obtained by electrochemical dissolution of Si. Following this discovery a large effort has been renewed to develop alternative Si based materials where visible light emission is predictable and observable. The driving idea is to realise a material where confinement, passivation and short-range crystallinity are all present. Indeed all these three items play a crucial role in p-Si.

2 How To Form Porous Silicon

Porous Si is obtained through electrochemical dissolution of Si in a solution of fluoridric acid and water or ethanol. This electrochemical process was initially developed for electro-polishing of Si wafers. When the current is low enough no electro-polishing occurs and a regime is entered where a random network of micropaths entering the Si is formed. This regime is that characteristic to form p-Si. As a result, a sponge-like layer is formed in the Si

wafer composed by porous and crystalline parts. The p-Si skeleton is composed by a hank of Si wires. Both n-type or p-type doped Si can be used. As holes are necessary to dissolve Si, one has to illuminate the wafer for etching n-type Si.

The thickness of the porous Si layer is usually around 1-10μm. The porosity, P, is measured through a gravimetric technique where the weight (m1) of the sample before the attack, the weight (m2) after the attack, and the weight (m3) after dissolution of the porous layer in KOH are recorded, then P=(m1-m2)/(m1-m3). The p-Si layers so formed have porosities dependent on the electrochemical parameters. The effect of the different parameters on the resulting layer is as follows [3]: increasing the current increases the porosity, increasing the etching time increases the p-Si layer thickness, increasing the HF concentration decreases the porosity, increasing the doping density of the sample decreases the porosity. Some formation mechanisms for p-Si have been proposed. These are reviewed in Refs. [4, 5, 6, 7, 8, 9].

It is worth-noticing that the porous Si samples freshly etched are different from the aged ones. In fact the p-Si samples are subjected to an aging process in which the chemical characteristics of the nano-crystal surface and of the surrounding matrix change. The nano-crystal surface is rich in hydrides for freshly etched samples while it is covered by an oxide matrix in aged samples. This is evidenced in the Auger lineshape of the LVV Si transition [10]. The Si lineshape changes from one characteristic of a covalent bonded Si atoms to one of an ionic bonded Si atom, i.e. H has been replaced by O. Theoretical calculations of the Si LVV lineshapes show that in the region of freshly etched samples investigated by the Auger probe the Si-H_2 bond is predominat [11]. The aging process induces a peculiar blue-shift of the visible luminescence band because the thin oxide layer formed on the surface of the Si nano-crystals reduces the size of the inner crystalline part. Sometimes an increase in the luminescence intensity is also measured in aged samples.

3 The Quantum Confinement Model

Room temperature visible photoluminescence is seen with the naked eyes in p-Si. The colour can be varied over the whole visible spectrum (from red, 1.8 eV, to green, 2.4 eV) by appropriate treatments which could involve oxidation steps. The spectral position of the luminescence band depends on the porosity, and shows a blue shift with increasing porosity. This observation together with TEM imaging [12] led Canham to propose the quantum model to explain the visible luminescence band of p-Si. In this model, p-Si is formed by a disordered array of undulating quantum wires (1-dimensional systems). Further refinements of the model consider the presence of interconnected quantum-dots (QD, 0-dimensional systems) where the excitons are confined.

According to the simple particle-in-a-box example [13], the electron-hole transition energy

is larger than the Si energy gap because it results from the sum of the Si energy gap, the electron and the hole confinement energies minus the exciton binding energy. In fact the excitonic recombination in p-Si occurs in the visible, while the Si energy gap is 1.1 eV. Since high porosity samples have more voids with respect to low porosity samples, one expects smaller Si nano-crystal sizes for the high porosity samples, i.e. a large quantum confinement, and, consequently, a blue shift in the luminescence. Indeed this is observed, which strongly supports the quantum confinement model. The 0.3 eV width of the visible band is explained by the distribution in the nano-crystal size, to which corresponds an energy distribution of the excitonic recombination energies.

Another direct evidence of the presence of nano-crystalline Si comes from Raman measurements [14]. A characteristic softening and broadening of the Si crystalline optical phonon mode is observed and associated with the confinement of the optical phonon in the nano-crystals. In addition, a contribution of an amorphous layer is present. The relative intensity of the two structures is sample and excitation wavelength dependent. By the TEM images and these data, a model of p-Si emerges where voids and nanocrystals interconnected by an amorphous matrix form the porous layer.

A further evidence of the validity of the model is provided by excitation spectroscopy [15]. In these experiments the luminescence is excited by changing the excitation energy. When the exciting energy is sufficiently low an emission band is measured with a stepped increase on the high energy side. The steps are attributed to phonon-assisted recombinations of the excitons. The energy separation of the steps is that typical of crystalline Si phonons. Hence the visible band is due to excitonic emission which are quantum confined (see the spectral position of the emission band) in crystalline Si (note the phonon energies). This result rules out other possible models for the emission either based on surface states or on chemical species.

From a theoretical point of view studies of H-terminated Si quantum wires based on both semiempirical [16, 17, 18, 19] and first principles local density calculations [20, 21, 22, 23] pointed out that Si atoms form a direct gap material, if arranged in a quantum wire geometry. The calculation of the ϵ_2 function has been used to investigate the origin of the luminescence transition. Buda et al. [22] found a low energy structure of the component of ϵ_2 along the direction parallel to the axis of the wire, characteristic of the quantum wire structure and strongly dependent on the size of the wire. This dependence can explain the blue shift of the luminescence band, found on varying the porosity of p-Si. Therefore these authors suggest that this structure is responsible for the luminescence transition. The origin of this luminescence band is still under debate: according to a cluster calculation it originates from quantum confinement effect [24], while other authors point out the importance of surface states [25], or the presence of a Si cristalline inside the wire [20, 26]. We have recently shown

that all the Si atoms of the wire are collectively involved in the luminescence transition [27].

4 The Siloxene model

Stutzmann and co-workers proposed Siloxene (a particular Si:O:H compound whose chemical formula is $Si_6O_3H_6$) as the luminescent agent in p-Si [28]. Very recently, Brandt and Stutzmann [29] complemented the Siloxene model by assuming that a unique unit cell exists in several Si based systems which exhibits luminescence. This unique cell is composed by a six Si atom ring and is proposed to act as the radiative centre in p-Si, a-Si:H, siloxene compounds, substoichiometric alloys of Si. The Siloxene model seems not suitable to interpret all the experimental data. Among them, the strong luminescence in p-Si samples grown in the absence of oxygen and the EXAFS analysis of freshly etched p-Si, showing a clear difference between the Si neighbors in Siloxene and in porous Si [30]. It may be that a Siloxene-like compound exists in the surface layer of the oxidized p-Si samples, even if its presence is not necessary in order to obtain luminescence from Si.

5 Perspectives

Many questions on p-Si are open and first-principles calculations and new ideas are necessary to investigate this field. For example a full description of the optical properties of a Si wire (ϵ_1, loss function, etc.) is still lacking. Furthermore the system studied up to now consists of an H-passivated quantum wire, ideal quantum wire with crystalline lattice and the simplest passivating agent, hydrogen. More realistic models should include the effect of disorder, both in the surface of the wire, by considering the formation of a disordered layer of unknown composition, and in the topology of the structure. It is important to understand why the replacement of hydrogen by oxygen does conserve luminescence. At present this point is not fully understood and calculations for O-passivated quantum wires are lacking. In addition all the first-principles calculations on Si quantum wires do not include exchange-correlation effects beyond LDA. To my knowledge the only evaluation consists of an average between bulk and molecular self-energies [23].

A second point regards other forms of luminescent silicon. It is now generally accepted idea that p-Si opened the way to a new class of nanostructures based on Si [31]. The driving idea is to obtain a material where confinement, passivation and short-range crystallinity are all present. It is not clear what system will be the best for photonic applications.

At last, a few words on electroluminescence, i.e. the emission of light after excitation with carrier injection. Light emitting diodes (LED) have been fabricated which operate at room

temperature though with a very low efficiency [10]. Many problems have to be solved in order to obtain efficient LED based on p-Si. The interested reader is referred to the paper of Lang et al. [32]. Maybe p-Si will not result as the right material but it has had the great merit to indicate the essential ingredients for obtaining a good light emitter based on Si.

References

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] L.T. Canham, in *Optical Properties of Low Dimensional Silicon Structures*, edited by D. Bensahel, L.T. Canham, and S. Ossicini, Kluwer, Dordrecht (1993), p. 81.

[3] M. I. J. Beale, J. D. Benjamin, M. J. Uren, N. G. Chew, and A. G. Cullis, J. Crystal Growth **73**, 622 (1985).

[4] H. Foll, Appl. Phys. A **53**, 8 (1991).

[5] R. L. Smith and S. D. Collins, J. Appl. Phys. **71**, R1 (1992).

[6] *Porous Silicon*, edited by Zhe Chuan Feng and R. Tsu (World Scientific Publishing Co., New York 1995)

[7] *Porous Silicon Science and Technology*, edited by J.-C. Vial and J. Derrien (Les Editions de Physique, Paris 1995).

[8] special issue Thin Solid Films vol. 255 (1995).

[9] *Microcrystalline and nanocrystalline semiconductors*, edited by L. Brus, R. W. Collins, M. Hirose and F. Koch, MRS Symposia Proceedings No. 358 (Materials Research Society, Pittsburgh, 1995).

[10] L. Pavesi, M. Ceschini, G. Mariotto, E. Zanghellini, O. Bisi, M. Anderle, L. Calliari, M. Fedrizzi, L. Fedrizzi, J. Appl. Phys. **75**, 1118 (1994).

[11] L. Dorigoni, L. Pavesi, O. Bisi, L. Calliari, M. Anderle, S.Ossicini and F.Bernardini, submitted to the EMRS spring meeting (Strasbourg, May 22-26, 1995), and to be published.

[12] A. G. Cullis and L. T. Canham, Nature **353**, 335 (1991).

[13] S. S. Iyer and Y.-H.Xie, Science **260**, 40 (1993).

[14] J. M. Perez, J. Villabo, P. McNeill, J. Prasad, R. Cheek, J. Kelber, J. P. Estrera, P. D. Stevens, and R. Glosser, Appl. Phys. Lett. **61**, 563 (1992).

[15] P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumhead, J. Phys: Condens. Matter **5**, L91 (1993).

[16] G. D. Sanders and Y. -C. Chang, Phys. Rev.B **45**, 9202 (1992).

[17] C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **48**, 11024 (1993).

[18] C-Y. Yeh,S. B. Zhang and A. Zunger, Appl. Phys. Lett. **63**, 3455 (1993).

[19] H. M. Polatoglou, Journ. of Lumin. **57**, 117 (1993).

[20] A. J. Read, R. J. Needs, K. J. Nash, L. T. Canham, P. D. J. Calcott, and A. Qteish, Phys. Rev. Lett. **69**, 1232 (1992).

[21] T. Ohno, K. Shiraishi, and T. Ogawa, Phys. Rev. Lett. **69**, 2400 (1992).

[22] F. Buda, J. Kohanoff, and M. Parrinello, Phys. Rev. Lett. **69**, 1272 (1992).

[23] M. S. Hybertsen, and M. Needels, Phys. Rev. B **48**, 4608 (1993).

[24] Fu Huaxiang, Ye Ling and Xie Xide, Phys. Rev. B **48**, 10978 (1993).

[25] F. Koch and V. Petrova-Koch, in Ref.[6], pag. 133.

[26] Y. H. Xie, M. S. Hybertsen, W. L. Wilson, S. A. Ipri, G. E. Carver, W. L. Brown, E. Dons, B. E. Weir, A. R. Kortan, G. P. Watson, and A. J. Liddle, Phys. Rev. B **49**, 5386 (1994).

[27] L. Dorigoni, O. Bisi, F.Bernardini and S.Ossicini, submitted to the EMRS spring meeting (Strasbourg, May 22-26, 1995), and to be published.

[28] M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber and M. Cardona, Solid State Commun. **81**, 307 (1992).

[29] M. S. Brandt and M. Stutzmann, Solid State Commun. **93**, 473 (1995).

[30] S. L. Friedman, M. A. Marcus, D. L. Adler, Y. -H. Xie, T. D. Harris, and P. H. Citrin, Appl. Phys. Lett. **62**, 1934 (1993).

[31] O. Dag, A. Keperman and G. A. Ozin, Advanced Materials **7**, 72 (1995).

[32] W. Lang, P. Steiner and F. Kozlowski, Journal of Luminescence **57**, 341 (1993).