

DISORDERED SEMICONDUCTORS: THE MOTT-ANDERSON LOCALISATION

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The domain of disordered (amorphous) materials has been pioneered by Stan Ovshinsky for many decades. In this article, we intend to show that these amorphous materials have not only been very successful in the fabrication of industrial products, but have also opened a new field of physics. As an example, we show how, for two almost identical systems - small particles of *crystalline* and *amorphous* silicon - the electronic wavefunction is profoundly affected by disorder.

(Received July 8, 2002; accepted July 22, 2002)

Keywords: Porous silicon, Amorphous silicon, Quantum confinement, Photoluminescence

1. Introduction

A celebration of the 80th anniversary of Stan Ovshinsky is also a celebration of more than half a century of research in the field of disordered materials. Indeed, for many decades, S. Ovshinsky has been defending with fervour that non-crystalline solids, far from being freakish materials, are interesting physical systems *per se*, introducing new concepts in physics and, what is more, with a great potential of industrial applications.

One of the most spectacular physical effect of disorder is the *localisation* of the quantum wavefunction of carriers in these materials. The object of this essay is to describe (or rather to discuss, since the experiment has been reported before [1] in an other context) an experiment *directly* showing this localisation of the electronic wavefunction in a disordered semiconductor.

2. Hydrogenated amorphous silicon: a "good" semiconductor

Quantum mechanics of *covalent* semiconductors should be, in first approximation, rather insensitive to a precise ordering of the lattice. In this type of material, it is indeed a good approximation to consider interactions mostly with first neighbours (the so called "tight-bonding approximation") and to neglect the effect of more distant atoms.

That is what has been done a long time ago by Weaire and Thorpe [2] in hydrogenated amorphous silicon, a-Si:H, where the effect of hydrogen was considered to "passivate" the large number of Si-Si broken bonds due to the disorder. The result is that the material should be a good semiconductor, with a conduction and a valence band separated by a proper gap with a very low density of states, even if the edges of the gap are slightly fuzzy compared to the sharp edges of the gap of a crystalline semiconductor. It is then possible to design devices (diodes, transistors, etc.) similar to that obtained with crystalline semiconductors.

And indeed, very successful industrial products have been fabricated with hydrogenated amorphous silicon, in particular inexpensive photovoltaic panels of large surface, and matrices of millions of transistors for the driving of the pixels of large displays.

3. The Mott-Anderson localisation

The tight bonding approximation, successful as it is for the description of many physical properties of disordered covalent semiconductors, hides an important difference between crystalline and non-crystalline solids. In a perfect crystal, a very important property is the *invariance by translation* of the lattice. The result of this strong symmetry is the existence of the famous Bloch's theorem [3]: the wavefunctions of the carriers are quite similar to that obtained in free space, they can be described in terms of pseudo-plane waves. The "pseudo" means here that the plane waves are modulated by a function having the lattice periodicity. The existence of Bloch's theorem greatly simplifies the problem and allows in general the complete resolution of the quantum equations of the system.

In an amorphous semiconductor the invariance by translation is not satisfied and Bloch's theorem is no longer valid. Although that does not change much the physical properties depending upon short range parameters (pn junction for example), it has a profound effect on the long range wavefunctions of the carriers. And indeed, P. Anderson [4] and N. Mott [5] have shown that in the presence of structural disorder the electrons in solids are not wavefunctions of the Bloch type anymore, but instead are spatially localised as wave packets of limited extend [6]. This Mott-Anderson localisation has indeed drastic consequences on the dc mobility of carriers in this type of material, like the well known existence of a "mobility gap" distinct from the optical gap. There are many consequences of the localisation due to the disorder that are verified by experiment and there is no doubt about the validity of this concept of localisation by disorder. However, these experimental illustrations of the effect are somewhat indirect. In the present article, we present a rather simple experiment which illustrates very directly and in a crucial manner the localisation induced by structural disorder in a semiconductor.

4. Luminescence in porous silicon

The observation of radiative luminescence is a simple and straightforward method to determine the quantum levels of carriers in a semiconductor. However, in practice with actual materials, the radiative recombination (transition from an excited level to the ground state with emission of a photon) is short-circuited by *non-radiative* recombination due to different defects: recombination centres in the gap and surface defects. For example, in "good" bulk silicon, the radiative recombination is some 10^{-3} weaker than non-radiative transitions, and photoluminescence at room temperature is very weak.

The discovery of "porous silicon" [7] provides an ingenious method to prepare silicon practically free of non-radiative centres, giving an almost ideal radiative photoluminescence. It is beyond the scope of this article to describe in detail the physics and chemistry of porous silicon. In an extremely simplified manner, sufficient for our purpose, let us say that it is a method - electro-chemical etching of silicon in hydrofluoric acid (HF) - that produces silicon in the form of small particles, from about 50 nm down to 2 nm. The photoluminescence of this type of silicon is very high for two reasons:

1°) The "Small is beautiful" effect. If the silicon particles are sufficiently small, a large number of them will not contain non-radiative recombination centres and thus will show pure radiative recombination. With the over-simplified picture of spherical shapes of radius a , the probability for a sphere to have no non-radiative recombination centre is given by $P = \exp(-4\pi a^3 N/3)$ where N is the concentration of non-radiative centres. For $N = 10^{17}/\text{cm}^3$ (a rather bad material) and $a = 6 \text{ nm}$ we obtain $P = 91\%$: more than 9 out of 10 of the spheres will not contain any mid-gap non-radiative recombination centre.

2°) But porous silicon, a highly divided material, has a very high internal surface that might induce a large number of surface states. Fortunately, it has been shown that HF-rinsed silicon surfaces have the smallest level of surface recombination [8], probably due to a very efficient surface passivation by the nascent hydrogen produced during the anodisation of the silicon surface. To avoid contamination by the atmosphere which in general induces unwanted surface states, it is imperative to leave the sample of porous silicon in the electrolyte containing a high concentration of HF, which is the case for the experiment described in this article.

In summary, porous silicon in HF provides an almost ideal system to study the quantum states of carriers in a semiconductor.

5. Quantum shift of luminescence due to confinement

It is a very elementary result of quantum mechanics that the spacing of the energy levels of electrons in a small particle increases when the size of the particle decreases: the so-called "quantum confinement" [9]. In a very simplified picture, let us visualise our porous silicon particles as forming 3 dimensional "wells" of size D with infinite walls at the surface of the particles.

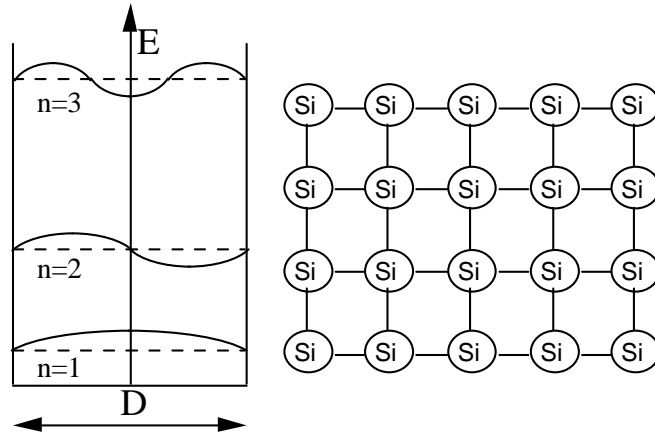


Fig. 1. Electronic wavefunctions in crystalline porous silicon in a very simplified picture of 3D potential wells of size D with infinite walls. The wavefunctions are Bloch's plane waves that are annulled at the walls. The energies increase like the inverse size as $1/D^2$ (quantum confinement).

In a crystal the electronic wavefunctions are plane waves (Bloch's theorem) which should vanish at the surface of the material (Fig. 1). The energy levels are then given by

$$E = \frac{h^2}{8m} (n_x^2 + n_y^2 + n_z^2) \frac{1}{D^2} \quad (1)$$

with $n_x, n_y, n_z = 1, 2, 3, \dots$

So the photoluminescence energy in this system (transition from the first excited state to ground state) should vary like the square of the inverse size of the structure, $1/D^2$.

This is indeed what is observed as shown in Fig. 2. Photoluminescence of crystalline porous silicon in an HF-based etching liquid is measured every 50 seconds. The particles of porous silicon are slowly etched down and their size decreases from about 60 nm down to 5 nm in 10 minutes. As shown in Fig. 2, a huge blue shift of the luminescence is observed from 800 nm to 550 nm (1.55 eV to 2.25 eV). This is a very direct illustration of the quantum confinement effect discussed above. After 10 minutes the porous material is etched out and the signal disappears.

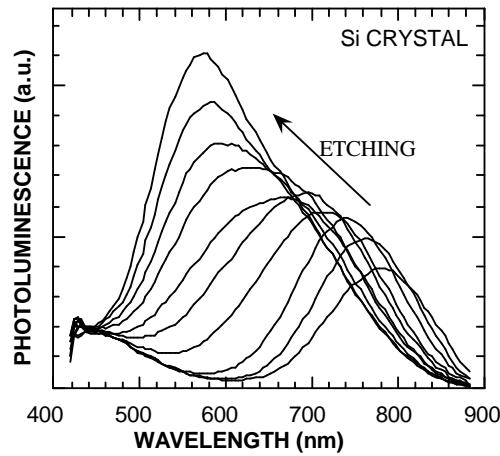


Fig. 2. Evolution of the photoluminescence spectra of crystalline porous silicon in ethanoic HF solution. There is a slow photo-etching of the microstructure and, as the particles become thinner, a large blue shift, due to the quantum confinement, is observed. The spectra are taken

every 50 s.

6. Localisation in amorphous silicon

Porous silicon can also be made from hydrogenated amorphous silicon films [10]. The preparation is somewhat different mostly because of its high resistivity compared to that of the crystal [9], but the produced porous material is almost identical. It is composed of small particles, many of them having zero non-radiative recombination centres (the "small is beautiful" effect) and, as long as it remains in an HF solution, it has no recombining surface states. So, as with crystalline porous silicon, amorphous porous silicon gives a strong photoluminescence signal.

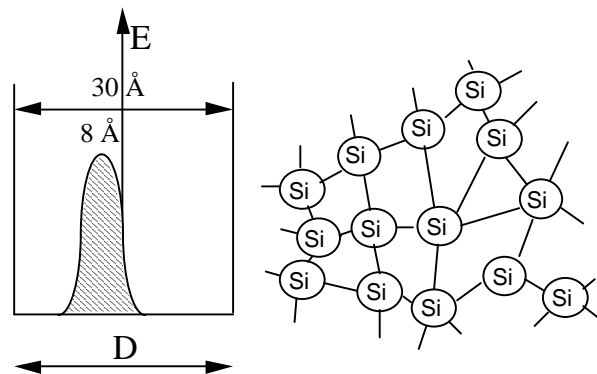


Fig. 3. In amorphous porous silicon, the electronic wavefunction is localised because of the disorder. If the wave packet is smaller than the size D of the particle (as shown in the figure),

the energy levels are independent upon the size D of the micro-structure.

There is however a difference between the two materials. Amorphous silicon is a disordered material and, as discussed above, the electronic wavefunctions are not plane waves as in a crystal, but are localised in wave packets as shown in Fig. 3. These wave packets in a-Si:H vary in size from about 0.6 to 1 nm, much smaller than the minimum size (5 nm) of the porous silicon particles. Then the wavefunction does not "see" the edges of the potential well (Fig. 3) and the quantum confinement effect described in Section 5 should not exist. This is indeed the case as shown in Fig. 4. The etching down of

amorphous porous silicon reduces the photoluminescence intensity but *does not induce any shift* of the line. And it should be so as long as the size of the localisation due to disorder remains smaller than the size of the particles, which is the case in the present experiment.

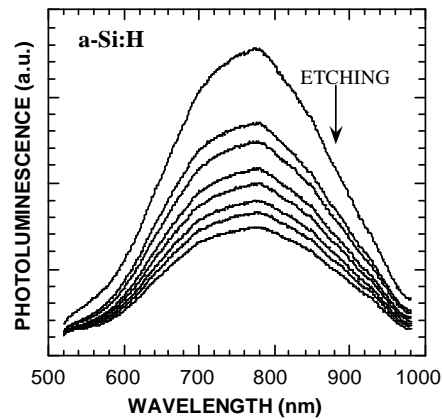


Fig. 4. Same experiment as in Fig. 2, but in amorphous porous silicon. Because of the localisation of the electronic wavefunction due to disorder, no shift is observed. The spectra have been taken every 10 s.

7. Conclusion

Within the picture of the tight-bonding approximation, crystalline and amorphous silicon are very similar materials. A small size (very small size!) observer, sitting on a silicon atom would see the same landscape in both materials ...provided this observer is slightly short-sighted. It is remarkable that a slight long range distortion in the amorphous material should be enough to induce very different physical properties. The wavefunction localisation due to disorder, as illustrated by the experiment described in this article, is one example to demonstrate that an amorphous material is not simply a crystal with some fuzzy features. It is really a new material, with its own new properties, depending upon new physical concepts.

And last but not least, there is also the repeated demonstration by Stan Ovshinsky, over many years, of the many benefits provided to industrial applications by these amorphous materials.

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