

# Quantum effects in amorphous superstructures

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## QUANTUM EFFECTS IN AMORPHOUS SUPERSTRUCTURES

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**Abstract:** A brief survey of quantum effects in amorphous superstructures is presented, with a particular attention to optical properties. The determination of interface properties by superstructure investigation is discussed, with a special emphasis on the amorphous silicon/amorphous silicon-carbon system.

### 1. Introduction

Amorphous superstructures are artificial materials prepared alternating thin layers of two amorphous semiconductors different either in doping [1] or in composition [2]. In the following we will deal only with compositional superstructures which exhibit a variety of novel properties, some of them resulting from quantum confinement effects, similarly to what happens in their crystalline analogues. With respect to crystalline superlattices amorphous superstructures exhibit two important differences: 1) quantum effects are observed only for layer thicknesses below 50 Å and in semiconductors with low defect density, typically hydrogenated amorphous silicon (a-Si:H) or hydrogenated amorphous germanium (a-Ge:H). 2) since large fluctuations of bond angles ( $\simeq 8\%$ ) and bond lengths ( $\simeq 2\%$ ) are present in amorphous materials the problems of "lattice mismatch" at the interface are less critical than for the crystalline case. Since hundreds of interfaces are present in the same sample the preparation of these superstructures offers also the possibility of investigating interface properties using techniques appropriate for bulk analysis. The most studied systems are those of a-Si:H with a-Ge:H, or with silicon based alloys (a-Si<sub>x</sub>C<sub>1-x</sub>:H, a-Si<sub>x</sub>N<sub>1-x</sub>:H). In the following we will briefly discuss the preparation of these materials, the evidence of quantum size effects and the interface characterization, with particular attention to the a-Si:H/a-Si<sub>x</sub>C<sub>1-x</sub>:H system that we have investigated more extensively.

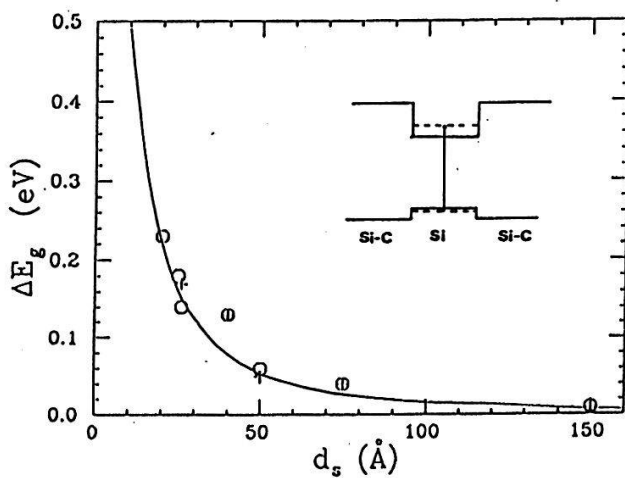
### 2. Sample preparation

The most widely used method for preparing amorphous silicon and its alloys is the plasma enhanced chemical vapor deposition, consisting in exciting a plasma

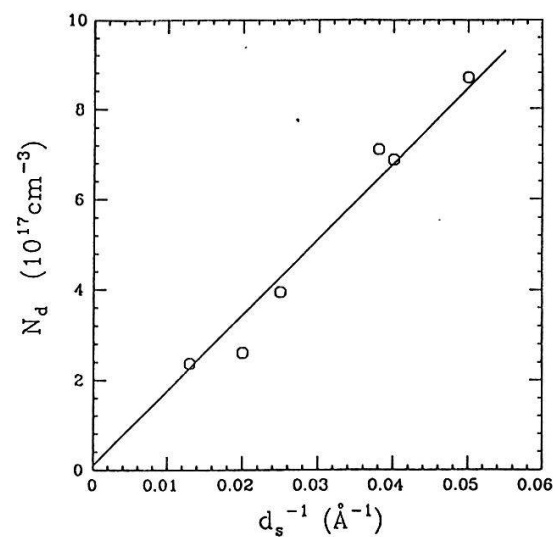
in a gas mixture appropriate for the desired material, e.g. in silane ( $\text{SiH}_4$ ) or in silane plus methane to prepare respectively a-Si:H and a-Si<sub>x</sub>C<sub>1-x</sub>:H alloys. In order to obtain the heterojunction the two different gas mixtures are rapidly interchanged in the reactor without interrupting the discharge. If the residence time of the gas is shorter than the time necessary to grow a monolayer the resulting interfaces are expected to be atomically abrupt. Structural characterizations performed by transmission electron microscopy [3] and X-ray scattering [4] have shown that this is indeed the case.

## QUANTUM EFFECTS

There are various evidences of quantum confinement effects in amorphous silicon based superstructures coming both from optical and transport measurements. As an example let us consider the behavior of the absorption coefficient  $\alpha$  for a series of superstructures of a-Si:H/a-Si<sub>x</sub>C<sub>1-x</sub>:H having a fixed thickness (120 Å) of a-Si<sub>x</sub>C<sub>1-x</sub>:H ( $E_g=2.8$  eV) and a variable thickness of the silicon layer ( $E_g=1.8$  eV). When the silicon layer thickness is decreased below 50 Å the absorption coefficient shifts to higher energies by a quantity  $\Delta E_g$  as indicated in Fig. 1.



**Fig. 1:** Gap shift  $\Delta E_g$  as a function of silicon layer thickness  $d_s$ . Absorption (o) and electroabsorption (+) measurements, theory (---).



**Fig. 2** Density of gap states  $N_d$  as a function of the inverse of the silicon layer thickness  $d_s^{-1}$ .

This shift can be explained assuming that the minimum transitions energy is now the one separating quantum states in the wells as sketched in the inset of Fig. 1. The energy position of the levels in the well can be computed using basic quantum

mechanics and depends on bands line-up (which determines the well depth) and on the effective mass of electrons in the valence and conduction bands. Using for bands alignment the results of photoemission measurements [5] the best fit to the data of Fig.1 is obtained with  $m_c=0.3 m_e$  and  $m_v=0.6 m_e$ . Similar data have been obtained on different systems like a-Si:H/a-Si<sub>x</sub>N<sub>1-x</sub>:H [6] and a-Si:H/a-Ge:H [7]. In the case of a-Si:H/a-Si<sub>x</sub>N<sub>1-x</sub>:H the same value of  $m_c=0.3 m_e$  is obtained from the fit. It has been pointed out that  $0.3 m_e$  is exactly the average over the different directions of the effective mass of electrons in c-Si [8] but the coincidence could only be accidental.

Very recently striking evidence of the presence of quantum levels in a-Si:H/a-Si<sub>x</sub>C<sub>1-x</sub>:H superstructures have been obtained from accurate measurements of photothermomodulation spectroscopy [8]. This technique gives directly the derivative of the absorption coefficient hence the sensitivity is considerably increased. Structures corresponding to transitions between sublevels are clearly observed in the spectra. Their position well agrees with the energy determined with the simple model described above using practically the same parameters.

Further evidences for the existence of quantum levels are obtained from transport measurements perpendicular to the layers. The I-V characteristics exhibit tiny structures [9,10,11] due to carrier tunneling as happens in crystalline superlattices. The position of the structures can again be explained in terms of a simple quantum model but a larger value of effective mass for the electron must be used in this case [10].

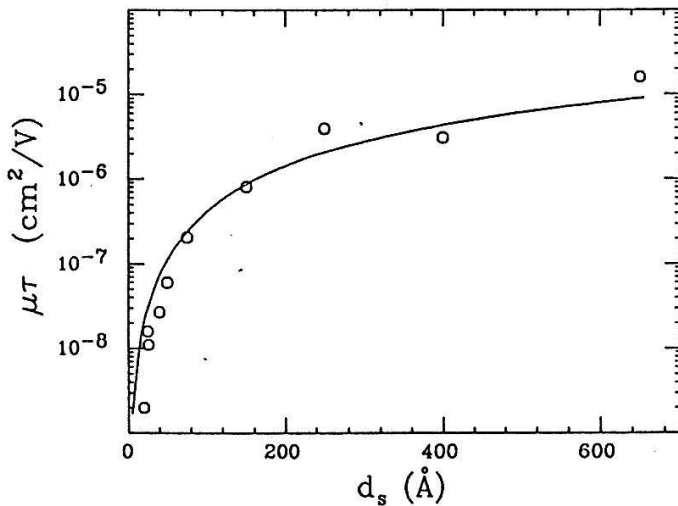
### 3. Interface characterization

Interface properties have been studied on superstructures by many groups and with different techniques like Infra-Red [12] or Raman [13] spectroscopy, absorption and electroabsorption [14]. In the following, as an example, we will discuss what information about interfaces can be obtained from measurements of photoconductivity and of absorption coefficient in the gap energy region. In amorphous materials the absorption coefficient  $\alpha$  in the pseudo-gap exhibits an exponential region, the so called Urbach tail, which extends a few tenths of eV below the onset of the band to band transitions and, at lower energies, a region where  $\alpha$  is a slow varying function which results from transitions between localized defect states and extended band states. Our measurements show that these general features are conserved in the multilayer structures but both the characteristic energy  $E_0$  of the exponential region and the absorption due to defect states increase with decreasing silicon layer thickness. The number  $N_d$  of defect states can be determined from the value of

$\alpha$  in the low energy region [15] and is reported as a function of the inverse silicon thickness  $d_s$  in Fig. 2. Since the total thickness of silicon was kept constant in all samples  $d_s^{-1}$  is proportional to the number  $n$  of a-Si:H/a-Si<sub>x</sub>C<sub>1-x</sub>:H interfaces. Therefore the linear increase of  $N_d$  with  $n$  points to the presence of a large density of localized states close to the interface. The spatial distribution of these defect states can be reasonably assumed to be an exponentially decreasing function with the maximum value  $N_d^0$  right at the interface and with a small decay length  $l$ . With this assumption and if  $d_s \gg l$ , the absorption coefficient is given by

$$\alpha \propto N_d^0 l \cdot \frac{1}{d_s} = N_s/d_s$$

where  $N_d^0 \cdot l$  can be defined as the number of defects at the interface  $N_s$ . The linear behavior of Fig. 2 confirms the hypothesis that  $l \ll d$  even for the smallest value of  $d_s$  (20 Å). From the slope of the linear behavior we deduce a value of  $2 \times 10^{11} \text{ cm}^{-2}$  for  $N_s$ .



**Fig. 3:** Behavior of the mobility-lifetime product as a function of the silicon layer thickness. Experiment (o), theory (—).

Turning now to the photoconductivity measurements we will show how they can give informations about the electrical behavior of defect states at the interface. From the value of photoconductivity parallel to the layers it is possible to derive the mobility lifetime product ( $\mu\tau$ ) for the majority carriers (i.e. electrons) in the silicon layer. This quantity decreases drastically with decreasing the a-Si:H layer thickness as reported in Fig 3. We ascribe this behavior to the large density of defect states at the interfaces. Their effect has been taken into account by introducing a surface recombination velocity  $v_s$  proportional to  $N_s$  itself and by solving the diffusion equation perpendicularly to the layers in order to determine the thickness dependent distribution of excited carriers [16]. From this distribution it is easy to compute the  $\mu\tau$  product and compare it with the experimental results. The best fit reported in Fig. 3 is obtained with  $v_s = 5 \times 10^6 \text{ cm/s}$ .

#### 4. Conclusions

We have briefly summarized the evidence of quantum confinement effects in amorphous superstructures. We have also shown that the study of heterostructures can be an effective way in determining the properties of the interfaces, which influences the performances of devices based on a-Si:H and possibly also the magnitude of quantum effects [17].

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