PHOTOLUMINESCENCE AS A SURFACE-EFFECT IN NANOSTRUCTURES

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Abstract — Nanocrystalline Si powder prepared by Laser Induced CVD (LCVD) showed photoluminescence (PL) at wavelengths of 400-900 nm when excited at 488 nm and 330 nm. The powder consists of spherical grains with an average diameter of 25 nm and log-normal size distribution. In this study we present a model which explains the origin of the photoluminescence: the latter is generated by electrons which jump from the regular bulk-states into the surface-states of the nanocrystals, which in turn are not populated after being excited by the illuminating photons. We present the effect of the surface potential on the surface states and, thus, on the possible transitions. The model is tested against experimental results which cannot be explained by the quantum size confinement effect such as photoluminescence from particles bigger than 10 nm and shift in the PL emission wavelength due to oxygen and nitrogen bonds at the surface of the particles.

The tools presented here can be applied also to porous silicon.

1. INTRODUCTION

Visible photoluminescence (PL) with a few percent quantum efficiency was observed in porous silicon at room temperature and was first reported in 1990 (1); the porous Si layer contains Si crystallites with a typical size of 2-5 nm (2). Photoluminescence, similar to that of porous Si (PS), has also been observed in clusters of nanosized grains (3-5). The great interest in this phenomena originates from its potential application in light emitting devices based on well-known silicon technology. Application of PL to Si-based devices requires an understanding of its mechanism and its dependence on microstructure and composition. Two main models have been proposed to explain PL in porous Si: (i) physical quantum size confinement effect, and (ii) chemical quantum size confinement effect; however, there are various experimental results which cannot be accounted for by either.

The most frequently quoted mechanism is the physical quantum confinement of electrons in nanometer size crystallites (2,6,7), in spite of the fact that no direct evidence for discrete quantum confinement levels has been demonstrated to date. According to this model, quantum confinement in fine silicon structures can lead to symmetry-allowed optical transitions across the gap with an energy in the visible range. In other words, the nanocrystals have a direct gap which
widens with decreasing grain-size to a value where visible luminescence can be observed. The physical quantum size confinement theory is based on the assumptions that: (i) the nanocrystals have small dimension in all three directions which are considered as quantum dots, (ii) the nano-size particles are spherical with no relaxation of the bulk lattice, and (iii) all dangling bonds at the surface of the particles are saturated; otherwise the gap would be completely masked by the dangling-bond states, namely no surface-states are present.

The density of dangling bonds can be reduced by the presence of SiH$_2$ or SiH$_3$ groups at the surface of the Si crystallites and, consequently, higher photoluminescence efficiency [8] was observed. Calculations of the band gap show an almost linear behavior of the band gap as a function of the inverse crystallite diameter. The physical quantum size confinement model cannot explain many experimental results such as observation of PL in porous Si under hydrostatic pressure, high enough to reach the phase transformation of silicon towards different metallic phases (9-10). This result demonstrates that PL is still observed in the high pressure metallic phases, therefore PL is not related to the diamond phase of the silicon, which in turn rules out the quantum size effect as a plausible explanation. Another example along this line is the observation of PL in Si powder having crystallites with an average size larger than 20 nm (11), which is larger than the theoretical size limit allowed according to the quantum size confinement theory. A third result, which is not supported by the quantum size confinement theory, is given by an experiment in which silicon surfaces were prepared by reactive plasma etching and plasma enhanced chemical vapor deposition, and they showed intense photoluminescence emission in the blue green range with decay times smaller than 5 ns (12).

As previously indicated, the second model used to explain the mechanism of PL in porous Si is based on the chemical (quantum size) confinement to sub-nanometer size silicon due to isolation effect of oxygen atoms. The main assumption of this model is that the shift of the gap is not a size-effect but rather a chemical substitution of the Si bonds at the surface. Some experimental data supports this model since the electronic properties of the crystalline Si surface can be systematically changed during the initial oxidation after HF treatment (13). These oxidizing agents are also used in the preparation of porous Si and they do affect the PL spectra (14). Another study which supports the chemical confinement model shows that post-anodic treatments of porous Si shift the PL spectra to short wavelengths (10-17). However, none of these treatments result in a large scale blue shift.

As indicated above, there are experimental results which cannot be explained in terms of either the physical or chemical quantum size confinement effect. As an example, let us quote the results reported in Ref. 18. In their experiment, intense violet and blue emission at wavelengths of 415, 437, and 465 nm at room temperature was observed from nanocrystalline silicon thin films prepared by crystallization of amorphous Si films which do not contain oxygen or nitrogen. The PL was observed only from nanocrystalline Si film and not from the amorphous Si film, and, therefore, it is associated with the crystal structure. After anodization, the samples showed a broader visible spectra from the violet to the red region. The conclusion from this result is that the presence of oxygen or nitrogen at the surface of the Si crystallites is not responsible for PL in the blue wavelength, but rather affects the PL at higher wavelengths.

The two models discussed above regard the bulk states as the main contributors to the PL, and the surface has only an impeding effect on the emitted photons (due to recombination). According to these models, the surface has no direct contribution to PL. This implies that the effect of the whole fraction of atoms which are at the surface of the nano-crystals is being ignored, and
these can be as high as 50% of the total number of atoms in the nanosize structure. Furthermore, when ignoring the contribution of the surface atoms, these models neglect the crystallography of the surface. It is well known that at the macroscopic level, the crystallography of the surface has a dominant effect on the electro-optical properties. When scaling down to nanosize structure, the crystallography of the surface is expected to have even a greater effect. Experimental data demonstrates that the surface structure of porous Si (25) has a high specific crystallographic orientation, depending on the pore structure. A strong preferential formation of (111) surfaces estimated to 50% of the total surface was observed in porous Si after vacuum annealing (20). In addition, preferential crystallographic orientations of crystallites with specific facets were observed in Si nanocrystallites (21-23).

In this study we present a model in which the potential experienced by an electron at the surface can be significantly different than that in the lattice. Consequently, energy states much lower than the usual bulk-states may develop. These energy states are associated with the surface. When a high energy photon removes an electron from such a surface-state, electrons from the bulk state may jump to this lower state, emitting in the process a lower energy photon. At the macroscopic level, this process renders itself to the photoluminescence effect as observed experimentally. Momentum conservation in transitions which involve these surface-states does not impose a stringent constraint. In contrast to bulk-states where the k number is well defined, in the surface states the wave function is localized; therefore, a broad "spectrum" of k's are associated with it. Although we use a 1D model, it possesses the main features of the experimental data available to date.

In principle, if we compare two samples of silicon, one with a large surface and the other with nanosize surfaces but both having the same crystallography, we may expect PL in both samples. However, for a given number of atoms, the nanosize crystallite has a much higher surface-to-volume atoms ratio and, therefore, the PL's intensity is expected to be correspondingly higher. Furthermore, the actual potential on the surface may be substantially different and so is the energy state. In addition, oxygen or hydrogen bonds on the surface may affect the surface states and therefore the spectrum of the emitted photons.

This study is organized as follows: in the next section we shortly review some experimental results. This is followed by a description of the 1D model. In the fourth section we calculate the eigen states of the system under consideration and from their structure we show the potential of the model to explain the photoluminescence phenomenon. An evaluation of the number of states which can contribute to PL is done in the fifth section.

II. EXPERIMENTAL RESULTS

We have prepared Si powder by a laser induced CVD system (23). An excimer laser operated at 193 nm with a pulse duration of 24 nsec, and repetition rate of 20-80 Hz was used to decompose SiH4 molecules from SiH4/Ar gas mixture. The laser system parameters such as energy and repetition rate, as well as the gas composition, flow rate and pressure, were varied in order to control the average size and size distribution of the Si grains. Electron diffraction patterns show that the Si grains have a circular shape and are arranged in a preferred crystallographic orientation. No amorphous Si or other amorphous phases were found in the Si powder. Lattice images obtained by HRTEM show negligible line and surface defects inside the Si grains and minimum facetting...
at their surfaces. Photoluminescence measurements of the Si powder show an emission peak that spans between 610-670 nm due to excitation at 488 nm. The PL peak increases in intensity and expands toward lower wavelengths as a result of decreasing the average grain-size. Only in the powder having the smallest average grain size of about 25 nm, excitation at 330 nm, resulted in two additional PL emission peaks at 510-550 nm and 430-510 nm. FTIR measurements of the Si powder showed small peaks which correspond to Si-H, and Si-O-Si bonds. The mechanism of photoluminescence from these Si powders was first suggested to be quantum size confinement model. However, the large size of the grains which emit (> 10 nm) cannot be explained by this model. In this paper we present a model which explains the origin of PL in our nanocrystalline Si powder from the crystals surface states. We believe that this model can be useful for the explanation of the PL in porous Si and nanosize Si clusters where the quantum size confinement model could not explain the experimental results.

III. 1D MODEL FOR NANOSTRUCTURES

In order to have an adequate description of the energetic states of an electron in the vicinity of the surface, we consider a one-dimensional model that consists of several cells which represent the potential experienced by an electron in the bulk, and two cells at both ends of the structure which represent the effect of the surface. The real potential in each cell is represented by a square well. Experimental data regarding silicon indicates that the width of the potential well can be taken as 2.86 Å, with a distance between two potential wells of 2.6 Å; the basic configuration is illustrated in Figure 1. The depth of the potential well (in the bulk region) is taken to be $V_a = -8.151 \text{ eV}$.

![Figure 1. One-dimensional model of potential wells in a nanosize Si crystallite. It consists of an arbitrary number of bulk cells (5 drawn) and two surface cells at both ends of the crystallite.](image-url)
According to the experimental data available (11), the distances between neighboring atoms do not change significantly comparing to the bulk, and, therefore, it is assumed dimensions of the potential well at the surface are the same as in the bulk. The value of this potential well depends primarily on the angles of the bonds and neighbor compounds. In the present analysis, we shall use this quantity as a parameter, but first let us determine the eigen-states of the system illustrated in Figure 1.

The Hamiltonian which describes this system is given by

\[ \mathcal{H} = \frac{1}{2m} p^2 + V(x) \]

where \( m \) is the electron mass, \( p \) is the momentum operator and \( V(x) \) is the potential well presented in Figure 1. The Schrödinger equation

\[ \frac{h^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x), \]

can be solved analytically in each domain separately since in each region the potential is constant. To the first vacuum region we assign the index \( v = 0 \), the first potential well is indexed \( v = 1 \), and the interface between the two is taken to be zero, i.e., \( x_{v-1} = 0 \). The formal solution in each region is given by

\[ \psi(x_v < x < x_{v+1}) = A_v e^{-q_v(x-x_v)} + B_v e^{q_v(x-x_v)}, \]

where

\[ q_v^2 = \frac{2m}{h^2} (V_v - E), \]

and \( V_v = V(x_v < x < x_{v+1}) \) is the potential in the corresponding region. This quantity can have one of the three values: either zero, \( V_a \), the potential which represents an atom in the bulk, or \( V_s \), the potential at the two ends, and it represents an atom at the surface. The transition from one region to another is determined by imposing the boundary conditions, i.e., the continuity of the wave function and its derivative. Specifically, the continuity of the wave-function implies that

\[ A_{v-1} e^{-q_{v-1}} + B_{v-1} e^{q_{v-1}} = A_v + B_v. \]

and, in a similar way, the continuity of the derivative gives us

\[ A_v - B_v = \frac{q_{v-1}}{q_v} (A_{v-1} e^{-q_{v-1}} - B_{v-1} e^{q_{v-1}}). \]

In these expressions \( q_v = q_v g_v \) and \( g_v \) is the width of the \( v \)th region. From these two expressions we can calculate the connection between the amplitudes in any two cells. For this purpose it is convenient to define the set \( s_v = (A_v, B_v) \) as the state vector in the \( v \)th cell, and it is related to the corresponding vector in the cell \( v-1 \) by a matrix \( T_{v-1} \), i.e.,
Figure 2. Calculated energy states distribution of the nanosize Si crystallite as a function of energy for two cases: 7 identical wells (thin curve), and 5 bulk + 2 surface wells (thick curve).

Figure 3. Calculated energy states in the nanosize crystallite as a function of phase shift. The upper surface state is at -0.21208 eV and the deeper surface state is at -4.36995 eV. Three cases are shown: infinite number of potential wells (continuous curve), 7 bulk identical wells (diamond), and 5 bulk + 2 surface wells (square).

\[ a_N = T_{N-1} a_{N-1} \]  

[7]

The last cell in the right has the index \( N \) and it corresponds to a vacuum state. Therefore, in principle we have

\[ a_N = T_{N-1} T_{N-2} \cdots T_2 T_1 T_0 a_0 = \tau a_0 . \]  

[8]

Before we proceed, we should emphasize that the condition on the convergence of the wave function at \( x = \pm \infty \) implies that \( A_0 = 0 \) and \( B_N = 0 \). Substituting these two conditions in [8], we obtain that the expression which determines the eigen-energies of this system is given by

\[ \tau_{22}(E) = 0. \]  

[9]

In the framework of this formulation, the eigen-frequencies of an infinite periodic structure are determined based on the Bloch theorem which applied on a single cell implies that \( a_N = e^{ikL} a_{N-2} \); therefore, in conjunction with [7] we have

\[ \text{det} \left[ T_{N-1} T_{N-2} T_{N-3} \cdots T_2 T_1 T_0 - e^{ikL} I \right] = 0 , \]  

[10]
where \( k \) is the wave number in the first Brillouin zone, \( L \) is the period of the structure, and the quantity \( kL \) represents the phase advance per cell.

**IV. EIGEN-ENERGIES**

The model presented in the previous section allows us to examine the effect of the surface potential on the energy states of the electron. In Figure 2 we plotted \( \log(\left| t_{22} \right|) \) as a function of the energy for two cases. In one case (thin line) we took 7 identical cells, i.e., \( V_s = V_a \). The plot illustrates 7 resonances which are all located in the pass-band of an infinite periodic structure. The dispersion relation of the latter is illustrated in Figure 3 after we solved [10] for the same parameters. Once the energies are determined, after solving [9], we can calculate the phase shift in one cell by using [10]. The resulting points on the \( k-E \) diagram are represented by the diamonds in Figure 3.

Let us now go back to Figure 2. When the surface potential is different than \( V_a \) there are 5 energy states in the pass-band and two states out of the pass-band. These two states are clearly revealed by the thick curve in Figure 2. We observe that although the pass-band is between -0.6 eV to -1.75 eV, the two surface energy-states are substantially different: one is at \( E = -0.212 \) eV and the other at \( E = -4.37 \) eV. The potential of the surface in this case is taken as \( V_s = -6.1 \) eV. It
is the latter state which can be responsible for the photoluminescence observed experimentally in both silicon nanocrystals and porous silicon.

Consider now a 3.76 eV photon (330 nm) impinging upon our structure. It extracts electrons from the lower surface-state (-4.37 eV) and puts them in the upper bulk-state. Electrons from the upper levels may now fill this state and emit a photon. If the initial photon was larger than 4.37 eV, then the electron from the upper surface-state may emit a photon of 4.16 eV. In reality (3.76 eV photon) the first bulk state’s electron may emit a photon of 3.56 eV as illustrated in Figure 5. In a similar way, the other energy states may generate photons of 3.29, 3.02, 2.8 and finally 2.60 eV; the probability for each transition is different. A direct result of this model, which is also supported by experimental data, is that there is virtually no emission beyond a certain wavelength. In our example, the lowest bulk state is -1.72 eV, and since the surface-state is at -4.37 eV, there will be no photons below 2.60 eV (obviously with the exception of intra-bulk-states transitions).

In the example presented above, the surface-potential was chosen such that the surface-states separation will be large in order to illustrate in a clear way their effect. Let us now use our model and examine the experimental data in Ref. (23). Specifically, a 330 nm light illuminates a powder of silicon nanocrystals and the measured spectrum has peaks at 420 nm, 455 nm, 485 nm and 530 nm (corresponding to 2.96, 2.73, 2.56 and 2.34 eV). In another experiment, the same powder was illuminated with 488 nm light and there was a broad peak which starts at 610 nm (2.04 eV), culminates at 630 nm (1.97 eV), and falls off at 670 nm (1.85 eV). We found that if we assume $V_s = -5.3$ eV and in addition we assume twelve rather than seven atoms, then the energy states are given in Figure 6; the high surface-state is above zero (vacuum) level. The low surface-state occurs at -3.664 eV. As the energetic photon (330 nm or 3.764 eV) impinges, it extracts electrons from the latter energy-state. As a result, electrons from higher (bulk) states may move into the lower (surface) state, emitting a photon in the process. In Figure 6, the transitions which correspond to the experimental data from the first experimental set are indicated with exp. 1. The transitions which correspond to the second experiment (exp. 2) are also illustrated. Note that in this case the photon is sufficient to bring an electron from the lower surface-state into the upper part of the ‘pass-band’ (bulk states).

Several points should be emphasized before we proceed: (i) In reality the nanocrystals are three-dimensional, therefore the surface potential may vary from one surface to another. Consequently, the surface-state may broaden and part of the photons observed experimentally may be due to transitions to these states. Variation of surface-potential may be caused also by various compounds such as hydrogen or oxygen, as well as edge effects. (ii) The phase advance per cell ($kL$) is meaningful only in the identical cells and it is meaningless in the two different cells; therefore, $k$ is meaningful in these states and meaningless in the surface-states. In other words, the wave function of the electron is localized; therefore, the momentum uncertainty is large and the momentum conservation is not a stringent constraint.

V. THE NUMBER OF SURFACE-STATES

Now that we have established the energetic states associated with the potential at the surface of the nanocrystals, we go one step further to give an estimate for the density of states. Let us assume that the average density of the material is $p$ and it does not change significantly when in bulk or as part of a nanocrystal. For adequate comparison we consider one spherical crystal of an
average radius $R$; thus, the total mass is $M = \rho m_A 4\pi R^3 / 3$ where $m_A$ is the mass of a single atom. In parallel, we consider $N$ nanocrystals of an average radius $r$, and we require that the total mass should be equal, i.e.

$$M = \rho m_A \frac{4\pi R^3}{3} = N \rho m_A \frac{4\pi r^3}{3}$$

[11]

which clearly indicates that the relation between the radius of the macroscopic crystal and the nanocrystal with the same weight is

$$R^3 = N r^3$$

[12]

We further assume that the average surface-states per unit surface, denoted by $v_s$ is the same in macroscopic structures as well as in nanostructures. Consequently, the number of states in the macroscopic crystal is $v_s \times (4\pi R^2)$, whereas in the nanocrystal powder of the same weight we have

$$N v_s \times (4\pi r^2)$$

[13]

The contribution to the photoluminescence of two samples of the same weight, one being a single crystal and the other being a powder of nanocrystals is

$$\frac{N v_s 4\pi r^2}{v_s 4\pi R^2} = \frac{N r^2}{R^2} = N^{1/3}$$

[14]

In order to have a rough estimate as for the surface-states effect, consider a bulk which has 1 mm radius and a powder whose nanocrystals have an average radius of 50 nm. In this case, the number of nanocrystals is of the order of $10^{16}$, and consequently the number of surface-states is $2 \times 10^5$. That is to say that if we compare the contribution of the surface-states of a “smooth” single crystal with a powder of nanocrystals where both have the same mass, the latter case has a contribution which is 5 orders of magnitude larger than the smooth single-crystal. Therefore, the surface-states effect may exist in a smooth sample but its magnitude is several orders of magnitude smaller than in a nanocrystalline state.

Let us now compare the number of surface-states in nanocrystalline powder with that in porous silicon. The number of surface-states in this case can be calculated by assuming that the surface consists of a distribution of cylindrical teeth whose average distance between two teeth is $l$, the average height is $h$, and the average radius is $r_2$ (the subscript 2 in this case indicates that this is the radius of the cylinder). We denote by $N_2$ the total number of teeth, thus the mass of all teeth is $M = n\left[N_2(2\pi r_2^2)h\right]$. The number of surface-states is $v_s\left[N_2(2\pi r_2^2)\right]$, thus, if we require that the mass is equal to the spherical case as assumed in the case of nanocrystals ($M = nN_3 4\pi r_3^3 / 3$) we obtain that

$$\frac{\text{No. surface - states porous}}{\text{No. surface - states nanocrystals}} = \frac{2 r_3}{3 r_2^2}$$

[15]
Thus, the number of states is proportional to the radii ratio; $r_3$ is the radius of the spheres discussed previously which means that the PL effects in the two cases are expected to be comparable.

VI. DISCUSSION

In this study we presented a simple model that explains in terms of the electron surface state in a nanocrystal the photoluminescence phenomenon which was observed in porous silicon and powder silicon nanocrystals. The model relies on the solution of the Schrödinger equation in a series of potential wells. With the exception of two, they are all identical. The two potential wells which are different model the potential experienced by an electron at the surface. The difference can be a result of the way the crystals were prepared, the crystallographic symmetry, the geometry, bonds at the surface, etc. We have shown that the photoluminescence can be explained in terms of extraction of electrons from "deep" energy-states associated with the surface potential and photon emission as a result of transition of an electron from the bulk-state to the surface vacant state. Although in the example presented above the number of bulk potential wells was small [5], we saw no difference in the surface-state; but obviously increasing the number of bulk wells will cause an increase in the number of bulk states respectively.

In order to emphasize even further the concept presented here, let us consider one aspect which has not been discussed yet; it is associated with the presence of compounds at the surface. For this purpose we shall examine the results of the experiment reported in Ref. 18. Before anodization, photoluminescence was observed at 415 nm (3 eV), 437 nm (2.84 eV), and 465 nm (2.67 eV); after excitation at 325 nm (3.82 eV) or 337 nm (3.69 eV). After anodization, additional peaks were observed at 530 nm (2.34 eV) and 680 nm (1.83 eV) with the same excitation energies. These additional peaks are related to Si-H bonds or Si-O bonds formed at the surface during anodization. These bonds cause a change in the effective potential at the surface of the crystal. Now, according to Figure 4, any change in the potential of the surface translates into a change in the energy state of the electron—in this particular model this relation is linear. The presence of oxygen or hydrogen atoms at the surface weakens the potential at the surface, therefore the surface energy state is now closer to the bulk-states. Consequently, additional transitions are possible. In order to quantify this statement let us follow the same approach as before. The bottom bulk state is close to 1.75 eV, almost regardless of the potential well at the surface (assuming the silicon parameters of Sect. IV). In order to get the lowest transition at 2.57 eV (465 nm), the potential well at the surface has to be $V_3 = -6.17$ eV and the energy state is at -4.45 eV. If the oxygen or hydrogen...
weakens $V_s$ to say -5.21 eV, then the surface energy state is up to -3.58 eV, and as a result photons with energies as low as 1.83 eV will be emitted, which is consistent with the experimental data. Note that if we could calculate the effect of these compounds on the surface potential, this experiment could be used to estimate the surface potential of the bare nanocrystals.

In another set of experiments, we have also prepared nanocrystalline Si powder by mechanical grinding in a high energy planetary ball mill. The average grain size was decreased from about 1 μm to about 10 nm, which is comparable to the dimensions of the LCVD
nanocrystalline powder reported in Ref. 23. The powder was illuminated with the same wavelengths (488 nm and 330 nm) and we scanned the same spectral range (400-900 nm), but no evidence of photoluminescence was found. This is an additional indicator that the PL in nanocrystalline Si powder is not only a size effect, but rather a surface effect governed by the surface crystallography. Finally, the photoluminescence yield depends on the grain size and we anticipate an optimal size in the sense of maximum yield. The reasoning behind this optimal value is the following. As the grain size is smaller, we have shown that the number of surface-states is larger, and obviously this tends to increase the yield. But the scattering cross-section of a grain is proportional to the square of its radius; therefore, if the radius decreases, the probability to excite a surface-state decreases and so is the yield. These two opposite trends are expected to lead to an optimal grain size.

REFERENCES