

Oscillations in the derivatives of broad structureless absorption spectra of silicon nanocolloids

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 L491

(<http://iopscience.iop.org/0953-8984/11/43/104>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.220

The article was downloaded on 15/05/2010 at 17:32

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Oscillations in the derivatives of broad structureless absorption spectra of silicon nanocolloids

Y Zhu and L D Zhang

Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

Received 6 April 1999, in final form 27 July 1999

Abstract. Two sets of fine structure were found in the derivatives of broad structureless ultraviolet and visible absorption spectra of silicon nanocolloids prepared by using an arc plasma with the gas flow method in Ar and Ar+H₂ atmospheres, separately. Calculation shows that these two sets of fine structure arise from oscillation–electron coupling of silicon electron transitions. The oscillations strongly depend on how many oxygen and/or hydrogen atoms are bonded to each silicon atom. This weak effect is an indication that the silicon nanoparticle surface and interface layer structure and chemical composition have a measurable effect on the electronic properties.

Nanometre-sized silicon, for example, porous silicon, silicon particles, silicon particles embedded in other materials and silicon colloids, has efficient luminescence in the visible region even at room temperature [1–5]. Many studies show that the structure of nanometre-sized silicon can be described by a core, interfacial and surface oxide silicon layer structure model [6]. The oxygen and/or hydrogen in the surface and interface layer (the localized states on the surface and interfacial layer [6]) and the quantum confinement effect of these kinds of material plays a very important role in the photoluminescence (PL) in the visible region [1, 6–8]. The behaviour of the Si(O) and/or Si(O, H) in the silicon nanoparticle surface and interfacial layer is different from that in bulk silicon [9, 10], and has attracted much attention. Here we present the results of the fine structure in the derivatives of ultraviolet and visible (UV/vis) absorption spectra of silicon nanoparticles dispersed in 2-propanol (silicon nanocolloids). The results indicate that the fine structure is from oscillation–electron coupling of silicon electron transitions. The oscillations strongly depend on how many oxygen and/or hydrogen atoms are bonded to each silicon atom. Although the measured effect is very small, there is an indication that the surface and interface layer structure and composition have a measurable effect on the electronic properties (which may be important for the PL process).

Samples were prepared in Ar or Ar+H₂ atmospheres by using an arc plasma with the gas flow method appropriate for colloid preparation, and characterized by transmission electron microscopy (TEM) and energy dispersed x-ray analysis (EDX) (the details have been reported elsewhere [11]). Briefly, the results are nearly the same as for samples prepared by a dc sputtering method except the particle size distributions [12]. There are some very large particles in the sample though half of the particles are less than 10 nm in diameter. In order to separate large particles from the sample, all samples were filtered by using filter paper with a pore size of 0.3 μm . The silicon particles are composed of a silicon crystal core covered by an oxidized amorphous silicon shell (SiO_x). The oxidized shell is thought to be formed during the discharge process due to the residual gas in the vacuum system. Hydrogen cannot be analysed by EDX, but there are two Si–H–Si stretching vibration peaks (in the region of 2000–2300 cm^{-1}) in the

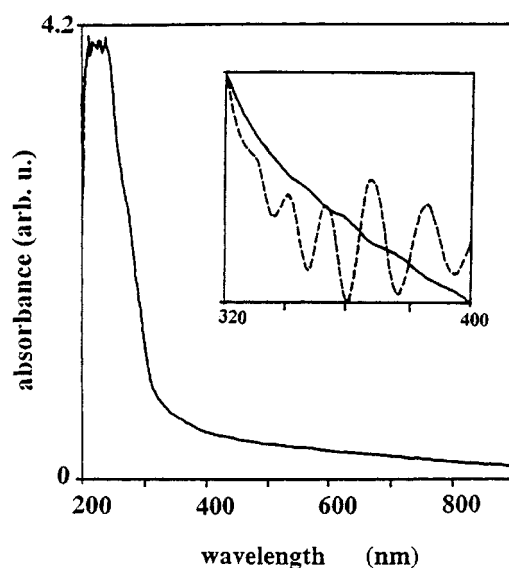


Figure 1. The UV/vis spectrum of silicon nanocolloids in the wavelength region from 200 to 900 nm. The sample was prepared by arc plasma with the gas flow method in Ar atmosphere. The inset is the expansion part of the spectrum, which highlights the fine structure (the dashed line is the derivative of the expansion part of the spectrum).

IR spectra for the sample prepared in Ar+H₂ atmosphere (IR absorption spectra were measured with a Horiba FT-210 FTIR spectrophotometer).

Figures 1 and 2 are typical UV/vis absorption spectra (which were measured with a Hitachi U-3210 spectrophotometer) in the wavelength region 200 to 900 nm, for samples prepared by using arc plasma with the gas flow method in Ar and Ar+H₂ (2:1) discharge gases respectively. The inset spectra are the expansion part of each spectrum, which highlights the fine structure of each spectrum, and the dashed lines are the derivative of the expansion part of each spectrum (no fine structure was found in other region of the spectra). We labelled peaks as 0, 1, 2, 3 and 4 from the high energy to the low energy side (the following are the same and only five peaks were found for these two sets of fine structure). After accurately measuring the peak position, in the fine structure of figure 1, we obtained peak 0 to be 337.1 nm. The subsequent peak positions are 348.7 nm, 360.4 nm, 374.8 nm and 391.2 nm (in the spectra of many other samples prepared in the same conditions, the peak positions are 337 ± 1.2 nm, 348 ± 1.1 nm, 360 ± 1.5 nm, 374 ± 1.4 nm and 391 ± 1.6 nm for peaks 0, 1, 2, 3 and 4 respectively), the difference of the wavenumbers between two neighbouring peaks being 937 cm^{-1} , 980 cm^{-1} , 1065 cm^{-1} and 1105 cm^{-1} from the high energy to the low energy side. In the fine structure of figure 2, peak positions are 353.6 nm, 384 nm, 417.6 nm, 430.8 nm and 446 nm (in the spectra of many other samples prepared in the same conditions, peak positions are 353 ± 1.6 nm, 384 ± 2.1 nm, 417 ± 2.3 nm, 430 ± 2.2 nm and 446 ± 1.8 nm), the difference of the wavenumbers between two neighbouring peaks being 2239 cm^{-1} , 2095 cm^{-1} , 734 cm^{-1} and 791 cm^{-1} from the high energy to the low energy side.

Based on the energy conservation law, in silicon electron transitions, we may have

$$E_f - E_i = h\omega + E_c \quad (1)$$

where E_f is the electron energy of the final state, E_i the electron energy of the initial state, $h\omega$ the energy of the absorption photons and E_c the energy from other (coupling) sources.

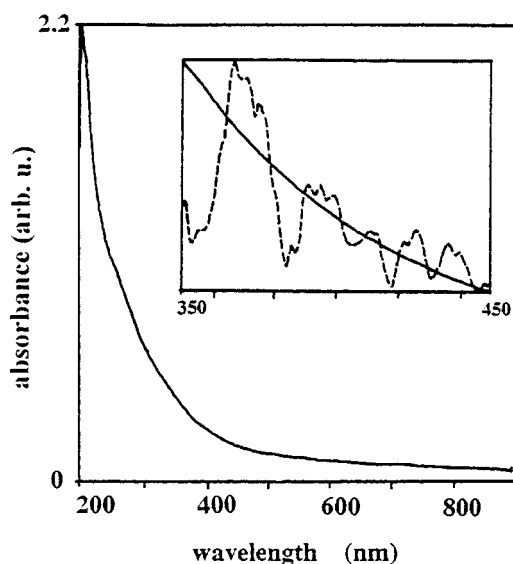


Figure 2. The UV/vis spectrum of silicon nanocolloids in the wavelength region from 200 to 900 nm. The sample was prepared by arc plasma with the gas flow method in Ar+H₂ (2:1) atmosphere. The inset curve is the expansion part of the spectrum, which highlights the fine structure (the dashed line is the derivative of the expansion part of the spectrum).

It is now widely accepted that SiO_x ($0 \leq x \leq 2$) contain five states, an unoxidized state and four different oxidation states of silicon [13–17]. The four oxidation states as well as the unoxidized state can be modelled as tetrahedral bonding units in which a central silicon atom is bonded to $(4 - n)$ O ($n = 0-4$). The structure of this SiO_x can be expressed as Si–Si_{4-n}O_n ($n = 0-4$). In the sample of figure 1, the main composition of some particle shells is in one of these five states; the others are in other states. For one particle, in different places in the oxidized shell, n may be different (for example, from the surface to the inside). Of course, some separation of oxygen- and silicon-rich phases can be evident at intermediate stoichiometries and can affect the fine structures of UV/vis spectra. For different n in each unit of Si–Si_{4-n}O_n structure, the quantity of oxygen atoms bonded to the silicon atom is different; that is, the quantity of Si–O–Si bonds is different. This leads to different Si–O–Si stretching vibration frequencies. In our previous work, we obtained results similar to that of figure 1, (in our previous work, samples were prepared by a dc sputtering method, and we directly obtained five peaks of the fine structure after expanding the absorption spectra; however, the peak positions of the fine structure were not accurately measured) and it is confirmed that the fine structure may relate to Si–O–Si stretching vibration [18]. Based on the reasoning above, we assume

$$E_c = h\Omega_n = nhP_n. \quad (2)$$

That is, the coupling energy is the oscillation energy or the sum of all Si–O–Si stretching vibration energies in each unit of Si–Si_{4-n}O_n (however, only some effective Si–O–Si bonds in which the Si–O–Si bonds neighbour defects and dangling bonds can be coupling [19]). Where n is the same number as in Si–Si_{4-n}O_n, $h\Omega_n$ is the oscillation energy (coupling energy) for each n ; hP_n is the energy of Si–O–Si stretching vibration for each n . Here we have taken $h\Omega_0$ ($n = 0$) as zero. For peaks 0–4, we have hP_0, hP_1, hP_2, hP_3 and hP_4 for $h\Omega_n$ that corresponds

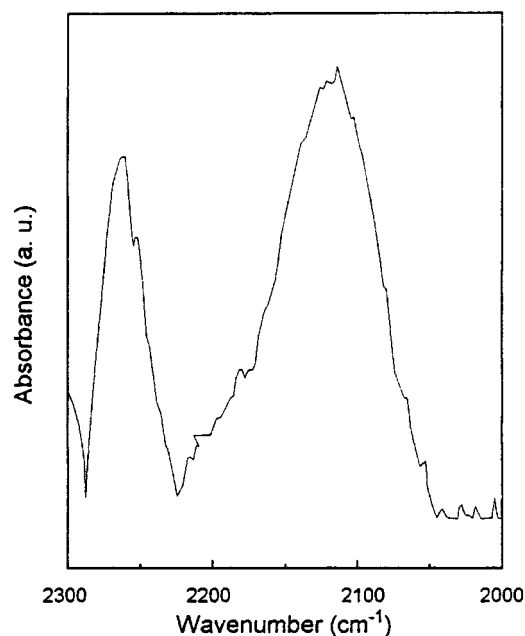


Figure 3. The IR absorption spectrum in the wavenumber region 2000–2300 cm^{-1} . The sample was prepared by arc plasma with the gas flow method in Ar+H₂ (2:1) atmosphere.

to $n = 0-4$. Then, take the differences:

$$\begin{aligned} \Omega_1 - \Omega_0 &= P_1 = 937 \text{ cm}^{-1} & \Omega_2 - \Omega_1 &= 2P_2 - P_1 = 980 \text{ cm}^{-1} \\ \Omega_3 - \Omega_2 &= 3P_3 - 2P_2 = 1065 \text{ cm}^{-1} & \Omega_4 - \Omega_3 &= 4P_4 - 3P_3 = 1105 \text{ cm}^{-1}. \end{aligned}$$

We can obtain:

$$P_1 = 937 \text{ cm}^{-1} \quad P_2 = 959 \text{ cm}^{-1} \quad P_3 = 994 \text{ cm}^{-1} \quad P_4 = 1022 \text{ cm}^{-1}.$$

The IR results of the sample prepared in Ar+H₂ atmosphere clearly show the stretching vibration of Si–H and Si–H₂ (figure 3). For the fine structure of figure 2, using the same model and method, and substituting some hydrogen atoms for oxygen atoms, we have

$$\begin{aligned} E_c &= h\Omega_n = nhP_n & (n = 0-2) \\ E_c &= h\Omega_n = 2hP_{2n} + (n-2)hP_n & (n = 3, 4). \end{aligned} \quad (3)$$

Here hP_n is the energy of the Si–H–Si stretching vibration when $n = 0-2$ or the Si–O–Si–H coupled vibration when $n = 3, 4$, hP_{2n} is the energy of the Si–H–Si stretching vibration (in H₂Si_{4-n}O_{n-2}) when $n = 3, 4$. Approximately, $hP_{24} = hP_{23} = hP_2$. Then, we can obtain

$$P_1 = 2239 \text{ cm}^{-1} \quad P_2 = 2167 \text{ cm}^{-1} \quad P_3 = 734 \text{ cm}^{-1} \quad P_4 = 791 \text{ cm}^{-1}.$$

The wavenumbers of the Si–O–Si stretching vibration based on the Si–Si_{4-n}O_n model were calculated from IR spectra of reactivity sputtering SiO_x films to be 987 cm^{-1} , 1019 cm^{-1} , 1052 cm^{-1} and 1085 cm^{-1} for $n = 1-4$ respectively [20]. Si–H–Si stretching vibrations are in the region of 2000–2300 cm^{-1} (see figure 3; one peak is at 2115 cm^{-1} and another is at 2255 cm^{-1}) and the Si–O–Si–H coupled vibration is around 800 cm^{-1} [3, 21, 22]. It seems the wavenumbers of our P_n should be shifted by several tens of cm^{-1} . This may be due to the following factors: (i) The effective mass of the Si(O) Si(O, H) is small, because the quantity

of the dangling bonds and defects (which may neighbour Si–O–Si, Si–H–Si and Si–O–Si–H bonds, then the oscillation–electron coupling occurs [16]) in our nanoparticle surface and interface layer are much higher than that in the above works, as our sample was prepared by arc plasma, and a low temperature (liquid nitrogen) trapping method; (ii) the measurement error of the peak position and (iii) for the calculation of the results for the sample prepared in Ar+H₂ atmosphere, we have an approximation of $hP_{24} = hP_{23} = hP_2$ and have not considered the cases of three or four hydrogen atoms or only oxygen atoms being bonded to the silicon atom.

Optical absorption occurred at the energy region with $E_f - E_i$ of about 3 eV, which might be associated with the onset of a strong direct transition in bulk silicon L₃–L₁ and another high energy gap. In the energy region of our fine structure spectra, there is a gap of Γ_{25} – Γ_{15} at the energy of about 3.5 eV (bulk value); therefore, we assume that there are oscillation–electron couplings of silicon electron transitions at this gap, and the fine structure may be associated with Si(O)- or Si(O, H)-like molecules [9, 10].

In conclusion, two sets of fine structure were found in the derivatives of broad structureless UV/vis absorption spectra of silicon nanocolloids, which arise from oscillations of Si(O) and Si(H, O) and electron coupling in silicon electron transitions. The oscillations strongly depend on how many oxygen and/or hydrogen atoms the silicon atom is bonded to; these may neighbour dangling bonds and defects in the silicon nanoparticle surface and interface layer. We may use this measurable effect as a micro-probe to measure the silicon nanoparticle surface and interface layer structure and composition.

This work is partly supported by the Chinese Academy of Sciences, National Climbing Project of China.

References

- [1] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
- [2] Littau K A, Szajowski P J, Muller A J, Kortan A R and Brus L E 1993 *J. Phys. Chem.* **97** 1224
- [3] Banerjee S, Narasimhan K L and Sardesai A 1994 *Phys. Rev. B* **49** 2915
- [4] Alivisatos A P 1996 *Science* **271** 933
- [5] Kimura K and Iwasaki S 1998 *J. Appl. Phys.* **83** 1345
- [6] Kanemitsu Y 1995 *Phys. Rep.* **263** 3
- [7] Canham L T 1995 *Phys. Status Solidi b* **190** 9
- [8] Cullis A G, Canham L T and Calcott P D J 1997 *J. Appl. Phys.* **82** 909
- [9] Gole J L, Dudel F P, Grantier D and Dixon D A 1997 *Phys. Rev. B* **56** 2137
- [10] Gole J L and Dixon D A 1998 *Phys. Rev. B* **57** 12 002
- [11] Zhu Y, Iwasaki S, Kimura K and Zhang L D 1998 *Chin. Phys. Lett.* **15** 928
- [12] Zhu Y, Kimura K and Zhang L D 1997 *J. Vac. Sci. Technol. B* **15** 2077
- [13] Hollinger G and Himpfel F J 1983 *Phys. Rev. B* **28** 3651
- [14] Finster J, Scuulze D and Meisel A 1985 *Surf. Sci.* **162** 671
- [15] Braun W and Kuhlenbeck H 1987 *Surf. Sci.* **180** 279
- [16] Feldman A, Sun Y N and Farabaugh E F 1988 *J. Appl. Phys.* **63** 2149
- [17] Furukawa S and Miyasato T 1988 *Phys. Rev. B* **38** 5726
- [18] Zhu Y and Kimura K 1995 *Chem. Lett.* **8** 643
- [19] Zhu Y, Kimura K and Zhang L D 1998 *Solid State Commun.* **108** 545
- [20] Lehmann A, Schumann L, Sobotta H, Riede V, Teschner U and Hubner K 1982 *Phys. Status Solidi b* **111** K103
- [21] Lucovsky G, Yang J, Chao S S, Tyler J E and Czubatj W 1983 *Phys. Rev. B* **28** 3225
- [22] Hayashi S, Kawata S, Kim H M and Yamamoto K 1993 *Japan. J. Appl. Phys.* **32** 4870