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Control of Silicon Dimensionality of Polysilanes and Their Optical Properties

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The effects of the silicon skeleton on the optical properties were studied for various kinds of polysilanes such as polysilylene, polysilyne, and soluble organosilicon nanocluster, which have one, two, and three dimensional silicon skeletons, respectively. The absorption and emission spectra of the polysilanes show the decrease of the optical band gap $E_{g,opt}$ with increasing the Si-dimensionality. The quantum size effects in the optical properties of the organosilicon nanoclusters with various Si-core sizes were discussed in comparison with those of inorganic silicons. $E_{g,opt}$ of the organosilicon nanocluster film heat-treated at 500°C is similar to that of a-Si, and it suggests the possibility of a-Si coating.

Keywords: polysilane; nanocluster; quantum size effects ; a-Si coating

INTRODUCTION

The various kinds of silicon materials with novel structures and properties have been studied recently. From a chemical point of view, the synthesis of soluble polysilanes opened the new field of low-dimensional silicon materials such as polysilylene (a quasi-one-dimensional silicon) and polysilyne (a quasi-two-dimensional silicon)[1,2]. On the other hand, from a physical point of view, the discovery of visible emissions from porous silicon attracted great interest in the optical properties of low-dimensional silicon materials[3-6]. These studies are linked to each other, and an interdisciplinary field between organic and inorganic silicon materials is formed. In this paper, we report the optical properties of polysilanes with various Si-dimensionalities, for

example, polysilylene, polysilyne, and organosilicon nanocluster which was first synthesized by us[7].

EXPERIMENTAL

Three-dimensional polysilane with an organosilicon nanocluster structure was synthesized by the reaction of tetrachlorosilane with magnesium metal, followed by capping the ends of the silicon nanocluster with tert-butyl (t-Bu) group in solution. The organosilicon nanocluster (PtBuSi) is soluble to common organic solvents. The detailed synthetic procedures have been reported in our previous paper[7]. The diameters of organosilicon nanoclusters were estimated by considering the size of the monodispersed polystyrenes which were employed as standards in the determination of the molecular weight of PtBuSi by size exclusion chromatography[4,7].

RESULTS AND DISCUSSION

The optical properties of polysilanes are strongly influenced by the Si skeleton because the σ-conjugation is caused by overlapping of the σ-electron of the Si atoms. In Fig. 1, the electronic absorption spectra calculated by the ZINDO method are depicted for four kinds of polysilanes consisting of 26 Si atoms. The spectra **a**, **b**, **c**, and **d** were calculated for poly-silanes ($Si_{26}H_x$) having linear (polysilylene), network (polysilyne), crystalline, and amorphous cluster structures, respectively. With increasing the Si-dimensionality, the lowest transition energy of the absorption band shows red shift: linear Si, 5.38 eV;

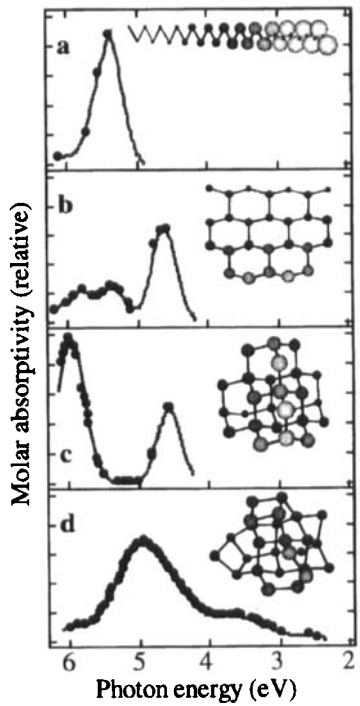

FIGURE 1 Absorption spectra calculated for polysilanes consisting of 26 silicon atoms. The ZINDO semi-empirical MO method were employed.

network Si, 4.60 eV; crystalline Si cluster, 4.57 eV; amorphous Si cluster, 2.46 eV. The amorphous Si cluster is formed by introducing 4- and 5-membered ring to the crystalline Si cluster consisting of 6-membered ring. The increase of the Si-Si bonds and the decrease of the distance between Si atoms enhances the σ-conjugation.

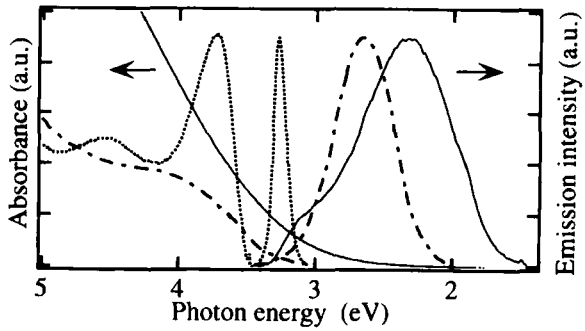

FIGURE 2 Absorption and emission spectra of polysilanes in THF: (·····) poly(methylphenylsilylene); (– · – · –) poly(n-hexylsilyne); (———) organosilicon nanocluster (PtBuSi).

The experimental absorption and emission spectra of polysilanes are also remarkably influenced by the Si skeleton as shown in Fig.2. The absorption edge and the emission maximum are shifted to lower energy region with increasing the Si-dimensionality from one-di-mensional polysilylene to three-dimensional organosilicon nanocluster (PtBuSi). The optical band gap $E_{g,opt}$ of PtBuSi (2.5 eV) is the lowest in the organo-soluble polysilane family. Fig.3 shows the far-IR spectrum of PtBuSi. From the comparison with the vibronic transitions calculated for cyclic silicons, it is evident that PtBuSi has an amorphous Si structure consisting of 4-, 5-, and 6-memberd rings.

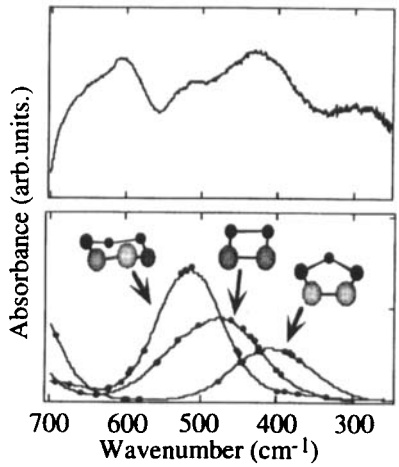

FIGURE 3 Far-IR spectrum of PtBuSi and the vibronic transitions of cyclic silicons calculated by MNDO method.

The quantum size effect in the optical properties of Si is an important subject in relation to the discovery of the visible emission from porous Si.

However, there are few studies of the Si cluster with smaller size than 2 nm.The organosilicon nanocluster supplements the lack of data in the smaller cluster size region. In Fig.4, the $E_{g,opt}$ values of PtBuSi are plotted against the diameter of the Si core in comparison with the reported values for inorganic silicon clusters such as surface-oxidized silicon nano-crystal[4], microcrystalline Si:H[6], and ultrafine Si particles in a Si oxide matrix[5]. The continuous change of $E_{g,opt}$ by quantum size effects is seen for organic and inorganic silicon nanoclusters.

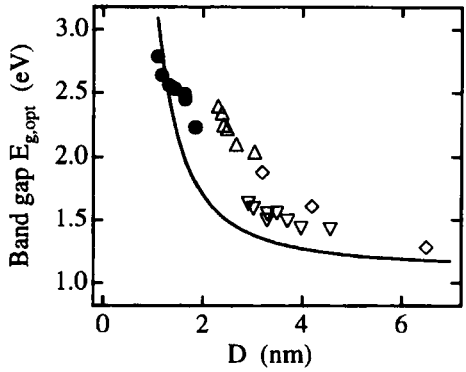

FIGURE 4 Quantum size effects on the optical band gap of silicon clusters: (●) this work; (◇) ref. 4; (▽) ref. 5 ; (△) ref. 6. The solid line is the band gap calculated for silicon quantum dot.

The organosilicon nanocluster is applicable to a precursor of inorganic films. A new route to a semiconducting film using soluble silicon nanocluster is expected. The TG-MS analysis of PtBuSi shows the elimination of t-Bu group by heat treatment forming 2-methylpropene. $E_{g,opt}$ of the spin-coated PtBuSi film decreased to 1.26 eV by the heat treatment at 500°C in vacuo. These results suggest the possibility of a-Si coating using the soluble organosilicon nanocluster as a precursor.

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