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Optical Properties of Porous Silicon and Small Silicon Clusters

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Very recently, a great deal of research effort is focused on low-dimensional nanostructures made from indirect-gap semiconductors such as Si[1] or Ge [2]. Especially, the discovery of the strong luminescence from Si nanostructures fabricated by electrochemical anodization, often called porous Si, is an extremely important scientific breakthrough with enormous technological implications. The origin and mechanism of strong visible luminescence in porous Si are currently under discussion. In this work, we have studied and compared the optical properties of both porous Si and the chemically synthesized Si-skeleton clusters. The rough surface of porous Si is regarded as a condensation of small Si clusters.

Porous silicon was formed on p-type (100) silicon. The anodization was carried out in HF-ethanol solution ($HF:H_2O:C_2H_5OH=1:1:2$) at a constant current density of 30 mA/cm^2 for 3 min. After the anodization, photochemical etching of the wafer was carried out for 2 min in HF-ethanol solution under illumination with a 500 W tungsten lamp from a distance of 20 cm. A planar Si-skeleton cluster (syn-tricyclooctasilane) and cubic Si-skeleton cluster (octasilacubane) were synthesized and used as model Si-based materials consisting of a small number of Si atoms. The structures are illustrated in Fig.1.

Figure 2(a) shows the excitation and PL spectra in porous Si. A sharp rise in the excitation spectrum is observed at photon energies above 3 eV. An excitation peak exists near ~3.25 eV, and broad PL spectrum under 325 nm excitation is observed at the peak value of 1.98 eV. Figures 2(b) and 2(c) show the molar extinction coefficients and PL spectra in planar and cubic Si-skeleton clusters, respectively. In a planar Si cluster, the lowest excitation state is observed at 3.09 eV and a broad PL spectrum is observed with the peak of 2.25 eV. In a cubic Si cluster, the absorption edge is observed at ~3.2 eV and a broad PL spectrum is also observed with the peak of 2.50 eV. Both the broad PL spectra and the large Stokes shifts in planar and cubic Si-clusters are different from those in one-dimensional chainlike Si clusters.[3,4] The characteristics of PL and excitation spectra of porous Si are similar to those of Si clusters.

Figure 3 shows the picosecond PL decay at peak energies in porous Si and planar and cubic Si-skeleton clusters. The PL decay exhibits non-exponential behavior even in picosecond time-scale. Based on the essential agreement between porous Si and Si clusters, the strong luminescence and fast initial decay of PL suggest that porous Si begins to have the character of a direct optical transition.

From our experimental findings, it is concluded that the entity causing the luminescence in porous Si shows similar optical characteristics to the Si clusters. Moreover, Brandt et al.[5] pointed out that the electronic properties of siloxene compounds with sixfold Si rings are similar to those of porous Si and that small Si-skeleton clusters also play an essential role in the luminescence process of these siloxene compounds. Therefore, the notion of a small Si-skeleton cluster gives a better understanding of the luminescent mechanism of porous Si.

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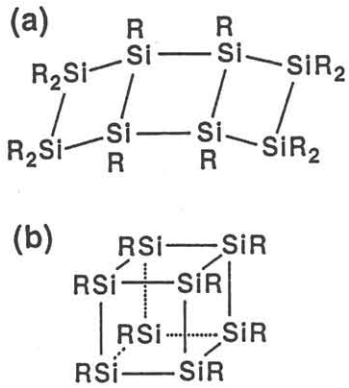

FIG.1. (a) A planar Si-skeleton cluster, syn-tricyclooctasilane (R=isopropyl) and (b) a cubic Si-skeleton cluster, octasilacubane (R=t-butyldimethylsilyl).

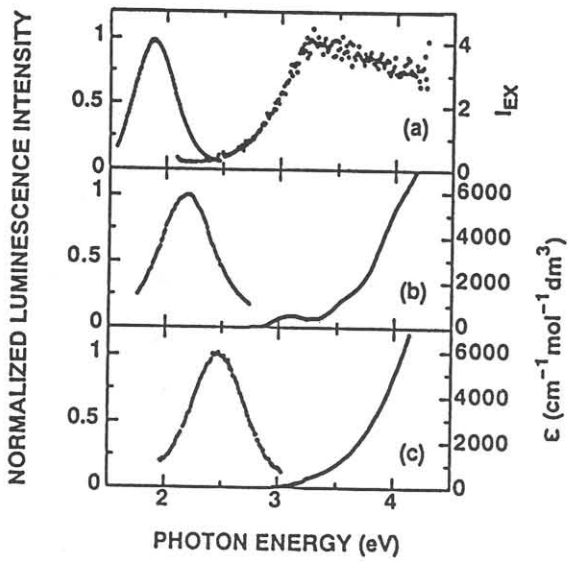

FIG.2. (a) Excitation (I_{EX}) and PL spectra in porous silicon. Molar extinction coefficients ε and PL spectra in a planar Si-skeleton cluster (b) and in a cubic Si-skeleton cluster (c).

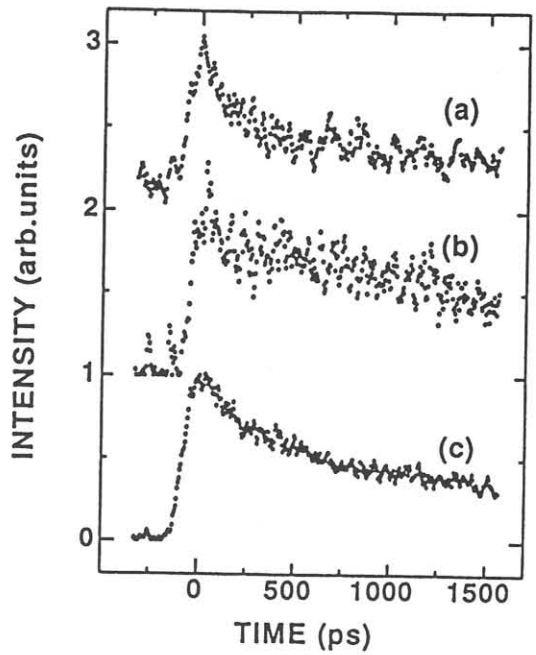

FIG.3. Picosecond PL decay of at the peak photon energies; (a) porous Si, (b) a planar Si-skeleton cluster, and (c) a cubic Si-skeleton cluster.