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LETTER TO THE EDITOR

The effect of atmospheric annealing on the photoluminescence of sandwich-structured thin films of silicon nanoparticles embedded in Al₂O₃ matrices

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Abstract

Sandwich-structured thin films of silicon nanoparticles embedded in Al₂O₃ matrices were prepared by using the pulsed laser deposition method. High-intensity photoluminescence (PL) with additional fine structures in the wavelength region of 300–550 nm was observed. There was a dramatic change in intensity of the main PL peak with different annealing conditions, and its peak position was gradually blue-shifted with increasing annealing temperature of the samples. However, no corresponding blue-shift of the PL fine structures was observed. The PL mechanism is attributed to quantum confinement within the nanoparticles, while the fine structures arose from the different oxidized states in the Si–Al₂O₃ interface coupled with the electronic transitions in the silicon nanoparticles.

The influence of quantum confinement on the optical properties, especially the photoluminescence (PL), of nanosilicon particles embedded inside appropriate insulators has been widely studied in recent years [1–5]. The most common insulator in this respect is SiO₂. However, the maximum concentration of silicon nanoparticles that can be packed inside the SiO₂ host is limited by the requirement that the spacing between adjacent silicon nanoparticles should be no less than 2–3 nm, in order to preserve their quantum confinement property [6]. Al₂O₃ is potentially a better host for enhancing the maximum allowable concentration of silicon nanoparticles since its band gap is similar to that of SiO₂ but its dielectric constant is over twice as high. In this letter we report on the high-intensity PL of our sandwich-structured thin films of silicon nanoparticles embedded in Al₂O₃ matrices and how it is affected by atmospheric annealing. The PL also exhibits fine structures at ordinary temperatures in the wavelength region of 300–550 nm which is contrary to the common presumption that the PL of silicon nanoparticles is mainly kinetic; this results in a dramatic increase in luminescence efficiency even though the emission and absorption spectra remain smooth and structureless, and is indicative of indirect optical transitions [7].

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Details of the sample preparation and characterization have been reported elsewhere [8]. The deposited films were composed of tiny silicon crystals with diameters of less than 6 nm embedded in Al_2O_3 matrices, in which the silicon nanoparticles lay in segregated layers sandwiched between Al_2O_3 layers. The set of samples (a)–(e) prepared for the present study were the as-prepared sample and ones which had been respectively annealed at 300 °C, 400 °C, 500 °C for one hour, and at 500 °C for six hours in the open but clean atmosphere. The same set of samples were used for the x-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and PL measurements.

Figure 1 shows the XPS curves for the Si 2p peaks for all of the five samples labelled (a)–(e). A small energy scale correction for the charge effect has been applied for all of the curves. The most significant feature of the results is the gradual change in the relative intensity of the low-binding-energy peak which decreased very much when the annealing temperature was increased and almost disappeared for samples (d) and (e). Since these samples were all annealed in the atmosphere, the main chemical change must be due to the oxidation of the film by the environmental oxygen. The low-energy peak in sample (a) corresponds to the Si–Si bonds, showing that the sample was initially largely unoxidized. When it was annealed, these bonds gradually disappeared through oxidation, causing a gradual decrease in the low-energy peak. Since XPS is sensitive mainly to the composition at or near the film surface, this implies that the oxidation occurred at least on the surface layers of the film.

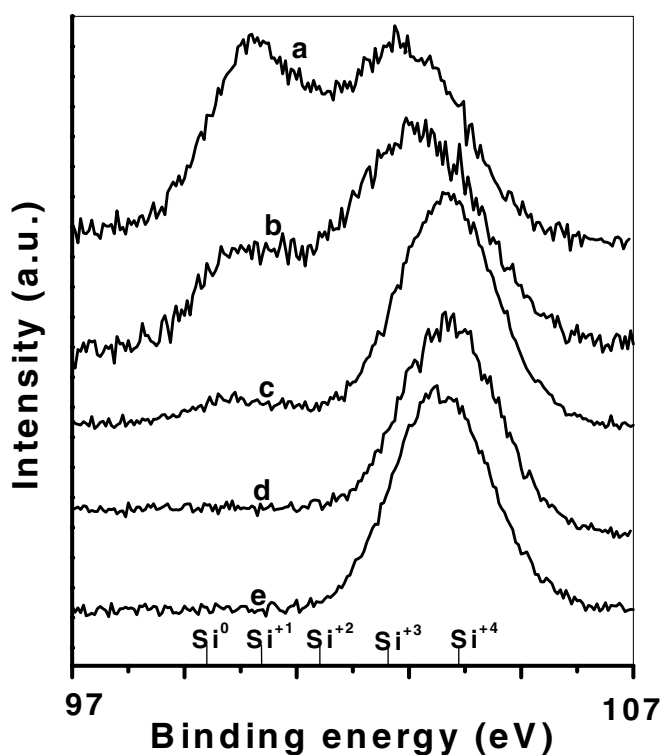


Figure 1. XPS results for the Si 2p peaks for all of the samples: (a) the original sample; (b) the sample annealed at 300 °C for one hour; (c) the sample annealed at 400 °C; (d) the sample annealed at 500 °C for one hour; and (e) the sample annealed at 500 °C for six hours. The samples were annealed in the open but clean atmosphere.

Figure 2 shows the transmittance FTIR spectra (a)–(e) for the same set of samples; these give information on the bulk material of the film. The large sharp band at about 520 cm^{-1} , which appears in all of the curves, is attributed to the silicon breathing vibration [9]. Unlike the weak breathing vibration in bulk silicon, the breathing vibration here is quite strong and is possibly due to the low-dimensional structures of the nanoparticles. This phenomenon resembles, for example, the unexpectedly high IR intensity at 525 cm^{-1} occurring in some special silicon clusters [10, 11]. Since the XPS data have indicated that the surface layers of the silicon particles were oxidized by atmospheric annealing, the slightness of the difference between the FTIR data for the different samples indicates that the silicon particles inside the films remain largely unoxidized, even after prolonged annealing in the atmosphere. This demonstrates that the Al_2O_3 host provided a compact and airtight seal preventing atmospheric oxygen from diffusing into the embedded silicon nanoparticles. In curve (a), there is a shallow broad peak at around 1140 cm^{-1} , which still persists in curve (b). The peaks at 1140 cm^{-1} and at 1080 cm^{-1} (in curves (d) and (e)) are attributed respectively to the out-of-phase and in-phase stretching vibrations of the oxygen atom in the Si–O–Si group [12]. However, the normal out-of-phase and in-phase motions of the Si–O–Si peaks are at 1150 cm^{-1} and 1075 cm^{-1} respectively [12]. The slight differences in vibrational wavenumbers arise because, in our samples, the Si–O–Si bonding is by Al atoms or Al–O atoms, unlike the case for normal samples. The 970 cm^{-1} peak for sample (c) is attributed to the stretching Si–O–Si vibration at low oxidation level [13]. It actually started to appear as a very broad shallow peak in curve (b), and became more pronounced in curve (c). This is consistent with the assumption that the silicon nanoparticles in sample (b) were only slightly oxidized.

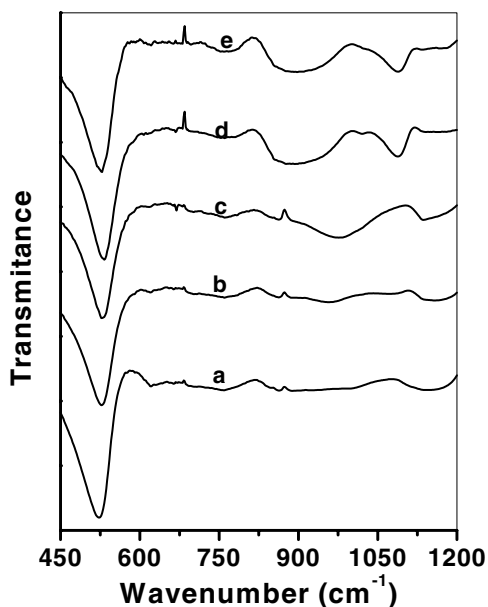


Figure 2. FTIR results for all of the samples (a)–(e) as defined in figure 1.

With increasing oxygen content, the in-phase vibrations would give way to out-of-phase vibrations, and the 1080 cm^{-1} peak in curves (d) and (e) suggests that the nanoparticles in the respective samples were increasingly more oxidized. Another broad peak at about 893 cm^{-1} appearing in curves (d) and (e), but not in curves (a), (b) and (c), is attributed to the formation of some new bonds in the interfacial region between the Al_2O_3 and silicon nanoparticles arising from the increase in oxygen content with prolonged annealing.

PL measurements were carried out in a fluorescence spectrophotometer using an excitation light wavelength of 280 nm. The peak at 560 nm is the secondary resonance at twice the excitation wavelength. Figure 3 shows the PL curves for all of the above samples labelled (a)–(e) respectively. Also included for the purpose of comparison is curve (f) representing the PL result for silicon nanoparticles prepared by direct dc sputtering of the silicon material onto the liquid-nitrogen-cooled surface of the stainless steel trap [14]. Each of the PL spectra including that of (f) displays a main broad peak on the short-wavelength side of the resonance line, and a shallower peak on the other side, which is more clearly seen in curve (c). There is a gradual shift of the main peak position from samples (a) to (e), which is located at 373, 353, 348, 343 and 342 nm respectively. Apart from this shift, all of the PL curves, including curve (f), are remarkably similar in shape and peak position despite their large differences in surface chemical compositions, as revealed by the XPS and FTIR measurements. The PL intensity of any of the present Si–Al₂O₃ samples is generally much higher than that of the directly sputtered sample shown by curve (f). It becomes extremely high for sample (c) which was annealed at 400 °C for one hour, but falls off again for the more intensely annealed samples (d) and (e).

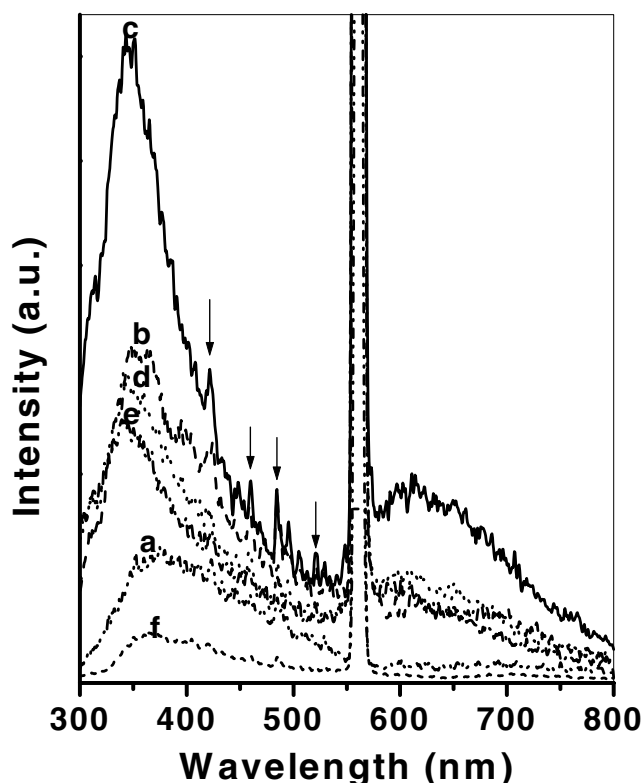


Figure 3. PL results for the samples (a)–(e) as defined in figure 1, and the sample (f) prepared by direct dc sputtering: (a) dash–dot–dot line; (b) dashed line; (c) continuous line; (d) dotted line; (e) dot–dash line; and (f) short-dash line.

A comparison of the PL and XPS results reveals no direct correlation between them. The large differences in our XPS spectra for samples (a)–(d) indicated that surface oxidation of the silicon nanoparticles took place gradually upon their annealing in the atmosphere. On the other hand, our PL intensity at first increased with annealing temperature up to 400 °C, but

it then decreased upon further increase in annealing temperature (samples (d) and (e)). Thus, it follows that the PL change of the film was not directly related to the change in chemical composition or structures of the films.

In our present experiments, the silicon nanoparticles embedded in Al_2O_3 matrices should possess a surface electronic structure which is different from that of the silicon nanoparticles prepared by the direct dc sputtering method [14]. This difference should show up as a difference between curves (a) and (f). Since the two curves have very similar peak positions and shapes, it follows that the PL structure arose not from the interfacial surface of the Si– Al_2O_3 boundary, but from the quantum confinement mechanism of the PL within the nanoparticle. That the PL intensity of the silicon nanoparticles embedded in the Al_2O_3 matrices was much higher than that of the sputtered silicon nanoparticles, which were surrounded by SiO_2 , shows that the Al_2O_3 host provided much better quantum confinement of the silicon nanoparticles than the SiO_2 host. Under the same environmental condition, the Al_2O_3 host requires only a thinner encapsulation layer to preserve the quantum well confinement of the silicon nanoparticles. The smaller insulator thickness required permits an increase in the packing density of quantum-confined Si nanoparticles, thus explaining the much higher PL intensity observed.

Under appropriate annealing conditions, it is possible that the tiny atomic silicon clusters aggregated together to form larger silicon nanoparticles. Under such conditions, some oxygen from the atmosphere could diffuse into the films and react with the silicon nanoparticles. This would lead to oxidation of the silicon nanoparticles thereby reducing their size and enhancing their PL quantum confinement effect as observed. The reduction in size of the silicon nanoparticles would also lead to an increase in the energy gap of the silicon particles, which would in turn lead to the observed blue-shift of the PL peak. With a higher annealing temperature, more oxygen from the atmosphere would diffuse into the films creating more localized oxygen sites. When an oxygen site occurs at, or migrates towards, a Si– Al_2O_3 interfacial region it provides a nucleus for forming special structures in the silicon– Al_2O_3 interfaces, including the formation of some silicon oxide composites. With excessive annealing, as in sample (e), the smaller silicon nanoparticles located near the film surfaces would be oxidized completely, and cease to be a quantum well, so the PL intensity would decrease.

At least four fine-structure PL peaks were observed for every sample, but their locations (as indicated by arrows in figure 3) do not change with different samples. Similar fine structures in the absorption spectra of silicon nanocolloids have been reported as arising from oscillation–electron coupling of the silicon electron transition [15–17]. However, we believe that our observed PL fine structures have a similar origin. Initially the oxygen sites from the Al_2O_3 migrate towards the silicon nanocrystal and combine with it to form special structures in the silicon– Al_2O_3 interfaces. Some oxygen atoms might get so close to the silicon as to produce silicon oxide in the silicon– Al_2O_3 interfaces. The XPS results indicate that different Si–O states with varying degrees of oxidation appeared in the Si– Al_2O_3 interfaces. These different silicon oxides, which can be expressed as $\text{Si-Si}_{4-n}\text{O}_n$ with $n = 0, 1, 2, 3, 4$, together with silicon nanoparticles and their surrounding Al_2O_3 material, give rise to different interface states which could couple with the electronic transitions of the silicon nanoparticles to produce the fine structures observed.

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