Significance of Surface Properties of CdS Nanoparticles

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This work shows that the surface properties of nanoparticles are very important for a particle size near 5 nm in diameter or less. A simple theoretical formula is derived to quantitatively predict the size of nanoparticles for which the surface properties become significant. Experimental evidence using electroluminescence from CdS nanoparticles of 5 nm in diameter is also provided to verify the significance of the surface properties. With different processing procedures or capping layers, the surface or surface states dominate the optical characteristics of the CdS nanoparticles and sometimes play even more important roles than internal atoms.   [DOI: 10.1143/JJAP.42.L610]

Nanoparticles have recently attracted much attention because of their versatile applications.[1,2] For light emission applications, nanoparticles have a great advantage over epitaxially grown quantum dots[3] because they can be applied on many substrates regardless of lattice matching. For example, they can be applied on Si wafers so that Si-based light sources can be monolithically integrated with electronics for optical interconnection[4] or easy control of display devices.[2,5] They can also be applied on bendable substrates like plastic to provide display devices on curved surfaces. While most studies have focused on the quantum effects confined in the nanoparticles due to their low-dimensional structures,[6] we quantitatively discovered that the surface properties of nanoparticles become very important as the particle size decreases to near 5 nm in diameter. In this work, a simple theoretical formula is derived to quantitatively predict the size of nanoparticles for which the surface properties become significant. Experimental evidence is also provided to show that surface atoms play even more important roles than internal atoms.

Surface states are known to be important for many semiconductor devices. For example, interface trap levels play an important role in metal-oxide-semiconductor (MOS) capacitors[7] and the surface roughness at the Si/SiOx interface of n-type metal-oxide-semiconductor field-emission transistors (n-MOSFETs) significantly reduces electron mobility.[8] However, surface states are usually treated as perturbations of normal functions provided by the majority of the atoms of the bulk material. If the perturbation is not negligible, they are mostly deemed as detrimental to the devices[8] and are seldom used for practical purposes. Here we show that when the nanoparticles are near 5 nm in diameter or less, the surface states become more important than the states of internal atoms. Those surface states could then be applied to practical use in addition to quantum states offered by the low-dimensional structures.

The significance of the particle surface can be estimated from the number ratio of surface atoms to internal atoms. For spherical particles with n atoms along the radius, the ratio of atoms in the top layer to internal atoms is given by

$$\frac{n^3 - (n-1)^3}{(n-1)^3}$$

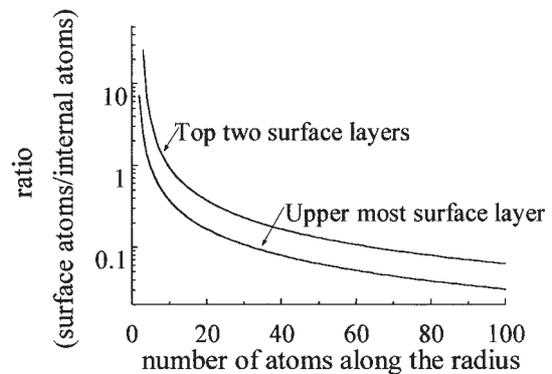If the surface atoms are considered to be those in the top two

Fig. 1. Number ratio of surface atoms to internal atoms vs number of atoms along the radius of the spherical nanoparticle.

layers, the ratio becomes

$$\frac{n^3 - (n-2)^3}{(n-2)^3}.$$

Figure 1 shows the calculated ratio as a function of atom number along the radius according to the above formula. We can see that the number of surface atoms becomes comparable to the number of internal atoms for $n \leqq 10$. An atom typically has a diameter of ~0.25 nm, so the surface atoms could dominate over the internal atoms when nanoparticles are near or less than 5 nm diameter. If the nanoparticles have other shapes, a similar estimation of surface significance can also be made according to their geometrical structures. Because other geometrical structures have a greater surface-to-volume ratio than spheres, the significance of their surfaces is certainly greater than the prediction given in Fig. 1.

To verify surface significance, CdS nanoparticles were prepared using Pietro's method[9] modified for this investigation. Solutions of CdS nanoparticles capped by p-hydroxyl thiophenol for spin-coating were produced. The diameter of the spherical CdS nanoparticles is about 5 nm. The capping thickness is less than 1 nm. The solutions of CdS nanoparticles were spin-coated on Si substrates and then treated under different processing procedures to examine the influence of surface states. The spin-coated layer of the CdS nanoparticles has a thickness of 500 nm. To deliver carriers into the CdS nanoparticles, metal contacts were

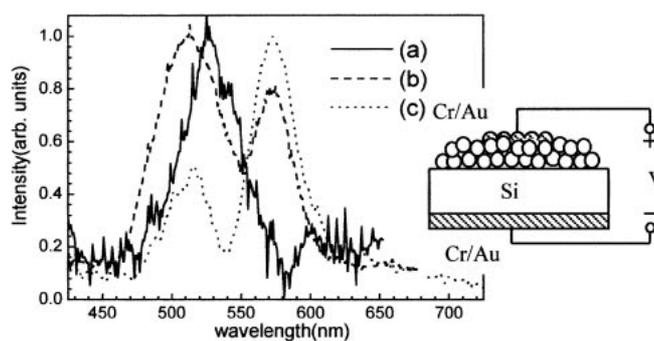Jpn. J. Appl. Phys. Vol. 42 (2003) Pt. 2, No. 6A

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Fig. 2. Measured EL spectra of the CdS nanoparticles treated by different processing procedures. The inset shows the schematic of the CdS-nanoparticle EL device used for spectroscopy measurement.
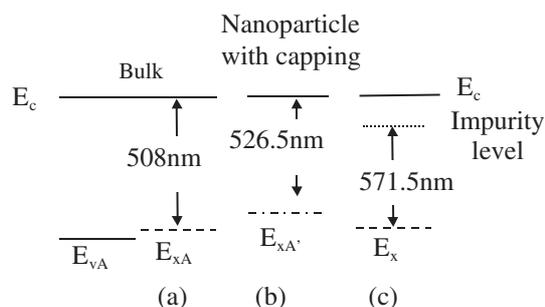

Fig. 3. The schematic of possible transitions between energy states in the CdS nanoparticle. (a) Transition from conduction band to the A-exciton level; (b) transition from the conduction band to the A-exciton level of the CdS nanoparticle modified by capping effect; (c) transition from the oxide-impurity level to the A-exciton level.

Table I. Processing procedures.

A	B	C
Clean Si surface; remove native oxide		
Spin on CdS nanoparticles		Spin on mixture of CdS and SiO$_2$ nanoparticles
Place in vacuum	RTA at 425°C for 5 min	RTA at 425°C for 5 min
Contact evaporation		

formed on top of the CdS nanoparticle layer and the bottom side of the Si substrate, as shown in the inset of Fig. 2. The top semi transparent contact is 3 nm thick Cr and 10 nm thick Au, while the bottom contact is 3 nm thick Cr and 150 nm thick Au.

A summary of these processing procedures is listed in Table I. The only difference between processing procedures A and B is that B involves rapid thermal annealing (RTA) at 425°C for 5 min, while A is conducted at room temperature. For processing procedure C, the CdS nanoparticle solution was first mixed with SiO$_2$ nanoparticles, held in isopropyl alcohol, and then spin-coated onto a clean Si substrate. Afterwards, samples were treated by RTA at 425°C to remove the solvent. Although SiO$_2$ nanoparticles are insulating, the nanometer size allows carriers to quantum-mechanically tunnel through. Thus carriers can be injected into CdS nanoparticles.

The electroluminescence (EL) spectra of the CdS nano-particles are shown in Fig. 2. Spectral curves (a), (b), and (c) correspond to processing procedures A, B, and C, respectively. Each spectrum is normalized with its own maximum value. For easy explanation of the emission spectra, the transition energies observed in spectral curves shown in Fig. 2 are illustrated in Fig. 3. Figure 3(a) shows the transition for bulk CdS. The transition usually involves A, B, and C excitons,[10] and lead to a spectral peak at 508 nm (2.441 eV) for room temperature and 513.7 nm (2.414 eV) for 65°C. Figure 3(b) shows the transition with the capping effect of p-hydroxyl thiophenol, which causes the transition to occur at a wavelength of 526.5 nm. Figure 3(c) shows the transition due to the increase in oxide-impurity levels. The oxide-impurity levels are mainly formed at the particle surface and lead to the emission peak at a wavelength of 571.5 nm.

Spectral curve (a) has a peak at 526.5 nm (2.355 eV),

which is red-shifted from the bulk CdS A-exciton transition energy.[10] Such emission energy is influenced by three factors. First, the small size of the nanoparticles should have the quantum effect that leads to the blue-shift of emission. Second, the injected current should cause the temperature to increase and thus bring about a red-shift. Third, the capping effect of p-hydroxyl thiophenol could modify the electronic states of the CdS nanoparticles and result in red-shift.[11] The total effect of the latter two factors exceeds the first one, so red-shift occurs. In particular, the capping effect has a significant influence on red-shift. Other studies[12,13] also revealed different red-shifts with different capping treatments. Because the capped p-hydroxyl thiophenol prevents the diffusion of oxygen into the nanoparticle, no emission from oxide-impurity levels occurs.

For curve (b), because the samples had been treated at high temperature, the capped p-hydroxyl thiophenol decomposed. As a result, two peaks appear in the emission spectrum. One is at 513.7 nm and corresponds to the A-exciton transition energy of bulk CdS at 65°C. The reason is two-fold. One is because the injected current raises the device temperature to above room temperature. The other is that nanoparticles partly coalesce, so the quantum effect disappears. In addition, the emission at the A-exciton transition energy indicates that the capping effect of p-hydroxyl thiophenol disappears. The other peak is at 571.5 nm, which corresponds to the oxide-impurity level. Because the CdS nanoparticles are now directly exposed to air, oxide impurity is formed at the surface for the corresponding emission.

For curve (c), there are also two peaks at 513.7 nm and 571.5 nm, indicating the disappearance of the capped p-hydroxyl thiophenol and the increase of oxide-impurity levels because the high temperature again causes p-hydroxyl thiophenol to decompose. In addition, the contact of CdS nanoparticles with SiO$_2$ nanoparticles makes the oxide-impurity levels very significant, resulting in the emission at 571.5 nm becoming much stronger than that at 513.7 nm. The measurement also shows that the contribution from the impurity levels causes the light emission for curve (c) to be ten times higher than that for curves (a) and (b). This clearly indicates that surface states become even more important than internal atoms for light emission.

The energy shift caused by the capping effect, shown in

Curve (a), also indicates that surface influence is very significant. A very thin capping layer at the surface is sufficient to force the entire nanoparticle to have different energy levels from those of the nanoparticles without capping, so the emission energy shifts. On the other hand, as the capping layer decomposes, the transition corresponding to the bulk material of nanoparticles is recovered. This indicates that the energy shift caused by the capping effect is not due to the chemical reaction of the nanoparticles with the capping material.

The variation of the emission energy with temperature for nanoparticles is also discovered to be very different from that of the bulk material. In this investigation, CdS nanoparticles capped with SiO_2 were prepared. The EL of the SiO_2-capped CdS nanoparticles was measured from 15 K to room temperature (300 K). Light emission is 10 times stronger at 15 K than at room temperature. The peak emission energy is shown against temperature in Fig. 4 and only slightly varies with temperature. This is very different from the behavior of normal bulk crystals. The variation of band-gap energy with temperature for bulk CdS crystals is also plotted in the same figure for comparison.

The small variation of emission energy with temperature for nanoparticles could be explained again as being due to the significant influence of the surface. The capped layer of SiO_2 influences the thermal behavior of the CdS nanoparticle through two factors. First, its coefficient of thermal expansion is smaller than that of the CdS crystal. Second, it is very thin and behaves like a two-dimensional crystal, so its thermal expansion is not the same as for a conventional three-dimensional crystal.[14] As explained before, a very thin capping layer could cause significant changes to the electron states. It also forces the thermal behavior of the entire CdS nanoparticle to deviate from the usual situation. Therefore, ambient temperature has much less influence on the energy states of nanoparticles, as shown in Fig. 4.

In conclusion, we used CdS nanoparticles to experimentally demonstrate the significance of the nanoparticle surface. With different processing procedures or capping layers, the surface or surface states demonstrate very important characteristics and sometimes dominate over the internal atoms. These phenomena can be easily explained using the number ratio of surface atoms to internal atoms.
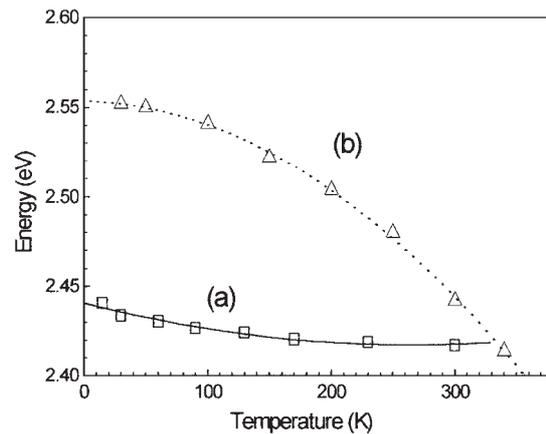
Fig. 4.   (a) Variation of the emission energy from the SiO_2-capped CdS nanoparticle with temperature; (b) variation of the band-gap energy of bulk CdS with temperature.

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