Fabrication of ZnO quantum dots embedded in an amorphous oxide layer

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ZnO quantum dots (QDs) have been fabricated by the growth of SiO_2/ZnO films/Si substrate and subsequent rapid-thermal annealing in a N_2 ambient. Transmission electron microscopy (TEM) results show that the ZnO QDs 3–7 nm in size are formed and embedded in the amorphous silicon oxide interfacial layer when annealed at 850 °C. Photoluminescence (PL) at room temperature from the 850 °C-annealed samples reveals only high-energy emission at about 3.37 eV, while PL at 10 K shows a broad spectra with a tail up to about 3.5 eV. The TEM and PL results indicate that the broad spectra are caused by the presence of the ZnO QDs and hence by the quantum confinement effect.

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ZnO material is of considerable technological importance because of its potential for use in short-wavelength devices, such as ultraviolet (UV) light-emitting diodes and laser diodes. ZnO has interesting characteristics, such as a large direct band gap of 3.37 eV, a large exciton binding energy of 60 meV, and low-power thresholds for optical pumping at room temperature, which is advantageous for excitonic-related device applications. In an effort to realize ZnO-based optoelectronic devices, research on growth and processing, e.g., thin-film growth, dry etching, and ohmic contact, have been performed. In particular, the growth of p-type ZnO has been known to be very difficult to achieve. Recently, Kim et al. reported that p-ZnO epitaxial layers could be grown on sapphire substrates through phosphorus doping followed by a rapid-thermal annealing process. Other research groups showed that nitrogen and As doping processes could be used to grow p-type ZnO layers. In addition, the growth of nanosized ZnO, such as ZnO quantum dots (QDs), ZnO nanowires, and ZnO-based quantum wells, has been largely investigated. In particular, QDs are of great interest because of their unique optical properties and potential for device applications. Kim et al. reported that the self-organized ZnO QDs could be grown on SiO_2/Si substrates by metalorganic chemical vapor deposition, whose size and density are small and high enough, respectively, to result in apparent quantum size effects. In this letter, we report on the fabrication of ZnO QDs embedded in an amorphous silicon oxide layer by the combined process of the growth of a thin film and subsequent rapid-thermal annealing.

ZnO thin films were grown on Si (001) substrates at room-temperature (RT) by radio-frequency (rf) magnetron sputtering. Sintered ZnO (99.999%) and a mixture of Ar and O_2 plasmas were used for sputtering. The working pressure in the growth chamber was kept constant at 10 mTorr. The Ar/O_2 gas ratio and the rf power were 5 and 100 W, respectively. SiO_2 thin films were deposited on the ZnO films by plasma-enhanced chemical vapor deposition. The SiO_2/ZnO/Si substrates were then rapid-thermal annealed (RTA) at temperatures ranging from 450 to 850 °C for 15 s–3 min in a nitrogen ambient. During the rapid thermal annealing process, the ramping rate of the temperature was kept at 25 °C/s. Photoluminescence (PL) of the ZnO films was measured using a He–Cd laser (λ = 325 nm) as an excitation source at RT and 10 K. The microstructures of the samples were analyzed by transmission electron microscopy (TEM). To characterize the extent of interdiffusion between the ZnO films and Si substrates, Auger electron spectroscopy (AES) was performed using a PHI 670 Auger microscope with an electron beam of 10 keV and 0.0236 μA.

Figure 1 shows the PL spectra of the ZnO films grown on the Si substrates, which were annealed for 3 min at 450, 650, and 850 °C. The PL spectra consist of several prominent components. As the annealing temperature increases, the intensities of the PL spectra increase and the PL peaks undergo a blueshift. A comparison of the present results and those reported in literature indicates that the characteristic PL components observed arise from different types of defects. The origin of the PL peak at 2.5 eV is attributed to defect levels associated with oxygen vacancies or Zn interstitials. The

![FIG. 1. PL spectra of the ZnO films grown on the (001) Si substrates annealed for 3 min at temperatures of 450–850 °C.](image-url)
3.02 eV peak is related to Zn vacancies and the PL emission related to free excitons is located at 3.21 eV. One very interesting feature is the observation of the PL peaks at 3.31 and 3.36 eV, which are located at a higher energy with reference to the near-band-edge emission of the ZnO thin film. The 3.31 and 3.36 eV peaks have not been hitherto reported in the RT PL study of ZnO. These features are not associated with the near-band-edge emission, but are believed to originate from the quantum confinement effect. It is noted that the 3.31 and 3.36 eV peaks are fairly intense, which is comparable to that of bulk ZnO. This implies that the high-intensity bands can be attributed to the formation of the ZnO QDs.

Figure 2 shows cross-section TEM images obtained from the ZnO films grown on the Si substrate before and after annealing. For the as-grown sample, there exists a thin amorphous native oxide (SiO$_2$) layer (~3 nm thick) at the ZnO/Si interface region. When the sample was RTA at 850 °C for 3 min, the amorphous oxide layer was grown up to ~20 nm thick. In addition, the high-resolution TEM image clearly shows that there are crystalline ZnO QDs (~3–7 nm in size) embedded in the amorphous oxide layer, as expected from the PL result.

To investigate the formation mechanism of the ZnO QDs embedded in the amorphous oxide layer, AES examination was performed on the ZnO films on the Si substrates before and after annealing at 850 °C. The as-grown sample reveals a well-defined ZnO/Si substrate interface. For the annealed sample, the contents of Si and O at the interface region largely increased compared to those of the as-grown sample. In addition, there is a small increase in the content of Zn at the interface region. This indicates that annealing causes the formation of Zn-incorporated amorphous Si oxide. Considering that the annealing temperature of 850 °C is not high enough to form crystalline SiO$_2$, the crystalline QDs embedded in the interfacial oxide layer are believed to be ZnO. The precise mechanism for the formation of the ZnO QDs is not clear at present. However, the ZnO QDs may be formed as a result of the reaction of the diffused Zn and oxygen atoms inside the amorphous silicon oxide layer. These QDs seem to be responsible for the occurrence of the high-energy emission observed in the PL spectra.

To improve the PL quantum efficiency through an increase of the QD density, ZnO (40 nm)/SiO$_2$ (20 nm) (×3) multilayers were grown and then annealed at 850 °C for different times. Figure 4(a) shows PL spectra (measured at RT) obtained from the annealed samples, exhibiting only high-energy emission related to the ZnO QDs. Annealing the samples at 850 °C caused the intermixing of the ZnO and SiO$_2$ layers, which consequently results in much thinner ZnO layers. Thus, it may be difficult to detect the PL peak of the ZnO layers, since the PL intensity of materials is related to their volume. Another interesting feature is that the PL intensity increases with increasing annealing time. This could be attributed to an increase in the QD density. Furthermore, regardless of the annealing time, the PL peaks in Fig. 4(a) are relatively narrow with a full width half maximum (FWHM) of 100–130 meV. This result indicates that the size of the ZnO QDs is reasonably uniform.

Figure 4(b) shows PL spectra recorded at 10 K from the samples of Fig. 4(a). The main PL peaks were observed at energies of 3.41–3.43 eV with a tail up to about 3.5 eV located at a higher energy relating to the band-edge emission of ZnO films where the free exciton emission is generally located at about 3.377 eV.
semiconductors, such as GaN and ZnO, the formation of QDs causes a blueshift in the PL spectra due to quantum confinement effect.\(^1,3\) Thus, the high-energy shift observed in 10 K PL [Fig. 4(b)] can be attributed to the formation of ZnO QDs, as confirmed by the TEM results, Fig. 2(b). It is shown that the PL spectra are somewhat broad with a FWHM of 32.21–89.96 meV compared with that of undoped ZnO films. This seems to be due to the size distribution of the ZnO QDs.\(^22\)

The blueshift of the main PL peak caused by QDs can be described as follows,\(^25\)

\[
E_{\text{gap,dot}} = E_{\text{gap,bulk}} + \frac{\pi^2 \hbar^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 0.248E_{\text{Ryd}},
\]

where \(E_{\text{Ryd}}\), \(R\), and \(h\) are the bulk exciton binding energy, the radius of the ZnO QDs, and Plank’s constant, respectively. Also, \(E_{\text{gap,bulk}} = 3.377\) eV,\(^1,3\) and \(m_e^* = 0.24m_0\) and \(m_h^* = 1.8m_0\) are the electron and hole effective masses, respectively. Let \(E_{\text{Ryd}}\) be 60 meV without considering an increase of the exciton binding energy caused by quantum confinement. According to the above equation, if the size of the ZnO QDs changes from 3 to 7 nm,\(^24\) the PL peak energy of the ZnO QDs will shift from about 4.15 to 3.51 eV. It is noteworthy that the calculated shifts are much larger than those observed experimentally, Fig. 4(b). This discrepancy is believed to arise from the use of an infinitely high barrier potential with vanishing wave functions at the boundaries of the equation. Regardless of the discrepancy, the shifts observed experimentally and theoretically indicate that the ZnO QDs are formed and the shifts are related to the quantum confinement and size effects.

To summarize, the ZnO QDs with the quantum confinement effects were fabricated by rf magnetron sputtering and subsequent RTA. The TEM results showed that the ZnO QDs 3–7 nm in size were embedded in the amorphous silicon oxide interfacial layer. The PL results showed that the blueshift and broadening of the 10 K PL main peaks are associated with the quantum confinement and quantum size effects. It was further shown from the PL measurements that the optical properties are improved with increasing annealing temperature and time.

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\(^22\) The RT PL results indicated that the present ZnO QDs are reasonably uniform in size, Fig. 4(a). Despite the reasonable uniformity, however, there is still a variation in the size of the ZnO QDs, resulting in the PL spectra with somewhat broad FWHMs.


\(^24\) The TEM results showed that the ZnO QDs varied from ~3 to ~7 nm in size and so this range was used for the calculations.