Optical Properties of CdS Microcrystallite-Doped Al_2O_3 Thin Films Prepared by Rf-Sputtering

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(Received February 6, 1991)

Synopsis. Al_2O_3 thin films containing CdS microcrystallites were successfully prepared by an rf-magnetron sputtering technique. Photoluminescence spectra of films exhibited blue band-edge emission at a higher energy than that of bulk CdS. The spectral change seems to arise from a zero-dimensional confinement of electrons and holes in CdS microcrystallites.

Semiconductor microcrystallites doped in solid matrices, such as glasses and polymers, exhibit a large optical nonlinearity due to the quantum size effect.[1-3] In fact, the diameter of semiconductor microcrystallites in bulk glasses was less than 100 Å, where the microcrystallites could be considered as "quantum dots".

In order to improve the uniformity of the crystallite size, the doping of semiconductors to glasses is carried out by alternative preparation processes such as melt-quenching,[1,2] sol-gel,[4-5] and sputtering methods.[6-8] Sputtering is one of the promising technique for the preparation of various types of semiconductor-doped glass thin-films. Most of the matrices investigated for the films were SiO_2. However, the effects of the matrices on the chemical bond of a doped semiconductor and on the optical properties of the films have not yet been investigated. To clarify the nature of the quantum size effect, it is important to study the relation between the chemical bond of doped semiconductors and the matrices.

In this paper, we report on the preparation of Al_2O_3 thin films containing CdS microcrystallites by the rf-magnetron sputtering technique. The optical properties of the films have also been investigated.

Experimental

Al_2O_3 thin films containing CdS microcrystallites were prepared by a conventional rf-magnetron sputtering systems. The targent used was an Al_2O_3 plate (100 mm in diameter with 5 mm in thickness) with a number of CdS tablets (10 mm in diameter with 1.5 mm in thickness). The concentration of CdS was controlled by changing the number of tablets. The substrates used were SiO_2 glass or GaAs. Sputtering was carried out for 5 h in Ar gas of 5.32 Pa while applying an rf power of 200 W. The substrate was not intentionally heated.

X-Ray photoelectron spectra (XPS) analyses were performed using a Mg$K\alpha$ X-ray source. Details of the measurements were described previously.[8] For calculating the binding energies of each peak, the peak position of the main component in the 1s core level spectrum of carbon was assumed to be 284.6 eV.

The composition of the films was determined by electro-probe microanalysis (EPMA) using the films on GaAs substrates. X-Ray diffraction measurements (XRD) were carried out in order to examine the crystallinity of the films.

The optical absorption spectra were measured in the range from 200 to 700 nm by a spectrometer. The photoluminescence spectra were measured at room temperature by using a spectrofluorophotometer with filters to eliminate the excitation light.

Results and Discussion

Figure 1 shows the Al2p electron spectra of a film with 25.4 cadmium wt%. In this figure, the arrows indicate the standard peak position for Al2p of Al metal[9] and Al_2O_3.[10] The peak of the film coincides with that of Al_2O_3. The Ols electron spectra of the film also coincided with that of Al_2O_3.[10] Thus, Al_2O_3 was

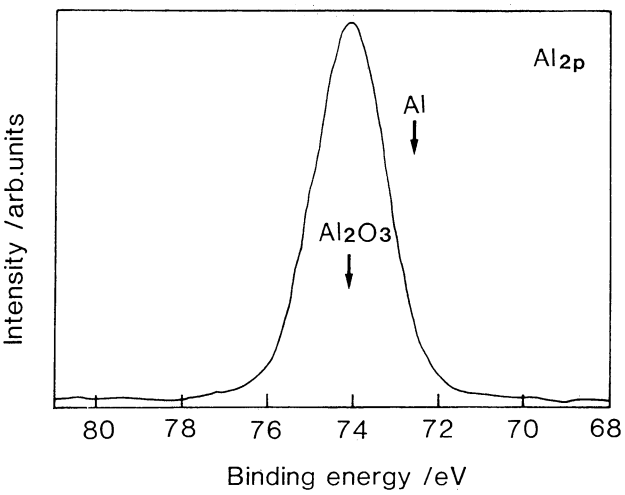

Fig. 1. A12p electron spectra of the film containing 25.4 cadmium wt%. Al indicates the standard peak position of A12p electron spectra of Al metal, Al_2O_3; A12p of Al_2O_3.

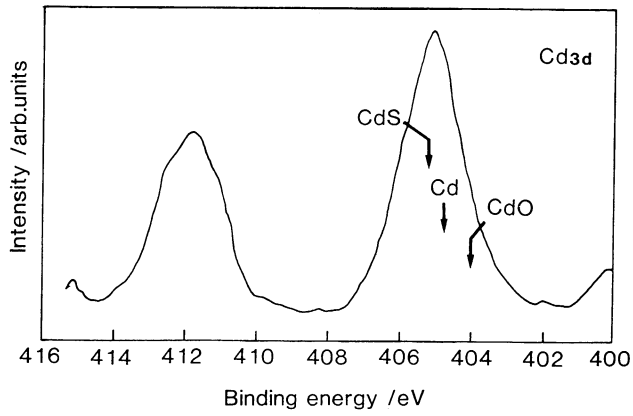

Fig. 2. Cd3d electron spectra of the film containing 25.4 cadmium wt%. CdS indicates the standard peak position of Cd3d electron spectra of CdS, Cd; Cd3d of Cd metal, CdO; Cd3d of CdO.

successufully formed by rf-magnetron sputtering.

Figure 2 shows the Cd3d electron spectra of the film. The film examined was the same as that shown in Fig. 1. The spin-doublet of $Cd3d_{3/2}$ and $Cd3d_{5/2}$ is given in Fig. 2. In this figure, the arrows indicate the peak position of the Cd3d electron spectra for CdS, Cd metal, and CdO.[11] These experimental peak positions are close to those of the standard CdS. The Cd and S atoms were reasonably doped in the Al_2O_3 matrix as CdS. In conclusion, CdS was successfully doped into Al_2O_3.

The XRD patterns of the films showed no reflection lines, suggesting that the Al_2O_3 thin film was amorphous. The crystal system of the doped CdS could not be identified in this expepriment. The doped CdS was too small to identify its crystal system by the XRD patterns.

By means of the EPMA measurements, the ratio of S to Cd atoms (S/Cd) of a film containing 25.4 cadmium wt% was estimated to be 0.83. This is because the reevaporation of S atoms from the substrates was larger than that of Cd atoms under the experimental condition. Although the Cd and S atoms were reasonably doped as CdS by XPS analyses, it seemed that part of the Cd atoms were doped as Cd metal and CdO.

Figure 3 shows the transmission spectra measured at room temperature for Al_2O_3 thin films containing CdS: (a) film with 10.9 cadmium wt%, (b) 20.0 wt%, and (c) 25.4 wt%. The thickness of the films was 0.4—0.6 μm. The films, thus, show interference oscillations (the waves in the spectra) in the transparent region. The three spectra are different in the region below 500 nm. From the figure, the power of the absorption coefficient, α, was plotted against the photon energy, $h\nu$. The α^2 varied linearly with $h\nu$, indicating that the direct interband transition took place. The optical band-gap energy, E_g, of the film (a) was estimated to be 2.66 eV from the α^2 vs. $h\nu$ plot. The E_g of the film (a) is clearly blue-shifted by about 0.25 eV, compared with that of the bulk CdS (2.41 eV). With increasing the concentration of CdS, E_g decreased. This is because the diameter of CdS microcrystallites became large.

In spherical semiconductor quantum dots enclosed by the insulating matrix, the blue shift, ΔE_g, is expressed by

$$\Delta E_g = h^2/8a^2\mu \quad (2)$$

where a and μ are the radius of the spherical dots and the reduced effective mass of an electron-hole pair, respectively; h is Planck's constant. This equation is valid when the radius, a, is smaller than the Bohr radius of the bulk exciton.[12] The diameter of the CdS-microcrystallites in the film (a) was 57 Å, as calculated by Eq. 2. The blue shift of an Al_2O_3 thin film with 25.4 cadmium wt% was 0.04 eV larger than that of SiO_2 thin films with 35.9 cadmium wt%.[8] The reasons for the larger blue shift of the films have not been clarified. However, the larger shift seems to represent the difference in the size between the CdS in an Al_2O_3 thin film and that in a SiO_2 thin film. Direct observations of CdS in Al_2O_3 thin films is the next problem.

The effect of the dielectric constant of the matrix on the blue shift has also been reported by Brus et al.[13] They calculated the blue shift for CdS microcrystallite in vacuum using an equation with three energy terms; kinetic, coulomb, and polarization. The polarization term was influenced by the dielectric constant of the matrices. According to the calculation: 1) the blue shift became small with increasing the value of the dielectric constant of matrices and 2) the contribution of the polarization term to the blue shift was rather small in comparison with the other two terms. The dielectric

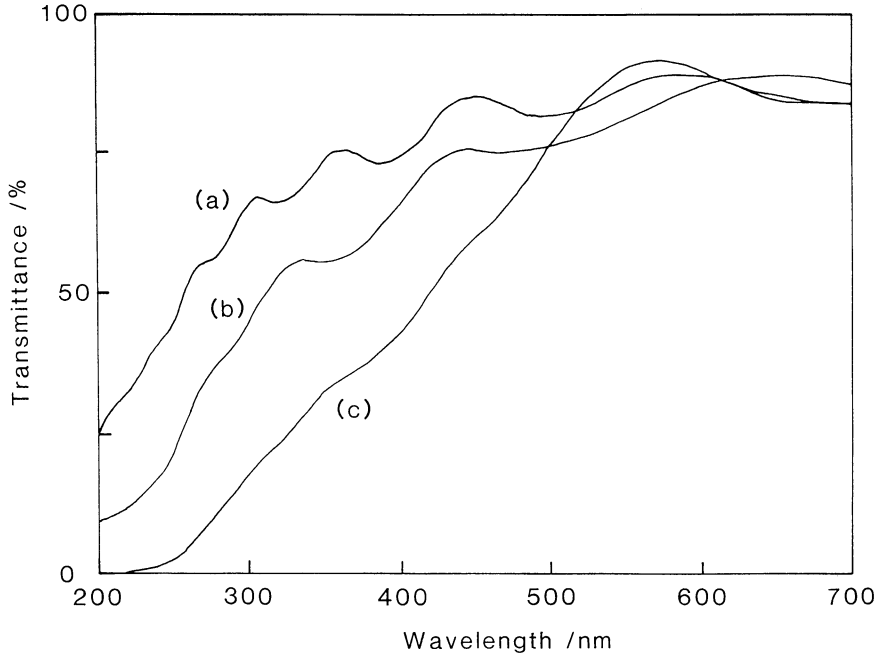

Fig. 3 Optical transmission spectra of the films at room temperature. (a) the films with 10.9 cadmium wt%, (b) 20.0wt%, and (c) 25.4 wt%.

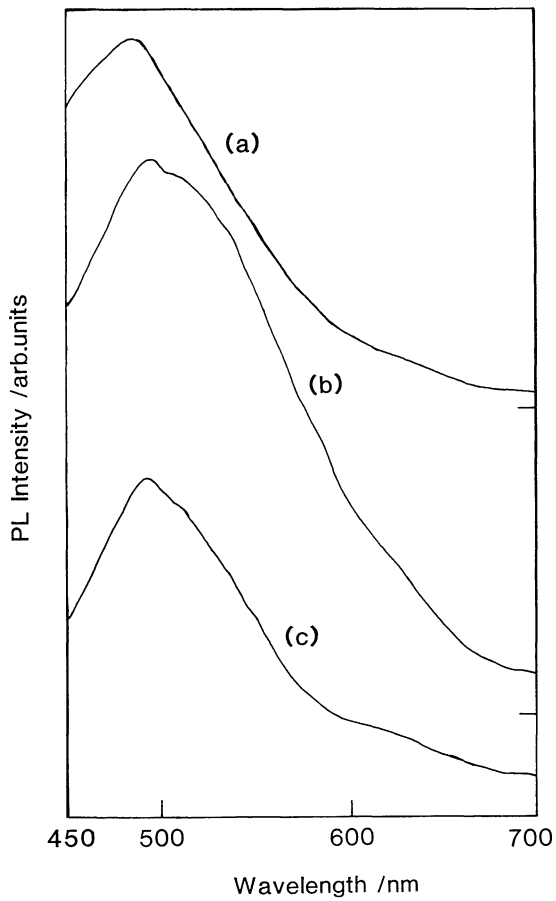

Fig. 4. Photoluminescence spectra of the films at room temperature. (a) the film with 10.9 cadmium wt%, (b) 20.0 wt%, and (c) 25.4 wt%.

constants of Al_2O_3 and SiO_2 were 8.6 and 4.5, respectively. Therefore, the larger blue shift of the Al_2O_3 thin films with CdS seems to be due to the smaller size of CdS.

Figure 4 shows the photoluminescence (PL) spectra at room temperature measured for films (a), (b), and (c). The emission of the films appears below 500 nm. It is reported that CdS deposited in porous vycor glass showed emission associated with a sulfur vacancy at 680 nm and band-edge emission at 520 nm.[14] The PL spectrum of CdS deposited in porous vycor glass was close to that of bulk CdS. The band-edge emission of the films examined were clearly blue-shifted in comparison with that of bulk CdS. The emission of the films is broad, suggesting that the size distribution of doped CdS was rather large. With increasing concentration of CdS, the PL peak position of the films shift to lower energy. In accordance with the results of the optical transmission spectra, the energy of the band-edge emission of the films is higher than that of bulk CdS. The shift to higher energy is attributed to a low-dimensional quantum size effect due to the confinement of electrons and holes in CdS microcrystallites.

The authors would like to thank Drs. T.Nitta and A.Nishino for their continuous encouragement. A part of this work was performed under the management of Japan High Polymer Center as a part of the R&D of Nonlinear photonics materials supported by NEDO (New Energy and Industrial Technology Development Organization).

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