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Two-photon-excited green emission and its dichroic shift of oriented thin-film CdS on glass formed by laser deposition

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The photoluminescence of oriented thin-film CdS on glass formed by laser deposition was investigated employing 200 fs, 1.54 eV laser pulses at room temperature. The ultrafast excitation caused a two-photon absorption process, which results in purely green emission at the band gap. The spectra are fitted very well by the application of the van Roosbroeck–Shockley relation, density of states, and Urbach’s rule demonstrating the intrinsic character of the radiative recombination. It is further shown that the energy position of the emission peak depends on the polarization of the impinging laser beam due to the dichroism of the highly oriented films. © 2002 American Institute of Physics. [DOI: 10.1063/1.1432756]

Modern photonics and optoelectronics address the relevant problem for many device applications of obtaining stable sources of green photoluminescence. Eye adapted light emission devices (LED’s) are of particular interest. Thin-film devices based on the II–VI compound semiconductor CdS appear to be a promising concept for adapted LED’s since the expected band gap emission at about 2.45 eV at room temperature lies very close to the highest sensitivity of the human eye. Indeed, in previous articles, it was demonstrated that thin-film CdS on glass formed by pulsed-laser deposition (PLD) at 1064 nm exhibit green light emission and lasing at 2.49 eV at room temperature. The films crystalize in a wurtzite structure and the c axis, which runs along the (001) direction, is perpendicularly oriented with respect to the glass surface independently of the incident laser intensity (laser fluence) applied for the PLD. On the other hand, CdS films on glass formed by PLD at 355 nm show different features from the crystallographic and optoelectronic points of view. The films also exhibit a wurtzite structure but the orientation of the (001) direction depends on the laser fluence applied to form the film; at 2 J cm−2 and ≥4 J cm−2, the (001) direction is perpendicular and parallel to the glass surface, hereafter referred to CdSc and CdSc, respectively. The details about the formation of oriented thin-film CdS by PLD have been published in previous articles.5,6 The photocurrent and transmission spectra measured with polarized light reflect the dichroism of the films by shifting the onset of the interband absorption of CdSc 55 meV below that of CdSc.7 The single-photon photoluminescence (SPL) excited with the continuous wave 325 nm line of a He–Cd laser, however, does not reflect the dichroism of the films and shows an opposite shift in energy. The emission peak of CdS and CdS centers at 2.45 eV and 2.27 eV, respectively.

In this letter, we demonstrate that the dichroism of oriented thin-film CdS is reflected by the emission properties if the bulk is excited. For this purpose two-photon excitation in the femtosecond regime at 1.54 eV was used.

The samples investigated were prepared by PLD by guiding the 355 nm emission of Nd:YAG laser (pulsed width 5 ns, repetition rate 10 Hz) onto a target of sintered CdS (99.999%) powder. The distance between the target and the fused silica glass substrate was 3 cm. During the PLD process, the substrate temperature and ambient pressure were kept at 250 °C and 10−3 Pa, respectively. The samples were formed with laser fluences of 2 J cm−2 and 5 J cm−2, resulting in CdS and CdS, as demonstrated by the x-ray patterns in Fig. 1. We should stress that the possibility to control the dichroism of thin-film CdS is interesting especially for the fabrication of photonic structures with a periodic dielectric structure.9,10 By means of transmission spectroscopy, the thickness of the films was found to be 1.70 μm and 0.82 μm for CdS and CdS, respectively.

The photoluminescence of the films was excited by an ultrafast laser system, which delivers 200 fs pulses with a repetition rate of 249 kHz at 1.54 eV (804 nm) and an energy per pulse of 1.5 μJ. The beam was focused to an e−2 radius of ∼30 μm resulting in an intensity of 200 GW cm−2. The laser beam exhibits linear horizontal polarization and therefore by placing CdS and CdS in the beam, the direction of the electric field vector is perpendicular (E∥c) and parallel (E∥c) to the c axis. The excitation caused clearly visible green light emission and was detected by a fiber optics spectrometer placed behind the sample. The emission intensity depends on the square of the impinging intensity revealing...
the two-photon character of the phenomenon. Figures 2(a) and 2(b) show the photoluminescence spectrum due to two-photon excitation (TPL) of CdS\(_{\perp}\) and CdS\(_{\parallel}\). The symbols show the experimental data and the solid lines the fit according to the van Roosbroeck–Shockley relation, i.e., the principle of detailed balance,\(^{11}\)

\[ I(h\nu) \propto \frac{(h\nu)^2 \alpha(h\nu)}{\exp(h\nu/kT_c) - 1}, \]

where \(h\nu\) is the photon energy, \(\alpha\) is the absorption coefficient, \(k\) is the Boltzmann constant, and \(T_c\) is the carrier temperature. The absorption coefficient versus energy is calculated by the density of states and Urbach’s rule, and is given by\(^3\)

\[ \alpha(h\nu) = \begin{cases} \left(\frac{h\nu - E_g}{2}\right)^{1/2} & \text{if } h\nu \geq E_{cr} \\ \left(\frac{E_{cr}}{h\nu - E_g}\right)^{1/2} & \text{if } h\nu \leq E_{cr}, \end{cases} \]

and

\[ \alpha(h\nu) = A \sqrt{\frac{kT}{2\sigma}} \exp \left[ \frac{\sigma}{kT}(h\nu - E_{cr}) \right] \]

where \(E_g\) is the band gap energy, \(A = 2 \times 10^5 \text{ cm}^{-1} (\text{eV})^{-1/2}\) represents \(\alpha(h\nu)\) for \(h\nu \geq E_g\). \(T\) is the lattice temperature, and the crossover energy between Eqs. (2) and (3) is expressed by \(E_{cr} = E_g + kT/2\sigma\). The dimensionless phenomenological parameter \(\sigma\) is a measure for the pureness of the material.\(^3\) For undoped intrinsic CdS, it is generally accepted that \(\sigma = 2.17\). Numbers below 2.17 are typical for thin-filmCdS and indicate tail states beyond the intrinsic density. The following parameters were used to fit the data for CdS\(_{\perp}\) in Fig. 2(a), \(E_g = 2.33\) eV, \(kT_c = 25\) meV, \(T_c = 55\) meV, and \(\sigma = 0.7\), and for CdS\(_{\parallel}\) in Fig. 2(b), \(E_g = 2.37\) eV, \(kT_c = 25\) meV, \(kT_c = 60\) meV, and \(\sigma = 0.6\). As it is known from photoluminescence investigations on GaAs, the carriers attain a temperature much higher than that of the lattice.\(^12\) It is noteworthy that the emission takes place according to the straightforward principle of detailed balance since CdS is known to show peculiar emission features far from the ideal case.\(^13\)

As shown in Figs. 2(a) and 2(b), the TPL peak is at 2.35 eV and 2.40 eV for CdS\(_{\perp}\) and CdS\(_{\parallel}\), respectively. In order to check if the energy shift of 50 meV is subject to the dichroism corresponding to the polarizations \(E_{\parallel}\) and \(E_{\perp}\), it is of importance to calculate the penetration depth of the fs-laser beam,

\[ d_p = \frac{1}{\beta I_0 (e - 1)}, \]

where \(\beta (=6.4\ \text{cm/GW})\)\(^{14}\) is the two-photon absorption coefficient and \(I_0\) is the impinging laser intensity (=200 GW cm\(^{-2}\)), and find \(d_p = 13\ \mu\text{m}\). Since the film thicknesses are clearly shorter than \(d_p\), the samples are homogeneously excited and the spectra in Figs. 2(a) and 2(b) represent the bulk emissions of the samples. The curves of Figs. 3(a) and 3(b) show the first derivative of the transmittance \((\Delta T)/d\nu\) of CdS\(_{\perp}\) and CdS\(_{\parallel}\) with respect to energy \((d\Delta T/d\nu)\). As indicated, the \(\Delta T\) threshold of CdS\(_{\perp}\) and CdS\(_{\parallel}\) takes place at 2.45 eV and 2.51 eV, respectively. Hence, in good agreement with our previous results shown in Refs. 7 and 8, and with the...
The pulse duration of 200 fs. This tremendous carrier density evokes charge carrier densities of up to $10^{19} \text{ cm}^{-3}$ within the pulse duration of 200 fs. This tremendous carrier density changes the emission behavior of the films in favor of the band gap emission.

In conclusion, excitation with 200 fs laser pulses at 1.54 eV causes room temperature single peak band gap emission in thin-film CdS$_i$ and CdS$_j$ due to two-photon absorption. The spectra are very well modeled by the principle of detailed balance. As a result, under high two-photon excitation, thin-film CdS formed by PLD can be considered as an intrinsic semiconductor. This observation is of considerable importance for the field of nonlinear optics since it demonstrates that excitation in the femtosecond regime reveals the intrinsic bulk features of the films, which are decisive in the fabrication of light emitting and laser devices. The work also stresses the possibility of PLD to form anisotropic CdS films. By comparing the emission spectra with the transmittance of the films, it was shown that the energy separation of 50 meV between the TPL peaks of CdS$_i$ and CdS$_j$ is caused by the dichroic shift of the absorption edge.