The influence of self-absorption on the photoluminescence of thin film CdS demonstrated by two-photon absorption

B. Ullrich[a], R. Schroeder[a,b], W. Graupner[c] and H. Sakai[d]

[a] *Department of Physics and Astronomy, Centers for Materials and Photochemical Sciences [*], Bowling Green State University, Bowling Green, Ohio 43403-0224, USA*
[b] *Department of Physics, Virginia Tech, Blacksburg, Virginia 24061-0435, USA*
[c] *eMagin Corporation, 2070 Route 52, Hopewell Junction, New York 12533, USA*
[d] *Faculty of Engineering, Hiroshima Kokusai Gakuin University, 6-20-1 Nakao, Aki-ku, Hiroshima 739-0321, Japan*

Abstract: By means of two-photon excited photoluminescence, we demonstrate the influence of self-absorption on the emission properties of thin (1.5 µm) film CdS formed by laser ablation. The excitation of the sample is performed with 200 fs pulses at 804 nm (1.54 eV). The photoluminescence spectrum takes the form of a single peak centered at 510 nm (2.43 eV) at 300 K. The spectrum is shifted about 45 meV to lower energies with respect to the photoluminescence excited by one photon absorption. By fitting the photoluminescence spectra with the Roosbroeck-Shockley relation and Urbach's rule, it is shown by Beer's law that the shift is caused by self-absorption. The results further provide evidence of low impurity concentration and excellent surface quality. They also confirm the outstanding optical properties of thin film CdS formed by pulsed-laser deposition and suggest the application of the films for effective up-conversion materials in ultra-fast experiments.
©2001 Optical Society of America

OCIS codes: (310.6860) Thin films, optical properties; (190.0190) Nonlinear optics

References and links

1. A. V. Nabok, A. K. Ray, A. K. Hassan, "Electron beam stimulated formation of CdS nanoparticles within calixarene Langmuir-Blodgett films," J. Appl. Phys. **88**, 1333-1338 (2000) and refs. therein.
2. C. Bouchenaki, B. Ullrich, J. P. Zielinger, "Luminescence investigations performed on differently prepared thin CdS layers," J. Lum. **48/49**, 649-654 (1991).
3. O. Zelaya-Angel, A. E. Esparza-Garcia, C. Falcony, R. Lozada-Morales, "Photoluminescence effects associated with thermally induced crystalline structure changes in CdS films," Solid State Commun. **94**, 81-85 (1995).
4. C. Mejía-García, A. Escamilla-Esquivel, G. Contreras-Puente, M. Tufiño-Velázquez, M. L. Albor-Aguilera, O. Vigil, L. Vaillant, "Photoluminescence studies of CdS films grown by close-spaced vapor transport hot walls," J. Appl. Phys. **86**, 3171-3174 (1999).
5. B. Ullrich, D. M. Bagnall, H. Sakai, and Y. Segawa, "Photoluminescence properties of thin CdS films on glass formed by laser ablation," Solid State Commun. **109**, 757-760 (1999).
6. B. Ullrich, H. Sakai, and Y. Segawa, "Optoelectronic properties of thin film CdS formed by ultraviolet and infrared pulsed-laser deposition," Thin Solid Films **385**, 220-224 (2001).
7. D. M. Bagnall, B. Ullrich, X. G. Qiu, Y. Segawa, and H. Sakai, "Microcavity lasing of optically excited cadmium sulfide thin films at room temperature," Optics Letters **24**, 1278-1280 (1999).
8. B. Ullrich, D. M. Bagnall, H. Sakai, and Y. Segawa, "Photoluminescence and lasing of thin CdS films on glass formed by pulsed-laser deposition," J. Lum. **87-89**, 1162-1164 (2000).
9. J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).

[*] Contribution#418 from the Center for Photochemical Sciences

10. R. Braunstein and N. Ockman, "Optical double-photon absorption in CdS," Phys. Rev. **134**, A499-A507 (1964).
11. J.-F. Lami and C. Hirlimann, "Two-photon excited room-temperature luminescence of CdS in the femtosecond regime," Phys. Rev. B **60**, 4763-4770 (1999).
12. B. Ullrich and C. Bouchenaki, "Bistable optical thin CdS film devices: All-optical and optoelectronic features," Jpn. J. Appl. Phys. **30**, L1285-L1288 (1991).
13. W. Van Roosbroeck and W. Shockley, "Photon-radiative recombination of electrons and holes in germanium," Phys. Rev. **94**, 1558-1560 (1954).

1. Introduction

The II-VI compound semiconductor CdS has various appealing features for technical applications, such as the "green bandgap" at around 2.45 eV, dichroism and a spectral dependence of the photocurrent action spectrum, which is very similar of that of the human eye. Furthermore, CdS enables the rather easy realization of nanoparticles [1]. Hence, large area thin CdS films on cheap and easily available substrates are of considerable interest for the formation of smart photonic structures. However, the properties of CdS films are far from theoretical expectations mainly due to an unbalanced stoichiometry. The largest divergence between theory and experiment is observed in the photoluminescence features. Films formed by vacuum evaporation, spray pyrolysis, closed space vapor transport and chemical bath deposition on various substrates (glass, pyrex and CaF_2) have been investigated [2-4]. As a result, at 300 K, either no photoluminescence was observed or the spectra are clearly shifted to the red spectral range with respect to the bandgap. It was shown however, that by pulsed-laser deposition the emission features of CdS films are appreciable improved. Thin film CdS deposited by pulsed-laser deposition on glass shows green photoluminescence at 2.45-2.48 eV at 300 K [5,6]. Beyond that, the observation of microcavity lasing at 2.45 eV of an optically pumped sample was reported [7,8].

In this paper, we demonstrate the influence of self-absorption on the photoluminescence of thin film CdS by two-photon photoluminescence. The investigation of two-photon photoluminescence is of both fundamental and technological importance since a nonlinear absorption process excites two-photon photoluminescence, i.e., two phase-coherent photons excite one electron to twice the energy of the single photon. As a consequence, electron-hole pairs are generated by this cooperative phenomenon, resulting in bandgap photoluminescence [9]. Two-photon photoluminescence in CdS is investigated since the early 1960's [10] and regained considerable interest recently because of the appearance of femtosecond lasers, whose excitation causes pure carrier effects without absorption variations due to undesired thermal effects [11].

2. Experiment

The sample investigated was formed on glass by pulsed-laser deposition at 1064 nm using the fundamental emission of a Nd:YAG laser with a pulse width of 150-180 μs and a repetition rate of 10 Hz. The deposition was performed by heating the CdS target of 99.999% purity with a laser fluence of 3 J cm^{-2}. During the ablation process the ambient pressure and substrate temperature were kept at 10^{-3} Pa and at 250°C, respectively. The thickness of the sample is 1.5 μm and x-ray analysis showed that the film exhibits wurtzite structure with the *c*-axis orientation perpendicular to the film surface. The optical excitation of the sample was performed with a 30 W argon laser pumping a femtosecond oscillator and amplifier. The system delivers 200 fs pulses at 804 nm (1.54 eV) with a repetition rate of 249 kHz. The energy per pulse is up to 3 μJ resulting in focused (100 μm diameter) intensities of 190 GW cm^{-2}. The two-photon photoluminescence signal was measured by guiding the emitted light via a glass fiber, which was tilted by approximately 30° with respect to the film plane, to a monochromator with attached charged-coupled device camera. The single-photon photoluminescence experiment was carried out with a continuous-wave (cw) line (325 nm) of

a He-Cd laser delivering to the sample an intensity of 3 W cm^{-2}. All spectra are measured at 300 K.

3. Results

In order to show that we observe two-photon photoluminescence, we have to demonstrate that the photoluminescence intensity (I_{out}) depends upon the square of the incident intensity (I_{in}). Indeed, the power law $I_{out} \propto I_{in}^2$ is found, as it is seen in Fig.1. Figure 2 shows the two-photon photoluminescence spectrum measured with an excitation intensity of 80 GW cm^{-2}.

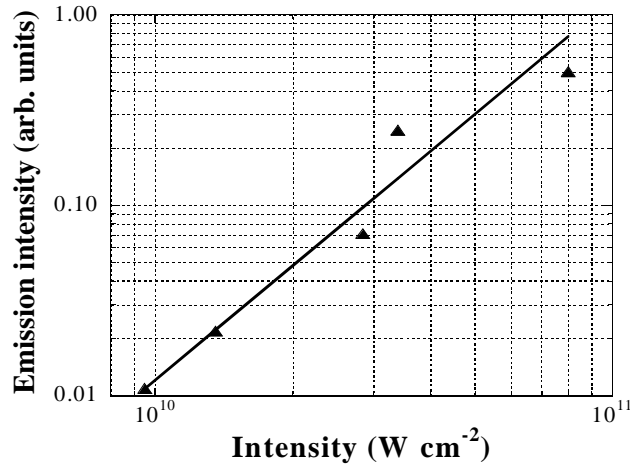Fig.1: Two-photon photoluminescence intensity vs. incident intensity. The line represents the power law $I_{out} \propto I_{in}^2$.
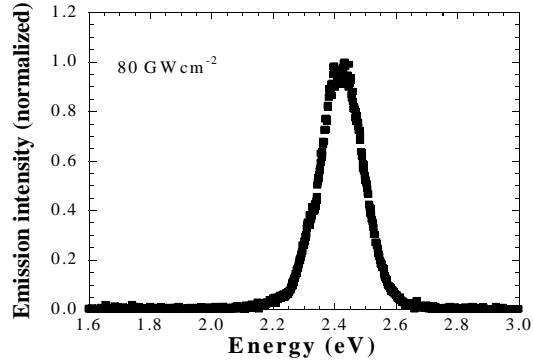

Fig. 2: Two-photon photoluminescence spectrum at an excitation intensity of 80 GW cm^{-2}.

Notably, no photoluminescence signal is observed in the red region of the spectrum, indicating a low impurity concentration. The energy position however, at 2.43 eV lies 45 meV below the peak energy, which is found with the He-Cd laser. This shift is explained by self-absorption due to different excited volumes. The 804 nm line of the fs-laser system penetrates the sample, whereas the 325 nm emission of the He-Cd laser is absorbed at the surface region (depth ≈ 0.1 μm) of the film. In other words, the single-photon photoluminescence is mainly surface emission, unaffected by self-absorption, and the two-photon photoluminescence in Fig. 2 represents the externally detectable fraction of the integrated photoluminescence over the excited volume of the film. In the following, we prove our qualitative statements quantitatively.

For this purpose the knowledge of the absorption coefficient of the samples is necessary. Most straightforwardly, one might believe that the absorption coefficient is easily measured via transmission measurements. However, we tried this approach several times in the past and it turned out that we are not able to fit photoluminescence spectra satisfactorily by absorption data achieved by transmission experiments. One reason is that we need quite accurate data for the absorption coefficient in the opaque range of the films above 2.45 eV, which are rather difficult to measure with transmission techniques and, a further difficulty is that Fabry-Perot fringes below 2.35 eV start to influence the transmission spectra. Much better results have been achieved by calculating the absorption coefficient using the density of states distribution and the modified Urbach rule [5,12],

$$\alpha(E) = A_0 \sqrt{E - E_g} \quad \text{for} \quad E \geq E_{cr} \tag{1}$$

and

$$\alpha(E) = A_0 \sqrt{\frac{kT}{2\sigma}} \exp(\frac{\sigma}{kT}(E - E_{cr})) \text{ for } E \leq E_{cr}, \tag{2}$$

where A_0 ($=2\times10^5$ cm^{-1} (eV)$^{-1/2}$) is a constant, which represents the saturation of $\alpha(E)$ for energies above the bandgap energy E_g, kT (=0.025 eV) is the thermal energy and σ is a dimensionless phenomenological fitting parameter, which is a measure for the intrinsic nature of the absorption process. The crossover energy E_{cr} is given by $E_{cr}=E_g+kT/(2\sigma)$. Absorption coefficient and emission intensity are related via the Roosbroeck-Shockley equation [13],

$$I(E) \propto \frac{E^2\alpha(E)}{(\exp(E/kT_c)-1)}, \tag{3}$$

where k is the Boltzmann constant and T_c is the actual carrier temperature. The following values were used to fit the two-photon photoluminescence spectrum in Fig. 3, E_g=2.400 eV, σ=0.84 and kT_c=0.048 eV. In a previous paper [5], which shows photoluminescence experiments with the cw line of the He-Cd laser at 300 K, we found kT_c=0.038 eV and σ=0.84. The increase of T_c indicates an increase of the photocarrier density in the current experiment and the identity of σ shows that the absorption edge of the film exhibits the same slope for bulk and surface region of the film.
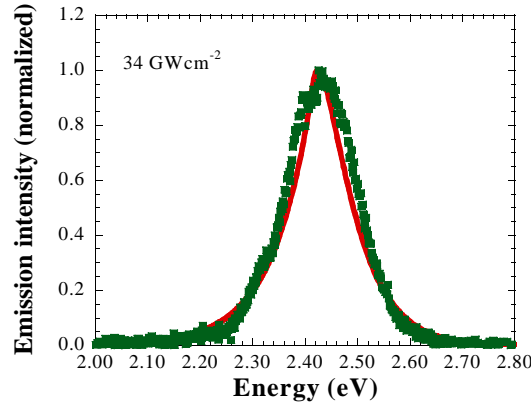

Fig. 3: Two-photon photoluminescence spectrum at an excitation intensity of 34 GW cm^{-2} (green squares) and theory (red line).

Applying basically Beer's law, the relation between $I(E)$ and the undisturbed intensity (I_0) is expressed by [9]

$$I_0(E) = \frac{\alpha(E)tI(E)}{(1-R)(1-\exp[-\alpha(E)t]}, \qquad (4)$$

where R (=0.2) is the reflection coefficient and t (=1.5 μm) is the thickness of the sample.

Figure 4 shows the comparison of the two-photon photoluminescence spectrum $I(E)$ [curve (a)] and its corrected "intrinsic" shape $I_0(E)$ [curve (b)] according to Eqs. (1)-(4). In addition, the single-photon photoluminescence spectrum is shown [curve (c)]. It is seen that the corrected two-photon photoluminescence spectrum coincides very well with the peak position and the high energy decay of the single-photon photoluminescence spectrum. Hence, the density of states at the surface and the bulk of the film are the same and the spectra are simply shifted by self-absorption and the energy position of the single-photon photoluminescence maximum is not influenced by surface defects. However, besides the fact that the single-photon photoluminescence spectrum is clearly dominated by the green emission, the films are not completely free of photoluminescence caused by impurities [7]. In fact, the rather flat decay of curve (c) below 2.44 eV is caused by the influence of impurities below the bandgap. Reinstating the aforementioned increased carrier temperature with fs-laser pumping in comparison with cw laser excitation, we think that the fs-pulses create such a high electron-hole density that only the band-to-band transition at the bandgap acts as the only effective radiative recombination mechanism and the remaining red emission is completely suppressed. A similar observation was reported for CdS crystals [10].
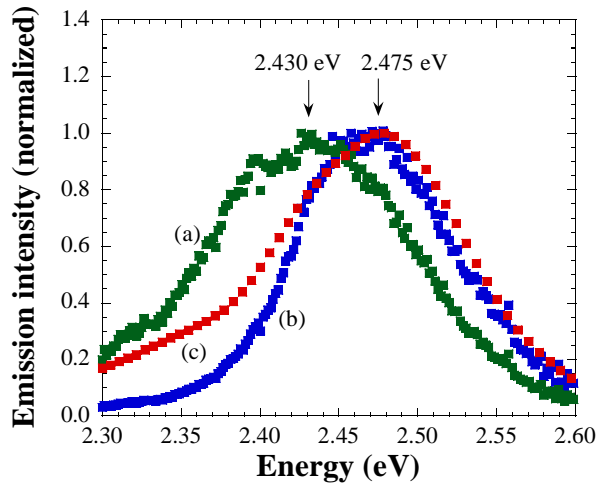

Fig.4: (a) Two-photon photoluminescence spectrum in Fig.2; (b) corrected two-photon photoluminescence spectrum; (c) single-photon photoluminescence spectrum.

4. Conclusion

In conclusion, as far as we are aware, the current study is the first application of two-photon spectroscopy to study self-absorption in thin film CdS. The results further show the capability of pulsed-laser deposition to form thin film CdS on glass with outstanding emission properties, which suggest the appealing technological challenge to consider this material for ultra-fast up-conversion applications in the green range of the spectrum.