

GROWTH AND CHARACTERIZATION OF CdZnS THIN FILMS BY SHORT DURATION MICRO WAVE ASSISTED-CHEMICAL BATH DEPOSITION TECHNIQUE

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Cadmium Zinc sulfide (CdZnS) thin films have been deposited on to ultrasonically cleaned glass substrates with various Zn^{2+} concentrations by Micro wave assisted-Chemical Bath Deposition (M_{wave} -CBD) technique. The structural studies were carried out by using X-ray diffraction (XRD) studies as a function of Zn^{2+} concentration. The surface morphological/ surface texture of the deposited films was characterized by SEM and AFM analysis. The optical band gap (E_g) tunability of the deposited films for various Zn^{2+} concentrations was successfully demonstrated by UV-VIS-NIR spectroscopy. The photoluminescence (PL) properties of the deposited CdZnS films have been investigated by PL emission spectroscopy.

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1. Introduction

Nano crystalline semiconductors of group II-VI have potential applications in many technical fields, including photo luminescence, solar cells and photo voltaic applications [1-3]. The control of the composition of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nano particles may lead to the development of ideal materials for short wavelength diode laser applications. Semiconducting CdZnS materials and also the related ternary compounds are promising materials for high density optical recording and for blue or even UV laser diodes. These applications are based on the structure of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ which exhibit fundamental absorption edges that can varied from green to UV [4-9]. In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ alloys has led to a decrease in window absorption loss and an increase in the short circuit current [10, 11]. In the present work, CdZnS thin films have been deposited by short duration Micro wave assisted CBD technique. The structural, surface morphological / surface texture analysis of the deposited films was investigated by XRD, SEM and AFM analysis. The optical absorption, transmittance and tunability of band gap (E_g) by the addition of Zn^{2+} concentration have demonstrated by using UV-VIS-NIR spectroscopy. The photoluminescence properties of the deposited films were characterized by the PL emission spectrophotometer at the excitation wavelength 370 nm. The investigated results are presented and discussed in detail.

2. Experimental

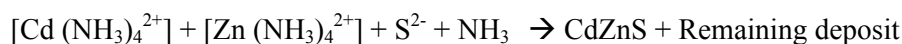
Analytical grade of CdCl_2 , ZnCl_2 and $\text{NH}_2\text{-CS-NH}_2$ were used as the source materials for Cd^{2+} , Zn^{2+} and S^{2-} ions, respectively. The volume ratios of the stock solution conditions are present in the table.1. The microscopic glass slides with ($1 \times 1 \text{ cm}^2$) are cleaned by using chromic acid for 24 hours at room temperature and placed vertically inside the chemical bath. The deposition was carried out for very short duration 600 seconds when compared to the usual CBD deposition. The Micro wave Owen was set at the temperature of 90°C . The deposition of a thin film takes place

through the condensation of the metals and sulfur ions on the initial layer, which acts as a catalytic surface.

Table 1. represents the experimental details of the three different Zn^{2+} concentrations in the formation of chemical bath to deposit CdZnS thin films.

CdCl ₂ (0.2M) ml	NH ₄ Cl (0.2M) ml	NH ₄ OH (2 M) ml	NH ₂ -CS-NH ₂ (0.4 M) ml	distilled-H ₂ O ml	ZnCl ₂ (0.2 M) ml
7.5	20	20	7.5	60	Lower
7.5	20	20	7.5	60	Intermediate
7.5	20	20	7.5	60	Higher

Ammonia solution is added to the Cd and Zn salt solution to form the cadmium tetraamine ions $[Cd(NH_3)_4^{2+}]$ and zinc tetraamine ions $[Zn(NH_3)_4^{2+}]$, respectively. All these source ions combine in the reaction mixture leading to the formation of CdZnS thin films.



The deposition of the CdZnS ternary thin film is based on the precipitation followed by condensation. After 10 min, the coated substrates are removed and washed with double distilled water to remove loosely bounded CdZnS particles. The fabricated CdZnS films are golden yellow, uniform, highly adherent and specularly reflective.

3. Results and discussion

3.1. Structural studies

Fig.1. shows the XRD patterns of CdZnS ternary thin films grows in the hexagonal form which could be indicated to scattering from (002), (101), (110) and (112) planes, respectively. With increasing Zn^{2+} concentration in the semiconductor CdZnS ternary thin films, the Zn^{2+} ions can substitute for Cd^{2+} site in the CdS lattice. The observed diffraction patterns are in good agreement with the standard JCPDS card data: 49-1302. The XRD pattern reveals that the (002) reflection is the most intensive in hexagonal phase, which indicates a general tendency that the c-axis of the CdZnS nanocrystallites is preferentially perpendicular to the thin film surface. The lower Zn concentrated CdZnS films exhibits the improved crystalline quality than the intermediate and higher Zn concentrated CdZnS films.

3.2. Surface morphological analysis

The surface morphology of the deposited CdZnS thin films was characterized by Scanning electron microscopy (SEM) analysis. SEM is a promising technique for the topography study of samples, as it gives important information regarding the growth mechanism, shape and size of the grains. Figure. 2 (a,b,c) shows the SEM images of the deposited CdZnS thin films for (a) lower, (b) intermediate and (c) higher Zn concentration. The growth of the CdZnS film with lower Zn concentration exhibits the less dissociated surface morphology and small sized flakes observed with in 100 nm range than the SEM images of the CdZnS thin films with intermediate and higher Zn content. All the three samples revealed the tendency of the well annealed samples with out applying any post thermal treatment and are in good agreement with the reported literature of well annealed CdZnS thin films [12].

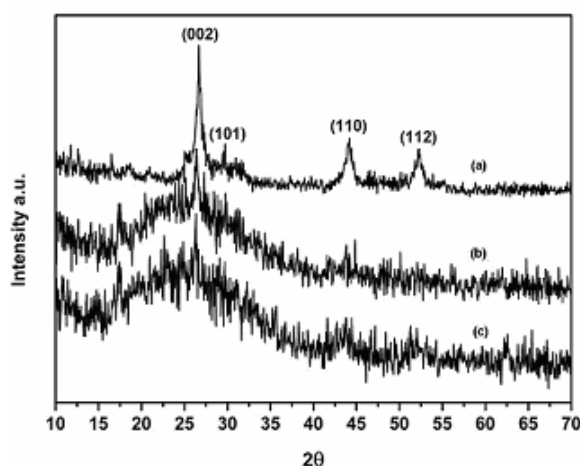


Fig.1 (a,b,c) shows the XRD pattern of the chemical bath contains (a) lower, (b) intermediate and (c) higher Zn concentrated CdZnS thin films.

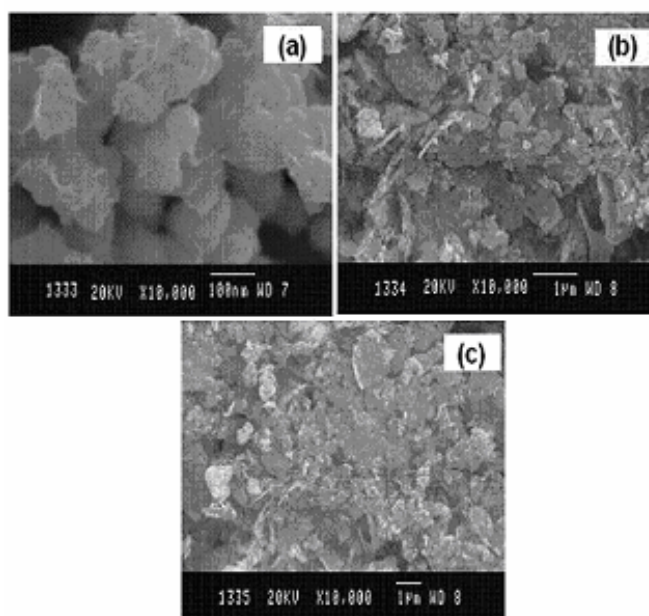


Fig.2 (a,b,c) represents the SEM images of the deposited CdZnS thin films for (a) lower, (b) intermediate and (c) higher Zn concentration.

3.3. Surface texture analysis

Atomic force microscopes (AFM) are well suited for visualize the surface texture of the deposited CdZnS thin films, especially when the surface feature sizes are far below one micron. Figure.3 (a,b,c) shows the AFM images of the CdZnS thin films with (a) lower, (b) intermediate, (c) higher Zn^{2+} concentrations. The atomic force microscopic analysis is ideal for quantitatively measuring the nanometric dimensional surface roughness and for visualizing the surface nano-texture of the deposited film. Measuring the surface texture of CdZnS thin films with horizontal length scale of less than 4 microns and a vertical length scale of 450 nm is critical for optoelectronic applications. For example, surface texture can alter the optical properties of materials.

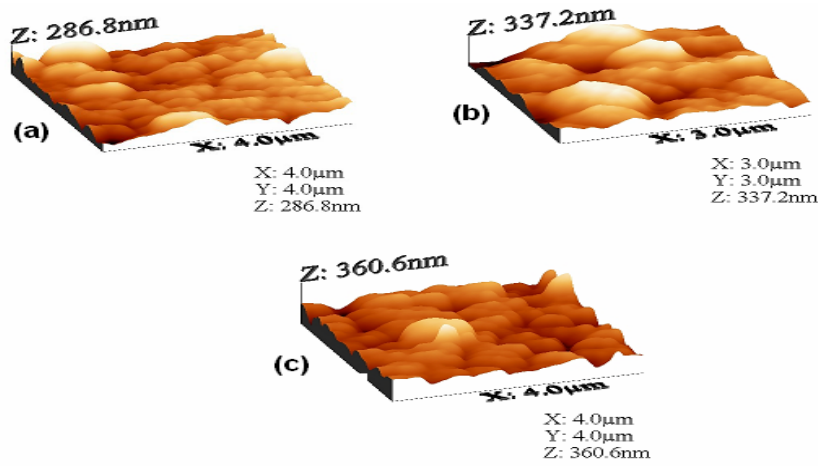


Fig.3. (a,b,c) shows the AFM images of (a) lower, (b) intermediate and (c) higher Zn concentrated CdZnS thin films.

The surface roughness profile was drawn by using the reported software [13]. Our investigated results shows three different Zn^{2+} concentrated CdZnS thin films exhibits different surface texture. The smooth surface texture was observed in the deposited CdZnS films with lower Zn^{2+} concentration. The investigated results of surface texture of the deposited films retrieving the possibilities on tailoring the surface texture of the CdZnS thin films by varying the Zn^{2+} concentration.

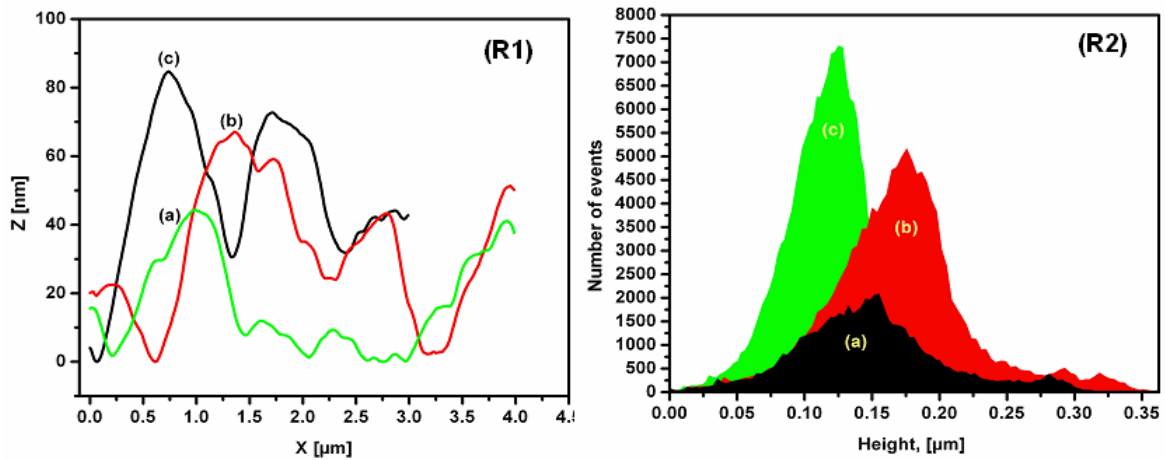


Fig.4. (R1, R2) shows the roughness profile and average roughness of the (a) lower, (b) intermediate and (c) higher Zn concentrated CdZnS thin films.

The roughness profile and average roughness of three different Zn^{2+} concentrated CdZnS thin films are shown in the Figure.4 (R1, R2). The measured root mean square surface roughness of the CdZnS thin films with (a) lower, (b) intermediate, (c) higher Zn^{2+} concentrations are shown in the table.2.

Table.2. shows the surface texture properties such as Root mean square surface roughness (μm), Average height (μm) and Maximum height of the deposited CdZnS thin films.

Zn ²⁺ content, (0.2 M), ml.	Root mean square surface roughness (μm)	Average height (μm)	Maximum height (μm)
Lower 4	0.03695	0.11762	0.26661
Intermediate 7	0.04026	0.14997	0.36619
Higher 10	0.05499	0.17468	0.32298

3.4. Optical studies

The optical absorption and transmittance spectra of CdZnS thin films at various Zn²⁺ concentrations were studied at room temperature in the wavelength range of 300-1200 nm by UV-VIS-NIR spectrometer. Figure.5 (a,b,c) Shows the absorption spectra of the deposited CdZnS thin films with lower, intermediate and higher Zn²⁺ concentrations, respectively. The absorption edges of the films were observed to shift towards shorter wavelengths with respect to the enrichment of Zn²⁺ concentration. The absorption studies revealed that the fabricated films are very low absorptive and is more suitable for the fabrication of solar cells.

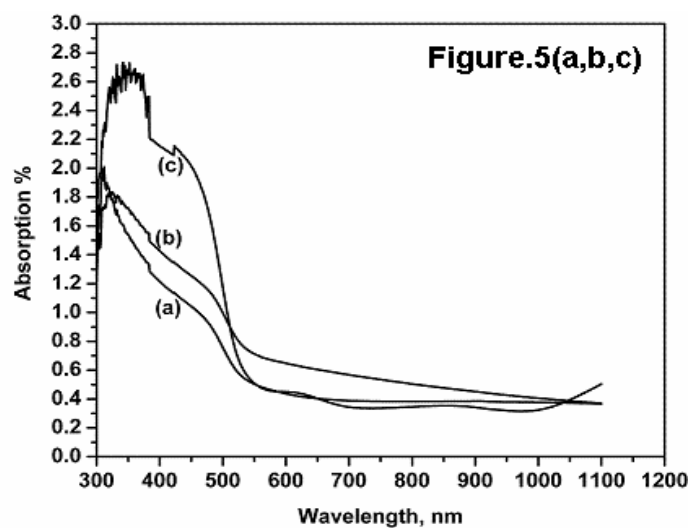


Fig. 5 (a,b,c) and Figure. 6 (a,b,c) Shows the absorption and transmittance spectra of the deposited CdZnS thin films with (a) lower, (b) intermediate and (c) higher Zn²⁺ concentrations.

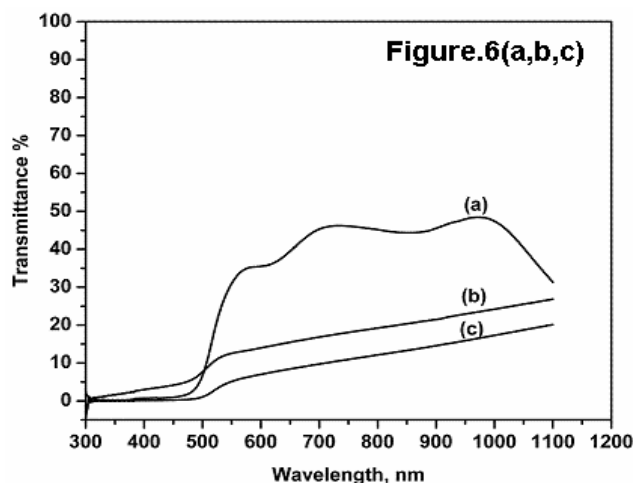


Fig. 6 (a,b,c) represents the transmittance spectra of the CdZnS thin films with lower, intermediate and higher Zn^{2+} concentrations.

The transmittance of the fabricated films decreases due to the incorporation of higher Zn^{2+} content in the chemical bath. The absorption studies revealed that the fabricated films are very low absorptive with a direct type of transition, which allowed the optical band gap (E_g) to be determined. The band gap energy (E_g) of the films was estimated as a function of photon energy ($h\nu$) in the range of 2.92 eV to 3.26 eV by measuring the thickness, transmittance and absorption of the films. The optical band gap (E_g) of the film to be determined by the experimentally observed values of $(\alpha h\nu)^2$ against $(h\nu)$ are plotted in the following Figure. 7 (a, b, c).

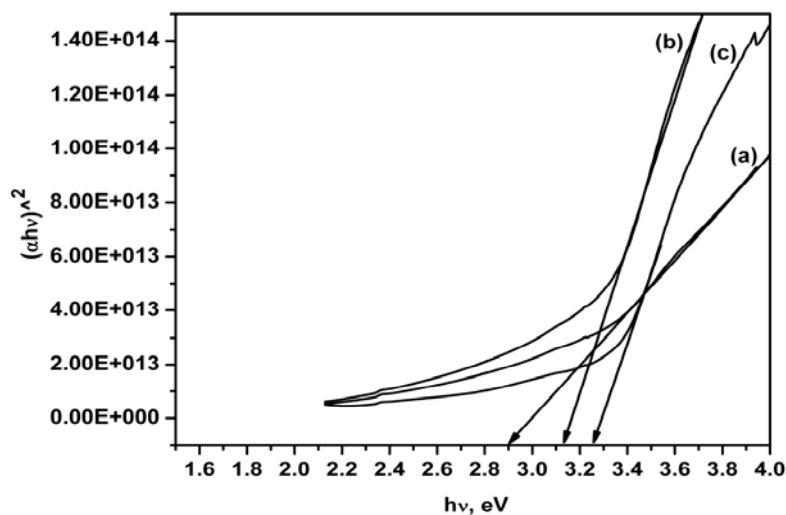


Figure. 7 (a,b,c) shows the band gap (E_g) of the (a) lower, (b) intermediate and (c) higher Zn^{2+} concentrated CdZnS thin films.

The band gaps (E_g) of the CdZnS films were tuned from 2.92 eV to 3.26 eV by tuning the incorporation of Zn^{2+} ion concentration in the chemical bath. The tunability of band gaps (E_g) is mainly due to the incorporation of Zn^{2+} enrichment in the fabrication of CdZnS thin films.

3.5. Photoluminescence measurements

Figure. 8 (a,b,c) displays the room temperature Photoluminescence (PL) emission spectra of micro wave assisted CBD-deposited CdZnS thin films following the 370 nm excitation wavelength. The PL spectra of CdZnS thin films shows the broad green emission peak in the visible range centered at 486, 500 and 515 nm for lower, intermediate and higher Zn^{2+} concentrations in the chemical bath originating from the surface states. It can be seen that for each sample, the PL peak energy always lower than its corresponding band gap (E_g). This evident that the radiative transition occurred from the surface states rather than excitonic transition. The broad PL peak exhibited a trend of shifting towards higher energies with increasing Zn^{2+} content in the fabrication of CdZnS thin films providing additional evidence for the formation of nanometric CdZnS crystallites in our deposited thin films. The higher Zn^{2+} in the fabrication of CdZnS thin films shows poor crystalline quality and increased structural and morphological disorders. This causes the greater broadening and asymmetry in the PL peaks. The decrease in the particle sizes of CdZnS thin films increases the separation of both inter and intra-band levels, which causes the high intensity emission. The intra band separation increases the trapped luminescence efficiency and inhibits the excitation emission via nonradiative surface recombination.

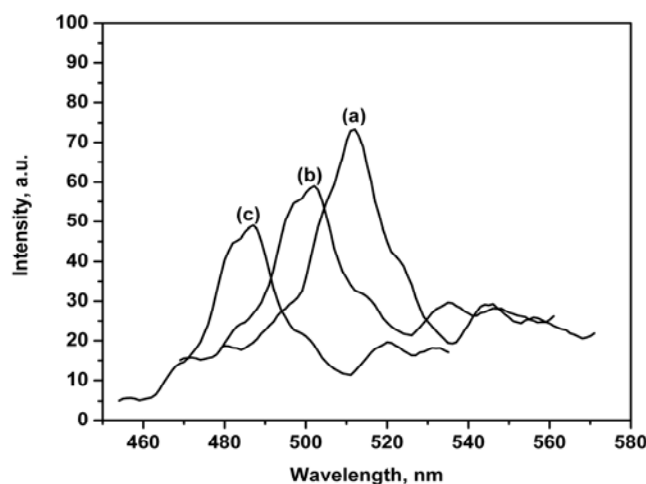


Fig. 8 (a,b,c) displays the room temperature Photoluminescence (PL) emission spectra of (a) lower, (b) intermediate and (c) higher Zn concentrated CdZnS thin films.

4. Conclusions

Micro wave assisted CBD of ternary CdZnS thin films with different Zn^{2+} concentration have been successfully fabricated with in short duration. The crystallographic studies show that the CdZnS thin films exist in hexagonal structure. The observed surface morphological analysis of CdZnS thin films with lower Zn^{2+} concentration shows the better surface features than the film at intermediate and higher Zn^{2+} concentration. The possibilities on tailoring the surface texture of the CdZnS thin films by varying the Zn^{2+} concentration have been demonstrated by surface texture analysis. All the three films show very low absorptive and exhibits direct type of transition. The band gap increases from 2.92 eV to 3.26 eV as the Zn^{2+} compositional parameter increased in the chemical bath. This strongly evident that the band gap tunability are mainly due to Zn^{2+} concentration in the formation of CdZnS thin films. The transmittance percentage of the film increases by decreasing the Zn^{2+} content. The surface morphology of the film changed according to the concentration of Zn^{2+} ions in the chemical bath. The close packed and less dissociated surface morphology was observed in the CdZnS ternary thin films with lower Zn^{2+} content than the intermediate and higher Zn^{2+} content. The degree of self-organization was, how ever, higher

for growth of CdZnS thin films at lower Zn^{2+} content. The high intensity PL emission was observed in the CdZnS thin films with lower Zn^{2+} content than the other two films.

Reference

- [1] J. Aguilar-Hernandez, J. Sastre- Hernandez, N. Ximello-Quiebras, R. Mendoza-Perez, O. Vigil-Galan, G. Contreras-Puente, M. Cardenas-Garcia , Thin Solid Films **511-512**, 143 (2006).
- [2] David Zubia, Cesar Lopez, Mario Rodriguez, Arev Escobedo, Sandra Oyer, Luis Romo, Scott Rogers, Stella Quinonez and John McClure, J.Elect.Mater. **36**, 12 (2007).
- [3] T, Chandra, S. Bhushan, J.Mater. Sci. **39**, 6303 (2004).
- [4] Wenzhong Wang, Igor Germanenko, M.Samy El-Shall, Chem.Mater. **14**, 3028 (2002).
- [5] T.Taguchi, Y.Endoh, Y.Nozone, Appl.Phys.Lett, **56**, 342 (1991).
- [6] B.J.Wu, H.Cheng, M.A.Guha, M.A.Haase, J.M.De Puydt, G.Meis-Haugen, J.Qiu, Appl.Phys.Lett, **63**, 2935 (1993).
- [7] S.Guha, B.J.Wu, H.Cheng, J.M.De Puydt, Appl.Phys.Lett. **63**, 2129 (1993).
- [8] M.A.Haase, J.Qiu, J.M.De Puydt, H.Cheng, Appl.Phys.Lett, **59**, 1272 (1991).
- [9] H.Geon, J.Ding, W.Patterson, A.V.Nurmikko, D.C.Xie Grillo, M.Kobayashi, R.L.Gunshor, Appl.Phys.Lett. **59**, 3619 (1991).
- [10] N.Gaewdang, T. Gaewdang. Mater. Lett. **59**, 3577 (2005).
- [11] G.C.Morris, R.Vanderveen. Sol.Energy Mater. Sol.Cells. **26**, 217 (1992).
- [12] S.D.Chavhan, S.Senthiklarasu, Soo-Hyoung Lee. Appl. Surface Science **254**, 4539 (2008).
- [13] I.Hprcas, R.Fernandez, J.M.Gomez-Rodriguez, J.Colchero, J.Gomez-Herrero and A.M.Baro. Rev.Sci.Instrum, **78**(1), 013705 (2007).