International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.2, pp 980-986, 2014-2015

ICONN 2015 [4th -6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Mg doping effects on the physical properties of lead sulphide thin films

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Abstract : Nanocrystalline ($Pb_{1-x}Mg_x$)S thin films were successfully deposited on suitably cleaned glass substrate at constant temperature of 60° C, using the chemical bath deposition technique. After deposition the films were annealed at 300°C for 2 hours. The film's structural, morphological and optical properties have been investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and UV–vis spectrophotometer. X-Ray diffraction patterns reveal that all of the films are polycrystalline cubic in nature with preferential orientation (200). Microstructural parameters like crystallite size, micro strain and dislocation density have been calculated using x-ray line profile analysis. The values of average crystallite size have been found to be in the range 20.03 to 15.12 nm. SEM analysis revealed that the films were polycrystalline nature with uniform and smooth surface. The energy band gap for thin films were revealed from the optical studies and were found to increase from 1.54 to 1.66 eV with increasing Mg doping concentration.
Keywords: Mg doping effects, lead sulphide thin films.

Introduction

In recent studies, II-IV and IV-VI semiconducting materials have been the subject of great interest due to the large practical application in the field of optoelctronics, infrared sensors, solar coating, gas humidity sensors and photoelectrochemical solar cells[1-4]. Among these materials, PbS is an important IV-VI material with the direct band gap of 0.4 eV and large exciton Bohr radius (18 nm) with small effective mass and high electron mobility[5].

PbS has a very wide spectrum of application which includes gas sensors[6], bio sensors[7], Pb^{2+} ion selective sensors[8], infrared detectors[9], solar radiation selective absorber coating[10], solar radiation control coating[11], decorative coating[12,13], field effect transistors[14].

Many techniques have been reported for the deposition of PbS thin films. These includes spray pyrolysis[15], electrodeposition[16], successive ionic layer adsorption and reaction (SILAR)[17], sol-gel[18] andvaccum evaporated synthesis[19]. Among these techniques chemical bath deposition technique is convenient, low cost and capable for the production of high quality films in large area[20,21,22].

In the present work, magnesium is doped with PbS thin films using chemical bath deposition techniques (CBD), with a view to investigate the structural, morphological and optical properties of these films.

Experimental

Synthesis of $(Pb_{1-x}Mg_x)S$ thin films

$(Pb_{1-x}Mg_x)S$ thin films of varying composition were deposited on the optically plane glass substrate of dimensions 25×75×2 mm by simple chemical bath deposition (CBD) technique. The reaction bath contained 1M of lead acetate ($Pb(CH_3COO)_2$. H_2O), Magnesium sulphate($MgSO_4.7H_2O$) and thiouria ($SC(NH_2)_2$) that were mixed in stoichiometric proportion such that x varies from 0 to 0.075. First, the solution of lead acetate and magnesium sulphate were mixed in the beaker and complexed with adequate quantity of triethonalamine (TEA). Finally thiouria was added. Ammonia was added in order to maintain the pH in the range of 11-12. Before the deposition, glass slides were boiled in chromic acid for 2 h and kept in it for 12 h. Then, they are washed with detergent, and again rinsed in acetone[23]. Cleaned substrate was dipped into the solution, without touching the bottom of the beaker with continuous stirring. The deposition was carried out at 60° C for 1 hour. After deposition, the films were washed with de-ionized water and alcohol solution to remove the loosely adherent precipitate during deposition, and allowed to dry in ambient air. The deposited films were annealed in air at 300° C in furnace for 1 hour. Various calculated quantities of Mg dopants ($0 \leq x \leq 0.1$) were added into the pure PbS solution. This allowed us to study of the material with different doping Mg levels. It was observed that, at higher concentrations ($x \geq 0.1$), of the dopant, the quality of the films decreases.

The techniques of characterization

The composition and crystalline status of the films were ascertained by an X-ray Diffractometer (PAnalyticalX'pert PRO). XRD plots were recorded in the 2θ range 20° to 80° using CuKα radiation. The surface morphology was examined by VEGA3 TESCAN Scanning Electron Microscope. The EDAX attachment (BRUKER) was used to carry out a semi-quantitative elemental analysis of the samples. The optical absorption and transmission spectra of the films were obtained by using Chemito, double beam UV–VIS–NIR spectrophotometer (SPECTRASCAN-UV-2600).

Results and discussion

XRD studies

Fig. 1, shows the XRD pattern of $(Pb_{1-x}Mg_xS)$ thin films grown on the glass substrate. All the diffraction peaks of $(Pb_{1-x}Mg_xS)$ clearly shows the polycrystalline nature corresponding to the diffraction angles approximately 26 (111), 30 (200), 43 (220), 51 (311), 62 (400) and 71 (420) with preferred orientation along (200) plane. By comparison with the data from JCPDS card No. 78-1901, all diffraction peaks can be indexed as a face centered cubic structure of PbS. It is evident from the XRD spectra that there are no additional peaks for the doped ones when compared to the PbS, which indicates that the incorporation of Mg ion into the Pblattice.

Table 1 shows the 2θ values, interplanar spacing d, lattice parameter, average crystal size (D), dislocation density (δ) , and micro strain (ε) of $(Pb_{1-x}Mg_xS)$ thin films. The values of interplanar spacing d and lattice constant a for cubic phase structure are calculated by reported formulas [24,25].

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \quad (1)$$

whered_{hkl} is the interplanar spacing. From the table 1, we can note that there is a significant change in the interplanar spacing and lattice constant for different doping concentration. The decrease in the lattice constant is attributed to the incorporation of Mg ions into the Pb lattice sites in the lattice. It may be due to smaller ionic radius of Mg ion (0.72 Å) compared with Pb ion (1.19Å)[26].

The average crystallite sizes of the films are estimated for the preferential peak $(200)_c$ by using the Debye Scherer's formula[27].

$$D = \frac{k\lambda}{\beta cos\theta} \quad (2)$$

Where k is the shape factor (0.9 here), λ is the x-ray wavelength (1.5406 Å for Cu-Kα), β is full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg's angle. The crystallite size is found to be in the range between 20.03 and 15.12 nm for x = 0- 0.075 and are tabulated in Table 1. It is found that

crystallite size decreases gradually with increasing dopant concentration.X-ray Diffraction results agree well with the observations on PbS thin films by earlier works[28, 29]. The change of the crystallite size with different compositions is prominent and it may be attributed to built-in strain and dislocations. Fig. 2, shows the variation of crystallite size with Mg content obtained from Debye Scherer's relation.

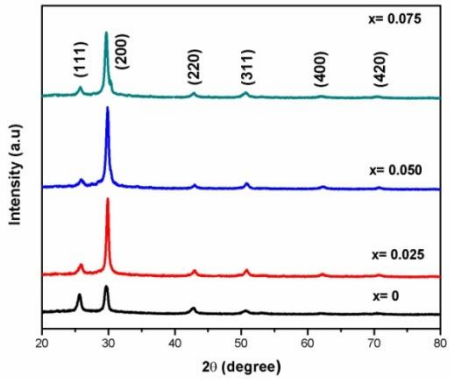

Fig. 1.XRD pattern of ($Pb_{1-x}Mg_xS$) thin films.

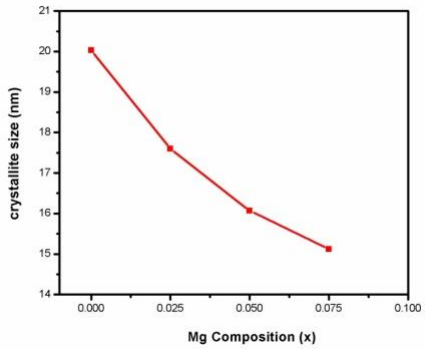

Fig. 2.Variation of crystallite size with Mg contentof ($Pb_{1-x}Mg_xS$) thin films.

The micro-strain (ε) can be calculated using the formula[30]

$$\varepsilon = \frac{\beta_{2\theta} \cos\theta}{4} \quad (3)$$

where θ and $\beta_{2\theta}$ are glancing angles and full width at half maximum. It is observed that, the microstrain decreases with increasing doping concentration. This type of change in strain is due to the predominant re-crystallization process in the polycrystalline thin films

The dislocation density can be calculated by Williamson and Smallman's relation[31].

$$\delta = \frac{n}{D^2} \quad (4)$$

where n is a factor, which equals unity giving minimum dislocation density and D is the crystallite size. Dislocation density are increasing with increasing doping concentration of Mg in pure PbS which may be attribute to the decrease in crystallite size as shown in Table 1.

Table 1.The 2θ values, interplanar spacing d, lattice parameter, average crystal size (D), dislocation density (δ) , and micro strain (ε) of ($Pb_{1-x}Mg_xS$) thin films.

x	2θ value (°)	d- value (Å)	Lattice parameter (Å)	Average crystallite size (D) (nm)	Dislocation density (δ) (10^{-15} lines/m^2)	Micro strain (ε)
0	29.90	2.965	5.93	20.03	2.4935	0.002232
0.025	29.85	2.9645	5.9292	17.60	3.2283	0.001345
0.050	29.68	2.9630	5.9261	16.07	3.8722	0.001213
0.075	29.54	2.9608	5.9217	15.12	4.4374	0.001048

SEM studies

Fig 4.(a)- (d), shows the SEM micrographs of PbS and ($Pb_{1-x}Mg_xS$) thin films. The SEM images of the pure PbS thin film shows the polycrystalline nature with smooth and uniform spherical grains without cracks or pinholes and well covered to the glass substrate. The chemical composition of PbS and ($Pb_{1-x}Mg_xS$) thin films was analyzed by EDAX. The typical EDAX spectrum of undopedPbS thin film shown in fig. 4(e). reveals the presence of Pb and S elements in the deposited film with a S/Pb atomic ratio of 0.82. There are no impurity atoms found in the report.

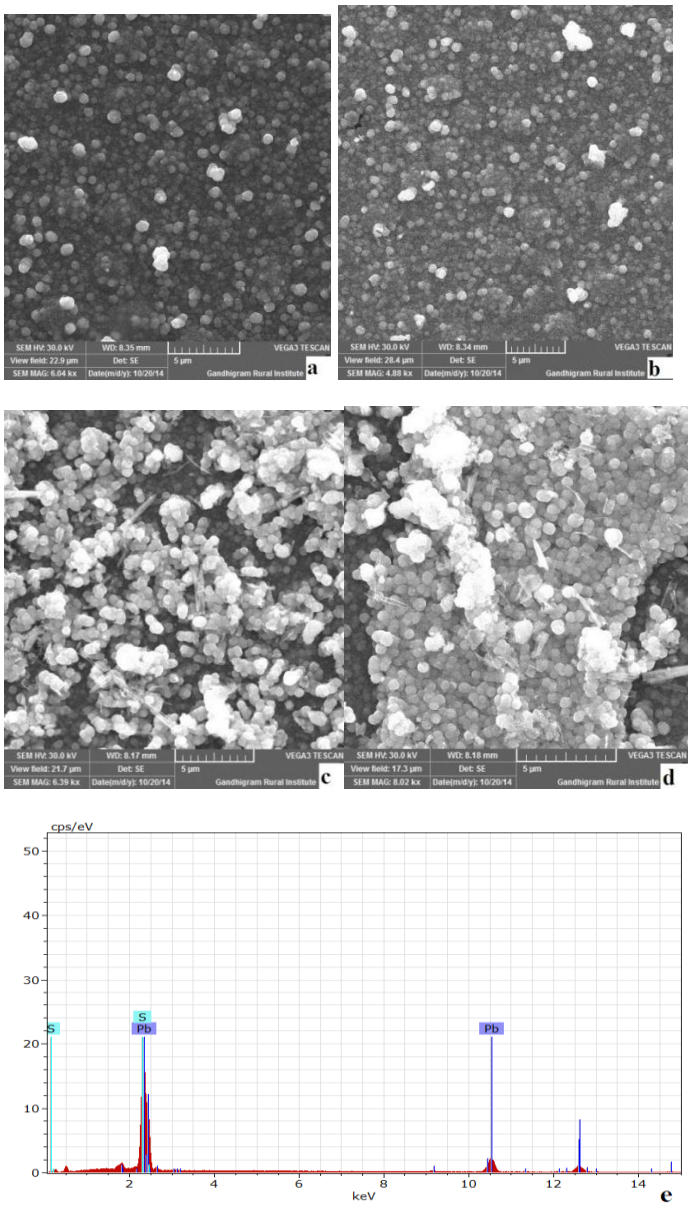

Fig 3.a, b, c and dare the SEM micrographs of x= 0, x= 0.025, x= 0.050 and x= 0.075 of ($Pb_{1-x}Mg_xS$) thin films.eis the EDAX spectrum of undopedPbS thin films.

Optical studies

The UV- Vis optical absorption and transmittance spectra of ($Pb_{1-x}Mg_xS$) thin films have been carried out at room temperature from 400 to 900 nm and are shown in fig. 6 and 7. It is observed that the absorption edge of the film shift towards shorter wavelength with increasing Mg doping concentration. The transmission spectra of ($Pb_{1-x}Mg_xS$) thin films are shown in fig. 6, shows just opposite trend of optical absorption spectra. From fig. 6, it is observed that the transmittance is generally increases with increasing in doping concentration. These thin films exhibit higher absorption in the visible range and on increasing the Mg doping concentration, the absorption of the films decreases.

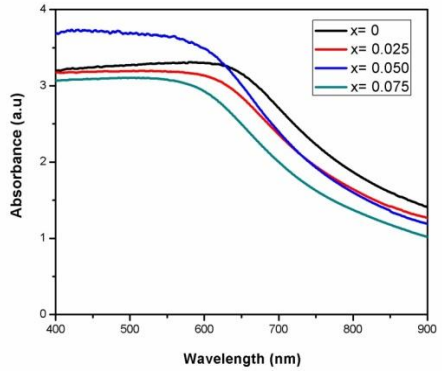

Fig. 5. Optical absorption spectrum of $(Pb_{1-x}Mg_xS)$ thin films.

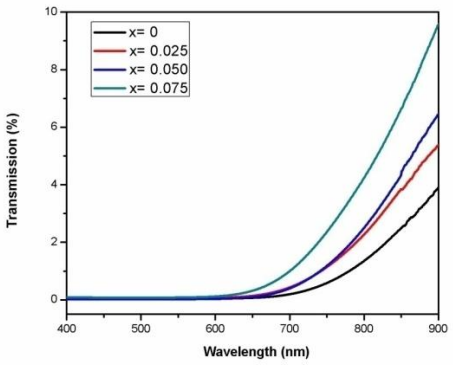

Fig. 6. Optical transmission spectrum of $(Pb_{1-x}Mg_xS)$ thin films.

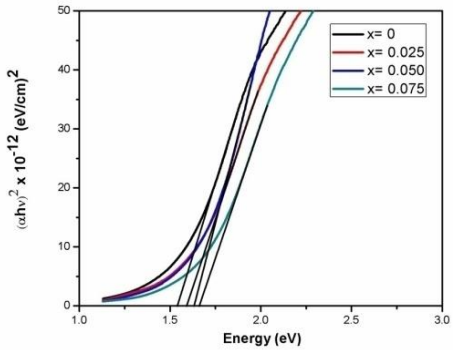

Fig. 7, Plot of (αhν versus hν) for $(Pb_{1-x}Mg_xS)$ thin films.

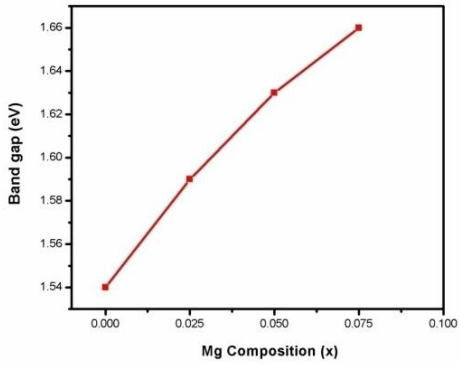

Fig. 8. Variation of energy band gap with Mg concentration of $(Pb_{1-x}Mg_xS)$ thin films

The optical band gaps were calculated using the Tauc relation[32]by plotting $(\alpha h\nu)^2$ versus hν. By extrapolating the straight line portion of the curve to intercept the energy axis as shown in Fig. 7, the value of the band gap energy has been calculated. The variation of energy band gap with Mg concentration of ($Pb_{1-x}Mg_xS$) thin films are shown in Fig. 8.

The band gap of nanocrystallinePbS thin film was found to be 1.54 eV which is quite high as compared to the bulk PbS. The optical band gap energy of Mg doped PbS films is increased with the increasing doping concentration. The band gap E_g values of x= 0.025 is 1.59, x= 0.050 is 1.63 and x= 0.075 is 1.66 eV. This increase of band gap is attributed to the decrease in the crystallite size and also due to the influence of Mg ions. However this proves that the incorporation of dopant ions into PbS lattice.

Conclusion

Nanocrystalline ($Pb_{1-x}Mg_x$)S thin films were deposited on the glass substrate at bath temperature of 60° C using chemical bath deposition technique. X- ray diffraction studies reveals that all the films are polycrystalline cubic phase in nature. The crystallite size of the films decreases from 20.03 to 15.12 nm with increase in the magnesium composition (x). The SEM micrographs shows that the present films are uniform, homogenous and well covered to the substrate surface with spherical grains. Optical absorption studies showed a blue shift on absorption edge and the estimated band gap values of present films increased with an increase in the Mg concentration. The optical band gap of ($Pb_{1-x}Mg_x$)S thin films varies from 1.54 to 1.66 eV.

References

1. Yu, J., Y. and Shengshui, H., The deposition of highly uniform and adhesive nanocrystallinePbS film from solution, Thin Solid Films, 516, 2008, 6048-6051.
2. Reddy,G.B.,Pandya, D.K. and Chopra, K.L., Solution grown $(PbS)_{1-x}$-$(CdS)_x$ composite selective surface, Solar Energy Materials, 15, 1987, 383-390.
3. Nair, P. K. and Nair,M. T. S., Versatile solar control characteristics of chemically deposited PbS-Cu_xS thin film combination, Semiconductor Science and technology, 4, 1989, 807-814.
4. Obaid, A.S., Mahdi, M.A., Hassan, Z. and Bououdina, M., Characterization of nanocrystallinePbS thin films prepared using microwave-assisted chemical bath deposition, Materials Science in Semiconductor Processing, 15, 2012, 564-571.
5. Puiso,J.,Tamulevicius,S.,Laukaitis, G., Lindroos, S.,Leskela, M. andSnitka,V., Growth of PbS thin films on silicon substrate by SILAR technique, Thin Solid Films, 403-404, 2002, 457-461.
6. Tiexiang, F., Research on gas-sensing properties of lead sulfide-based sensor for detection of NO_2 and NH_3 at room temperature, Sensors and Actuators B, 140, 2009, 116-121.
7. Xiaofang, S., Zhaoxia, L., Yan, C. and Yuehong, P., Glutathione-assisted synthesis of hierarchical PbS via hydrothermal degradation and its application in the pesticidalbiosensing, International Journal of Electrochemical Science, 6, 2011, 3525-3535.
8. Hiroshi, H. and Kenji, H., Analytical study of lead ion-selective ceramic membrane electrode, Bulletin of the chemical society of Japan, 44, 1971, 2420-2423.
9. Jamie, H. W. and Norman, H., HalinaRubinsztein-Dunlop, Non-linear photoluminescence from purified aqueous PbSnanocrystals, Materials Letters, 60, 2006, 3332-3334.
10. Gupta, B. K., Thangaraj, R. and Agnihotri, O. P., High absorptivity Al-PbS selective surfaces for solar photothermal conversion, Solar Energy Materials, 1, 1979, 481-487.
11. Ileana, P., Cristina, N., Vioteta, I., Indrea, E. andBratu,I.,Structural and optical properties of PbS thin films obtained by chemical deposition, Thin Solid Films, 307, 1997, 240-244.
12. Nair, P. K., Garcia, V. M., Hernandez, A. B.and Nair,M. T. S.,Photoaccelerated chemical deposition of PbS thin films: novel applications in decorative coatings and imaging techniques, Journal Physics D: Applied Physics, 24, 1991, 1466-1472.
13. Pawara,S.B.,Shaikhb, J.S., Devanc, R.S., Mac, Y.R., Haranathd, D., Bhosalea, P.N. and Patil, P.S., Facile and low cost chemosynthesis of nanostructured PbS with tunable optical properties, Applied Surface Science, 258, 2011, 1869-1875.
14. Colvin,V. L.,Schlamp, M. C. andAllvisatos,A. P., Light emitting diodes from cadmium selenidenano crystals and a semiconducting polymer, Nature, 370, 1994, 354-357.
15. Mahdi, H.S., Structural and optical properties of ZnS, PbS, $Zn_{1-x}Pb_xS$, $Zn_xPb_{1-x}S$, $PbZn_xS_{1-x}$ thin films, Indian Journal of Pure and Applied Physics, 50, 2012, 380-386.

16. Han, W., CaoL.Y., Huang, J.F. and Wu, J.P.,Influence of pH value on PbS thin films prepared by electrodeposition, Materials Technology, 24, 2009, 217-220.
17. Puiso, J., Tamulevicius, S., Lindroos, S., Leskela, M. andSnitka, V., Growth of ultra thinPbS films by SILAR technique, Thin Solid Films, 428, 2003, 223-226.
18. Alessandro, M., Jochen, F., Serge-Emile, L.,Michael, L.and Alain, H., Optical properties of PbS quantum dot doped sol–gel films, Journal of Non-Crystalline Solids, 345-346, 2004, 639-642.
19. Sushil, K., Sharma, T.P., Zulfequar, M. and Husain, M., Characterization of vacuum evaporated PbS thin films, Physica B, 325, 2003, 8–16.
20. Chattarki, A.N., Kamble, S.S. andDeshmukh, L.P., Role of pH in aqueous alkaline chemical bath deposition of lead sulfide thin films, Materials Letters, 67, 2012, 39-41.
21. Rakesh, J,K. and Sehgal, H. K., Structure, conductivity and Hall effect study of solution grown $Pb_{1-x}Fe_xS$ nanoparticle films, Nanotechnology, 14, 2003, 592-596.
22. Barote, M. A., Yadav, A. A., Chavan, T. V. andMasumdar, E. U., Characterization and photoelectron chemical properties of chemical bath deposited n-PbS thin films, Digest Journal of Nanomaterials and Biostructures, 6, 2011, 979-990.
23. Muthu, K.S. and Ashok, K.M., Size dependent structural, optical and morphological properties of ZnS:Cu thin films, Journal of Materials Science: Materials in Electronics, 23, 2012, 811–815.
24. Klug, P.H., and Alexender, L.E., X-ray diffraction, Addision-Wilson Publishing Company Inc, 1974, 132.
25. Cullity, B.D., Elements of X-ray diffraction, Addison-Wilson Publishing Company Inc, 1959, 42.
26. Shannon, R. D., Handbook of Chemistry and Physics, CRC Press Boca Raton, 74th Edition, A32, 1974, 751.
27. Muthu, K., S.and Gopalakrishnan, R., Structural, optical and photoluminescence properties of $Zn_{1-x}Ce_xO$ (x = 0, 0.05 and 0.1) nanoparticles by sol–gel method annealed under Ar atmosphere, Journal of Sol-Gel Science and Technology, 62, 2012, 193–200.
28. Seghaier, S., Kamoun, N., Brini, R. and Amara, A.B., Structural and optical properties of PbS thin films deposited by chemical bath deposition, Materials Chemistry and Physics, 97, 2006, 71–80.
29. Anusuya. M.,Saravanan, V.,Ramesh, T. and Mahaboob, B. M., Physical properties of spray pyrolytically li doped pbs thin films, 5, 2013, 33-37.
30. Hankare,P. P., Chate, P. A., Sathe, D. J., Chavan, P. A. and Bhuse, M., Effect of thermal annealing on properties of zinc selenide thin films deposited by chemical bath deposition, Journal of Material Science: Materialsin Electronics, 20, 2009, 374-379.
31. Rajesh, K., Das, R., Mukul, G. and Ganesan, V., Compositional effect of antimony on structural, optical, and photoluminescence properties of chemically deposited $(Cd_{1-x}Sb_x)S$ thin films, Superlattices and Microstructures, 59, 2013,29–37.
32. Mageswari, S., Dhivya, L., Balan, P. and Ramaswamy, M., Structural, morphological and optical properties of Na and K dual doped CdS thin film, Journal of Alloys and Compounds, 545, 2012, 41–45.

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