J. Nano- Electron. Phys.
3 (2011) No1, P. 460-468

PACS numbers: 78.20. – e, 73.61.At, 73.61. – r, 78.30.Er, 68.55.J –, 67.80.F –

OPTICAL, ELECTRICAL AND RAMAN PROPERTIES OF ANNEALED HYDROGENATED Mg/Co BILAYER THIN FILMS

M.K. Jangid, S.P. Nehra, M. Singh

Thin Film & Membrane Science Laboratory, Department Of Physics,
University of Rajasthan, Jaipur-302055, India
E-mails: maheshjangid2008@gmail.com, mangej_singh@yahoo.com

Bilayer Mg/Co thin films prepared using thermal evaporation method at pressure 10^{-5} *torr at room temperature. The films were rapid thermal annealed (RTA) using halogen lamp for different times to get a homogeneous structure of Mg/Co thin films. The hydrogen gas was introduced in hydrogen chamber, where samples were kept at different pressure of* H_2 *for thirty minutes. The UV–VIS transmission spectra of annealed and annealed hydrogenated films have been carried out at room temperature in the wavelength range of* 300-800 *nm. The optical band gap was found to be increased due to hydrogenation and decrease with annealing time and also conductivity has been found to be decreased with hydrogen and increased with annealing time. Raman spectra show decreasing intensity of peaks with annealing and hydrogenation. Relative resistivity varies nonlinearly with time and decreases with annealing time. Surface morphology of annealed and annealed hydrogenated bilayer thin films has been confirmed by optical microscopy.*

Keywords: *BILAYERS, ANNEALING, HYDROGENATION, OPTICAL, ELECTRIC, RAMAN, SURFACE MORPHOLOGY.*

(Received 04 February 2011, in final form 16 June 2011)

1. INTRODUCTION

Metal hydrides find a wide range of applications of which the most prominent is reversible hydrogen storage. Hydrogen is the most abundant element on earth, scores over all renewable fuels regarding reversibility, energy density and compatibility with the environment [1]. The behavior of hydrogen in metals has attracted scientific attention for many decades and is interesting from both basic research and technological points of view. Most of hydrogen's interesting properties relate to the high mobility of the hydrogen atoms, which reaches to the values similar to those of ions in aqueous solutions. This high mobility exists because the hydrogen atoms occupy interstitial positions in the host lattice due to an interstitial diffusion mechanism and the contribution from quantum-mechanical tunneling [2]. Mg is considered to be one of the most promising materials for hydrogen storage. It is light and abundant. In spite of the fact that MgH_2 satisfies the requirement set by the U.S. Department of Energy, with a theoretical capacity of 7.6 wt. % hydrogen, lightweight and low cost [3]. The three different families of metals and alloys have been identified to exhibit switchable properties from metallic to transparent during hydrogenation: (I) rare earth hydrides RE–H, [11] (II) RE–Mg–H, [4] and (III) Mg–TM–H (TM = transition metal such as Fe, Co, and Ni) [5-7]. Most of them have a band gap whose energy corresponds to the range of visible radiation. Richardson et al. [8, 9], discover that Mg based films absorb hydrogen very easily, While in bulk samples hydrogenation requires high temperatures (500 to 600 K) and pressures of 10^5 to 10^6 Pa , for thin films it occurs readily at room temperature at low pressures, and it opened the way to the third-generation switchable mirrors. Mixed metal thin films containing magnesium and a first-row transition element exhibit very large changes in optical and electrical properties on exposure to hydrogen gas [10, 11]. Similar behavior was subsequently found in Mg-rare-earth films and magnesium transition-metal alloys, such as Mg_2CoH_5 [12], $Mg_6Co_2H_{11}$ [13] and Mg_2FeH_6 [14], the band structure calculations which support experimental evidence for semiconductor behavior in these materials [12, 14]. The various scientists observed variation in optical band gap of complex hydrides and found 1.6 eV in case of Mg_2NiH_4 [15], 1.9 eV in case of Mg_2CoH_5 [16] and 2.56 eV for Mg_3MnH_7 [17]. The optical properties of Mg-TM (Ni, Co, Fe, Mn) also carried out by Lohstroh et al. and they suggested that the nucleation of hydrides start at the film substrate interface and remarkable optical black state of intermediate hydrogen concentration [18]. Electrical measurements provide detailed information about the electronic effects of hydrogen in thin film. A «universal alignment» model successfully describes the electronic behavior of hydrogen in a wide range of materials. The conductivity of semiconducting thin film has been found to be decreased with hydrogenation [19, 20]. The interaction of hydrogen in a metal hydride can be understood by using the anionic model [21]. The increase in resistivity ratio with increasing hydrogen absorption time means that hydrogen takes more electrons from the conduction band of the intermetallic compound and accelerates the hydrogen absorption capacity of samples [30-32]. The second generation switchable mirrors exhibit an absorbing, black state at intermediate hydrogen concentrations, due to the coexistence of nano-crystalline reflecting and transparent phases [7, 22]. The magnesium based hydrides can be used in several applications such as switchable mirrors as indicator layers, smart windows [23], switchable absorbers [24] and fiber optic hydrogen sensors [25]. In the present work we have been studied the effect of hydrogenation and rapid thermal annealing time on optical, electric properties, Raman spectra and surface morphology of Mg/Co bilayer thin films.

2. EXPERIMENTAL

Bilayer thin films were prepared by thermal evaporation method using vacuum coating unit at pressure order of 10^{-5} torr Mg granules (99.999 %) & Co powder (99.998 %) pure were purchased from Alfa Aesar, Jonson Matthay Company, U.S.A. used for present study, were placed into two different boats of tungsten material in the vacuum chamber. The glass substrates and ITO plates cleaned by plasma sputtering technique were placed in the substrate holder above the boats carrying materials. The bilayer thin films of Mg/Co (Mg-200 nm, Co-200 nm) had been prepared by stacked layer method in situ evaporation. Prepared bilayer thin films were rapid thermal annealed (RTA) by Halogen light lamp (1000 W) to get homogeneous mixture of MgCo films. For this process, bilayer thin films were kept in quartz tube at 200 °C and then rapid thermal annealed by halogen light lamp for different times (2 min and 4 min) to get homogeneous mixture.

The hydrogenation of RTA Mg/Co bilayer thin films has been performed by keeping these in hydrogenation cell, where hydrogen gas was introduced at pressure 30 psi and 45 psi for half an hour. UV–VIS transmission spectra of RTA and RTA hydrogenated Mg/Co bilayer thin films are taken at room temperature in the wavelength range of 300–800 nm with the help of Hitachi-330 spectrophotometer. Transverse I-V characteristics of thin films have been observed by Keithley-238 high current source measuring unit. The applied voltage was in the range of – 2.0 to + 2.0 V with increasing step of 0.1 V. For I-V characteristics, electrode contacts have been made using silver (Ag) paste on the thin films. I-V characteristics of bilayer thin films have been monitored with the help of SMU Sweep computer software. Raman spectra of thin films have been taken by a continuous wave-Green laser with a constant wavelength 532 nm at room temperature with the help of R-3000 Raman system. Resistivity of the thin films was measured by the Van der Pauw method at 300 K & various constant hydrogen pressures. Optical micrographs have been observed with the help of labomed optical microscope at 10 x magnification having resolution of the order of 1 mm and the microscope was kept in reflection mode.

3. RESULTS AND DISCUSSION

3.1 Optical transmission and band gap of Mg/Co bilayer

The optical transmission spectra of Mg/Co bilayer films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 300-800 nm. The variations of transmission (T %) with wavelength (λ) are shown in Fig. 1 & 2. These show that the transmission increase due to hydrogenation and decrease with RTA time. By studying transmission spectra of Mg/Co thin films, very useful information can be obtained about the energy gap, position of impurity levels in forbidden band, characteristics of optical transitions, etc. The optical band gap of these films have been calculated by using Tauce relation [26] $\alpha h\nu = A\,(E_g - h\nu)^{1/2}$ where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap and A is a constant. In this work, direct band gap was determined by plotting $(\alpha h\nu)^2$ vs $h\nu$ curves, with

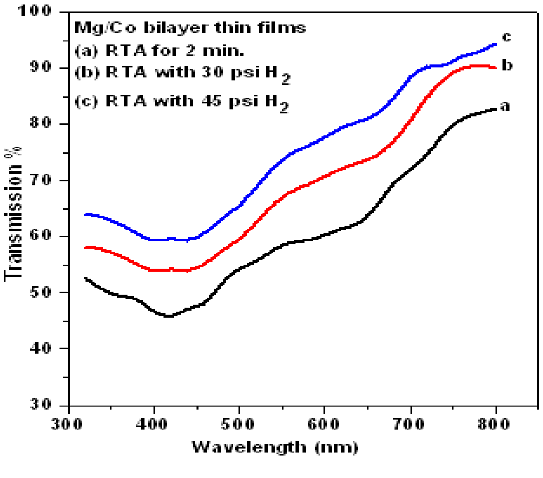


Fig. 1 – Transmission spectra of Mg/Co bilayer thin films for 2 min

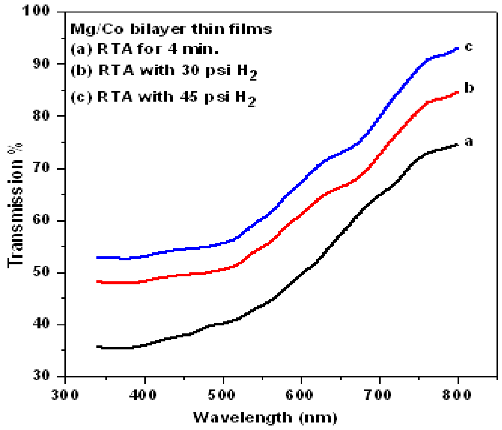


Fig. 2 *– Transmission spectra of Mg/Co bilayer thin films for* 4 *min*

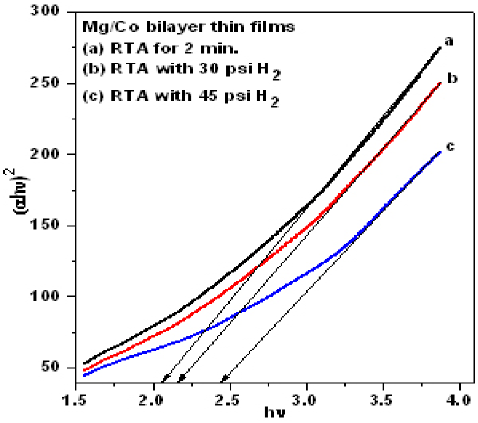


Fig. 3 *– Optical band graph of Mg/Co bilayer thin films for* 2 *min*

the extrapolation of the linear region to low energies. Fig. 3 & 4 show the graph between $(\alpha h\nu)^2$ versus energy (eV) of photon on Mg/Co thin films assuming it to be the direct band gap material. The intercept of straight line to energy axis has been used to find out the optical band gap. The value of optical energy band gap increases due to hydrogenation (Table 1), It may be due to hydrogen accumulates at interface and takes electrons from the Mg/Co thin film which support the anionic model for hydrogen interaction with intermetallics and variation in optical band due to hydrogenation suggests phase changes from metal to semiconductor [27] and decrease with annealing time (Table 1), it is due to crystallization and increase in grain size of the films with annealing [28].

3.2 Current - Voltage characteristics

Fig. 5 & 6 show the current voltage characteristics of thin films and found that the effect of rapid thermal annealing on the bilayer structure indicating the possibility of mixing of bilayer structure at the interface showing the partially semiconducting nature and the conductivity has been found to be increased with annealing time (Table 1), it may be due to increase in grain size with increase of annealing time [28] and conductivity has been found to be decreased due to hydrogenation (Table 1). It means hydrogen takes electrons from the conduction bands due to hydrogenation and blocks the flow of charge carriers across the interface and current decreases in forward as well as reverse direction [19, 20].

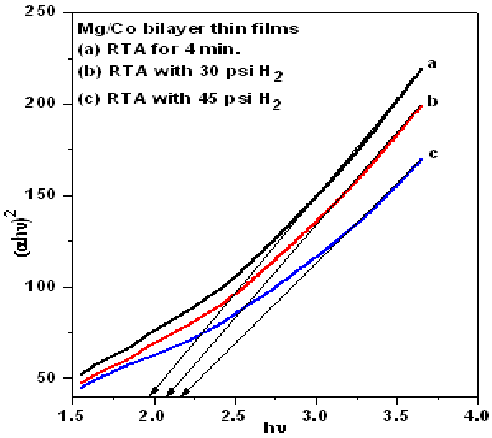


Fig. 4 – Optical band graph of Mg/Co bilayer thin films for 4 min

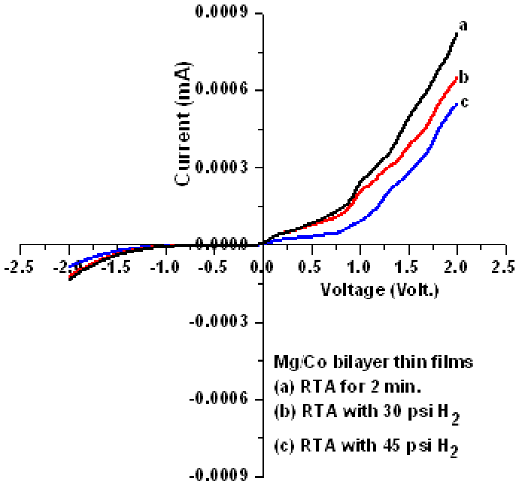


Fig. 5 – Current Voltage spectra of Mg/Co bilayer thin films for 2 min

Table 1 *– Optical Band Gap and Conductivity of Mg/Co bilayer thin films*

Annealing time	Optical Band Gap (eV)			Conductivity ($10^{-5}\Omega^{-1}$-m^{-1})		
	RTA	RTA with 30 *psi* H_2	RTA with 45 *psi* H_2	RTA	RTA with 30 *psi* H_2	RTA with 45 *psi* H_2
2 min	2.0540	2.1503	2.4342	5.5343	4.4405	3.7549
4 min	1.9693	2.0679	2.1605	8.2199	6.9805	5.1239

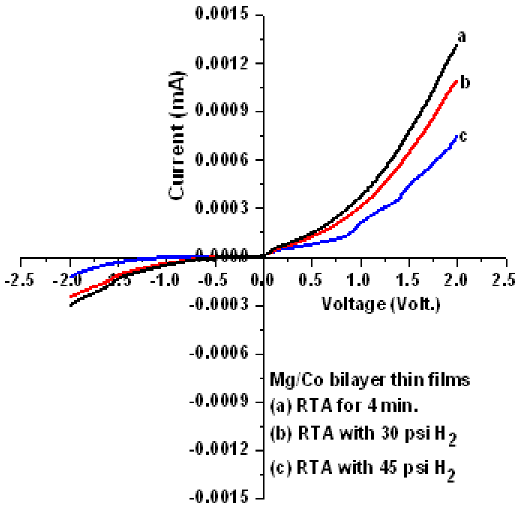


Fig. 6 – *Current Voltage spectra of Mg/Co bilayer thin films for* 4 *min*

3.3 Raman spectroscopy

Fig. 7 shows the variation in intensity versus wave number of Raman spectroscopy. In these spectra intensity of Raman peaks is decreased with annealing and hydrogenation and decrease in broadening of peak has also been noted. It suggests that hydrogen may change the phase or make the bonding with metal interstitial as well as surface locations. In case of Si crystalline structure, hydrogen absorption peaks were observed at 590 cm $^{-1}$ by Fukata et al. [29].

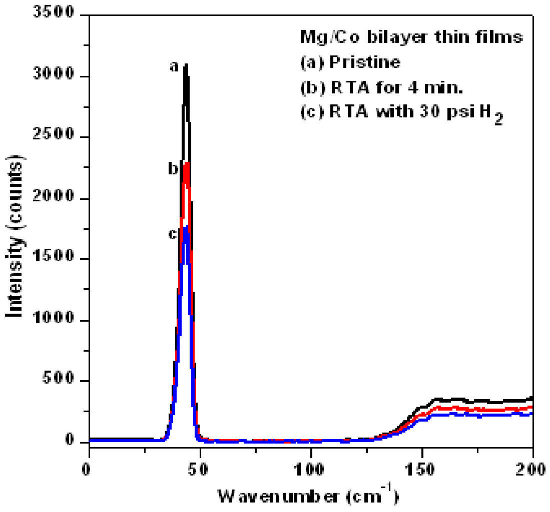


Fig. 7 – *Raman spectra of Mg/Co bilayer thin films*

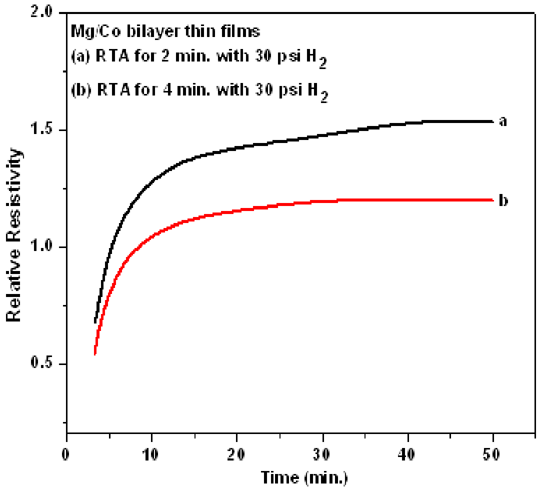


Fig. 8 – Hydriding kinetics of Mg/Co bilayer thin films

3.4 Resistivity Measurements

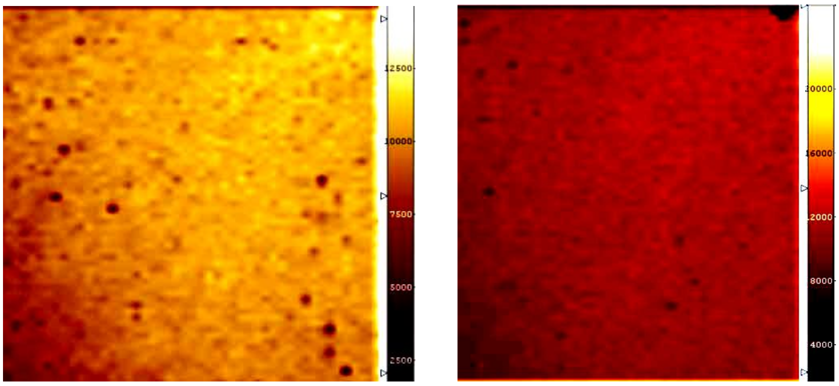
Fig. 8 shows that hydrogen absorption decreases with annealing time, which is indicated by the increasing resistivity ratio (ρ_H/ρ_o) due to the net effect of hydrogen absorption, where ρ_o is the resistivity before hydrogen absorption and ρ_H is the resistivity of the sample after hydrogen absorption. The resistivity ratio increases slowly with hydrogen absorption time and finally reaches the equilibrium position. It is suggested that resistivity increases as hydrogen takes electrons from the conduction bands of each of the samples during the hydrogen absorption process [30-32].

3.5 Surface morphology

Fig. 9 shows the optical surface morphology of (a) RTA for 4 min and (b) RTA Hydrogenated Mg/Co bilayer thin films. These are recorded in reflectance mode of optical microscope and observed pure black state with hydrogenation. The black state of film is suggesting an intermediate hydrogen concentration state to sustain in our bilayer thin film. The nucleation of hydrides starts at the film substrate interface and suggested remarkable optical black state of intermediate hydrogen concentration and concluded the enhanced hydrogen affinity at the film substrate interface and suggested the study of complex hydride formation in thin films might give valuable information for the use of these Mg/Mn bilayer structure for hydrogen storage as well as solar collector materials [7, 22].

4. CONCLUSION

Hydrogenation and rapid thermal annealing tailored optical, electrical and Raman properties of nanostructure Mg/Co bilayer thin films. Optical band gap has been found to be increase with hydrogenation; it may be due to hydrogen accumulation at interface and decrease with annealing time due to removal of defects and increase in grain size. The conductivity has been



(a) (b)

Fig. 9 *– Surface Morphology of Mg/Co bilayer thin films (a) RTA for 4 min. (b) RTA hydrogenated at 30 psi* H_2

found to be decreased due to hydrogenation and increased with annealing time and also intensity of Raman peaks is decreased with hydrogenation and annealing time. Surface morphology confirms the uniform deposition and proper mixing of bilayer structure and also optical black state of intermediate hydrogen concentration. These results indicate that Mg/Co bilayer structures can be used to hydrogen storage purpose.

The authors are highly thankful to Department of Physics, University of Rajasthan, Jaipur for providing experimental facilities.

REFERENCES

1. R.K. Singh, M.V. Lototsky, O.N. Srivastava, *Int. J. Hydrogen Energ.* **32,** 2971 (2007).
2. D. Richter, R. Hempelmann, L.A. Vinhas, *J. Less Common Metals* **88,** 353 (1982).
3. K.H.J. Buschow, P.C.P. Bouten, A.R. Miedema, *Rep. Prog. Phys.* **45,** 937 (1982).
4. P. van der Sluis, M. Ouwerkerk, P.A. Duine, *Appl. Phys. Lett.* **70,** 3356 (1997).
5. T.J. Richardson, J.L. Slack, R.D. Armitage, R. Kostecki, B. Farangis, M.D. Rubin, *Appl. Phys. Lett.* **78,** 3047 (2001).
6. T.J. Richardson, J.L. Slack, B. Farangis, M.D. Rubin, *Appl. Phys. Lett.* **80,** 1349 (2002).
7. W. Lohstroh, R.J. Westerwaal, B. Noheda, S. Enache, I.A.M.E. Giebels, B. Dam, R. Griessen, *Phys. Rev. Lett.* **93,** 197404 (2004).
8. H. Blomqvist, *Ph.D. thesis*, Stockholm University (2003).
9. J.J. Reilly, R.H. Wiswall, *Inorg. Chem.* **7,** 2254 (1968).
10. T.J. Richardson, J.L. Slack, B. Farangis, M.D. Rubin, *Appl. Phys. Lett.* **80,** 1349 (2002).
11. J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, *Nature* **380,** 231 (1996).
12. P. Zolliker, K. Yvon, P. Fischer, J. Schefer, *Inorg. Chem.* **24,** 4177 (1985).
13. R. Cerny, F. Bonhomme, K. Yvon, P. Fischer, P. Zolliker, D.E. Cox, A. Hewat, *J. Alloy. Compd.* **187,** 233 (1992).
14. J.J. Didisheim, P. Zolliker, K. Yvon, P. Fischer, J. Schefer, M. Gubelmann, A.F. Williams *Inorg. Chem.* **23,** 1953 (1984).
15. J. Isidorsson, I.A.M.E. Giebels, R. Griessen, M. Di Vece, *Appl. Phys. Lett.* **80,** 2305 (2002).

16. E. Belin, M. Gupta, P. Zolliker, K. Yvon, *J. Less. Common. Metals* **130,** 267 (1987).
17. E. Orgaz, M. Gupta, *J. Alloy. Compd.* **330,** 323 (2002).
18. W. Lohstroh, R.J. Westerwaal, A.C. Lokhorst, J.L.M. van Mechelen, B. Dam, R. Griessen, *J. Alloy. Compd.* **404,** 490 (2005).
19. J.I. Pankove, D.E. Carlson, J.E. Berkeyheiser, R.O. Wance, *Phys. Rev. Lett.* **51,** 2224 (1983).
20. S.P. Nehra, M.K. Jangid, S. Srivastava, A. Kumar, B. Tripathi, M. Singh, Y.K. Vijay, *Int. J. Hydrogen Energ.* **34,** 7306 (2009).
21. G. Chris, Van de Walle, J. Neugebauer, *Ann. Rev. Mat. Res.* **36,** 179 (2006).
22. I.A.M.E. Giebels, J. Isidorsson, R. Griessen, *Phys. Rev. B* **69,** 205111 (2004).
23. M.S. Dresselhaus, I.L. Thomas, *Nature* **414,** 332 (2001).
24. J.L.M. van Mechelen, B. Noheda, W. Lohstroh, R.J. Westerwaal, J.H. Rector, B. Dam, R. Griessen, *Appl. Phys. Lett.* **84,** 3651 (2004).
25. R.D. Smith, P. Liu, S.H. Lee, E. Tracy, R. Pitts, *Proceedings of the 2002 U.S. DOE Hydrogen Program Review,* NREL/CP-610-32405 (2002).
26. J. Tauc, *Amorphous and liquid semiconductors* (London, New York: Plenum Press: 1974).
27. M. Singh, *Int. J. Hydrogen Energ.* **21,** 223 (1996).
28. H. Kim, J.S. Horwitz, A. Piqu'e, C.M. Gilmore, D.B. Chrisey, *Appl. Phys. A* **69,** S447 (1999).
29. N. Fukata, S. Sasaki, K. Murakami, *Phys. Rev. B* **56,** 6642 (1997).
30. M. Singh, Y.K. Vijay and I.P. Jain, *Int. J. Hydrogen Energ.* **16,** 485 (1991).
31. M. Singh, Y.K. Vijay and I.P. Jain, *Int. J. Hydrogen Energ.* **16,** 477 (1991).
32. M. Singh, Y.K. Vijay and I.P. Jain, *Int. J. Hydrogen Energ.* **17,** 29 (1992).