

Effect of substrate temperature on microstructural, optical and electrical properties of V₂O₅ thin films

P. Rosaiah^{1,2}, G. Lakshmi Sandhya¹, S. Suresh¹, Jinghui Zhu², Yejun Qiu², O. M. Hussain^{1*}

¹Thin Film Laboratory, Department of Physics, Sri Venkateswara University, Tirupati, 517 502, India

²Shenzhen Engineering Lab of Flexible Transparent Conductive Films, Department of Material Science & Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen, 518055, China

*Corresponding author, E-mail: hussainsvu@gmail.com; rosaiah.svu@gmail.com; Tel: (+91) 9440249072

Received: 30 March 2016, Revised: 03 August 2016 and Accepted: 30 August 2016

DOI: 10.5185/amp.2016/219

www.vbripress.com/amp

Abstract

Vanadium pentoxide (V₂O₅) thin films have been prepared onto ITO coated flexible Kapton substrates by electron beam evaporation technique. The influence of substrate temperature on the structural, morphological, optical and electrical properties has been investigated. The XRD results reveals that the films prepared at lower temperatures are amorphous in nature and the films prepared at 300 °C is exhibited predominant (001) orientation with an orthorhombic crystal structure. AFM study showed that the grain size varies from 80 nm to 150 nm. The optical studies revealed that the transmittance decreased with increasing substrate temperature. The optical absorption coefficient 'α' determined from the experimentally measured transmittance and reflectance data for V₂O₅ films was found to give a better fit for the exponent $n = 3/2$ suggesting the direct forbidden transitions with an estimated optical band gap of 2.31 eV for the films prepared at 300 °C. The electrical conductivity has been observed to be increased from 2×10^{-6} S/cm to 3×10^{-2} S/cm by varying temperature from 30 °C to 300 °C. The electrochemical experiments exhibited the discharge capacity of about 60 μAh/(cm²-μm) for the films deposited at 300 °C. Copyright © 2016 VBRI Press.

Keywords: V₂O₅, thin films, e-beam evaporation, microstructure, optical properties.

Introduction

Vanadium pentoxide (V₂O₅) is one of the most widely investigated multifunctional materials for microelectronic and optoelectronic devices [1]. V₂O₅ is the saturated oxide, and therefore the most stable one in the V-O system. It crystallizes in the orthorhombic unit cell structure. It has a layer like structure and composed of distorted trigonal bipyramidal coordination polyhedra of O atoms around V atoms. The layer structured V₂O₅ is one of the potential cathode materials, because of its high electrochemical potential towards lithium, the possibility to insert upto 3 lithium ions per V₂O₅ leading to a high specific capacity, high energy density and ease of preparation in thin film form [2]. V₂O₅ films exhibits multicoloured electrochromism and have high potential for use in electrochromic display devices and other optical device applications [3-4]. V₂O₅ undergoes a semiconductor/metal transition which changes electrical properties. Since electrical and optical behavior is coupled, V₂O₅ is especially interesting in thin film form due to the possibility of integration into microelectronic

circuitry. Several investigators prepared V₂O₅ thin films by using different techniques such as sputtering [5-6], pulsed laser deposition [7-8], electron beam evaporation [9-10], sol-gel [11-12], thermal evaporation [13] etc, and studied their microstructural, optical and electrochemical properties. Very few investigators studied microstructural and optical properties by using electron beam evaporation technique, especially on flexible substrates though this technique has its industrial viability [14-15]. The microstructural properties of V₂O₅ thin films are depends upon the type of deposition technique and the process parameters involved during the growth. Electron beam evaporation is one of the potential techniques to deposit metal oxide thin films as it offers excellent material utilization, the possibility of precise control of deposition rate and film composition [16-18]. Today's world wide interest is in the development of light weight, high compact, flexible solid state micro-power sources for bio-sensors and MEMS. Synthesis of V₂O₅ thin film cathodes onto flexible Kapton substrates opens a broad study to investigate [19]. The flexible substrates have unique advantages in

comparison to solid glass substrates, such as (1) they can bend and stick to any curved shape object without altering their basic properties, (2) they are weightless, so that easy to carry and can be fold. Hence, in the present investigation, it is aimed to prepare V_2O_5 thin films by using electron beam evaporation technique on ITO coated flexible Kapton substrates. The V_2O_5 films are prepared by varying deposition temperature from room temperature to 300 °C and studied its structural, optical, electrical and electrochemical properties.

Experimental

Synthesis of V_2O_5 thin films

V_2O_5 thin films have been deposited by electron beam evaporation technique using Balzer BA 510 high vacuum coating unit. Pure V_2O_5 powder (99.9 % purity, Sigma Aldrich) pressed into one-inch diameter pellet and subsequently annealed at 500 °C is employed as target material. The vacuum chamber has been evacuated to a base pressure 1×10^{-6} mbar. Pure oxygen is introduced into the chamber and an oxygen partial pressure of about 2×10^{-4} mbar maintained during deposition. The power density of electron beam spot is maintained at 1.2 kW/m². The source to substrate distance is fixed at 12 cm. The films are deposited on ITO coated flexible Kapton substrates maintained at different deposition temperatures ranging from room temperature to 300 °C.

Characterization of V_2O_5 thin films

The structure of the films is characterized by a Siefert X-ray diffractometer (Siefert computerized X-ray diffractometer, model: 3003 TT) with CuK_{α} radiation source filtered by Ni film operated at a voltage of 40 kV and current 30 mA at a scan speed of $0.05^{\circ} s^{-1}$. The peak positions are determined precisely using REYFLEX-Analyze software. The Raman spectrum of V_2O_5 is recorded in the wavenumber region 200-1200 cm^{-1} at room temperature with Jobin Yvon (model HR 800 UV) Raman spectrometer using an excitation wavelength of 532 nm (Nd-YAG laser). The laser power on the sample is measured by a PM 100D consol with a C-series photo diode sensor (Thorlabs GmbH). The surface morphology is recorded with AFM (Digital Instrument: Dimension 3100 series). The optical transmittance of the films is recorded in the wavelength range 300 – 1500 nm using Perkin Elemer UV-Vis-NIR double beam spectrophotometer. The electrical conductivity measurements are performed by using four probe technique. The electrochemical characterization of deposited films was conducted using electrochemical analyzer (CH-Instruments, USA). Discharge profiles of the deposited films are recorded by exposing the effective area of 1.44 cm^2 in at a constant current density of 20 $\mu A/cm^2$ and lithium foil used as an anode.

Results and discussion

X-Ray diffraction

Fig.1(a) shows the X-ray diffraction spectra of V_2O_5 bulk and thin films deposited on ITO coated flexible Kapton substrates at 300 °C. The films grown at ≤ 200 °C exhibited a broad and diffuse patterns (not shown), which indicate their characteristic X-ray amorphous nature [20]. Other orientations such as (200), (110) and (002) are exhibited along with predominant (001) orientation for the films deposited at 250 °C. The appearance of first (001) reflection suggests that the crystallization starts in the films deposited at substrate temperature >200 °C. The films deposited at 300 °C showed well resolved and intense characteristic (400) (101) peaks along with predominant (001) orientation which corresponds to the orthorhombic structure of V_2O_5 with P_{mnm} space group. The subsequent appearance of these additional characteristic orientations in XRD spectrum of the V_2O_5 films is related to the in-plane organization of V-O-V chains. The evaluated lattice parameters from the obtained XRD data are $a = 1.152$ nm, $b = 0.356$ nm, and $c = 0.436$ nm, which are in good agreement with the previous reported values [21]. The full width half maximum (FWHM) of (001) is also increased by increasing the substrate temperature. The estimated crystallite size is 95 nm calculated using Scherer's formula for films deposited at 300 °C. The electron beam evaporated species reach the surface of the ITO coated polymer substrate maintained at a substrate temperature of 300 °C with high kinetic energy.

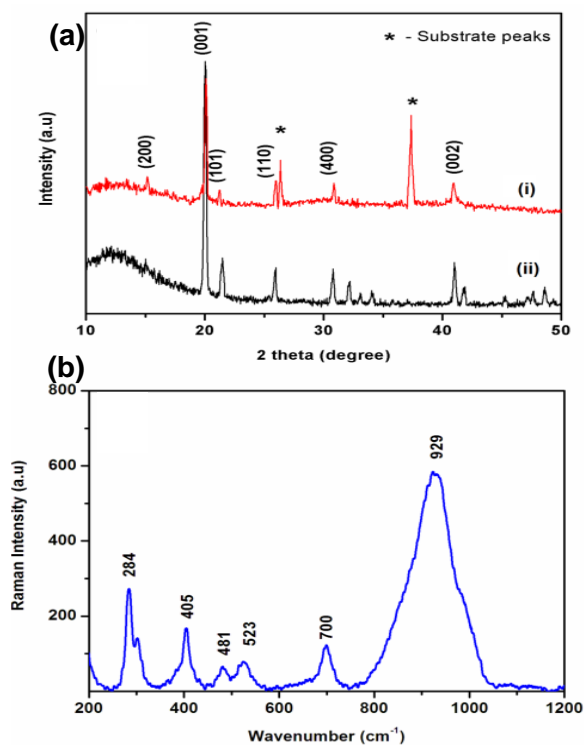


Fig. 1. (a). XRD spectra of V_2O_5 (i) Bulk powder (ii) Films deposited at 300 °C; (b). Raman spectrum of V_2O_5 films deposited at 300 °C.

The impinging species are attracted to the surface by instantaneous dipole quadrupole moments of substrate surface and interacts the condensation of vapor species and favors the formation of a greater number of crystallite centers due to low adatom mobility on polymer surface rather than coalescence of islands. Hence, vertical growth of grains perpendicular to the substrate surface in (001) orientation is observed. This may be responsible for more stress and stain components in the films. The tensile stress generated may be calculated from the c/a ratio and found to be 0.37. The estimated strain generated from the inter atomic attraction forces along the constructed grains is 1.1×10^{-3} . At higher substrate temperatures, the film surface is more pronounced by the coalescence of crystallites in (001) orientation with low crystalline micro-stress leading to the formation of orthorhombic layered structure.

Raman studies

Raman studies are performed in the range of 200 cm^{-1} to 1200 cm^{-1} for the V_2O_5 thin films deposited on flexible substrates. Raman spectrum of V_2O_5 thin film deposited at 300°C is shown in fig.1(b). The spectrum consists of internal modes in high frequency region and external modes in low frequency region [22]. Three peaks at 929 cm^{-1} , 700 cm^{-1} and 523 cm^{-1} were observed in the high frequency region. The first peak is the stretching mode of vanadyl mode terminal oxygen which is due to unshared oxygen.

The second peak is stretching mode of doubly coordinated oxygen (V_2O) which is due to corner-shared oxygens. The third peak is the stretching mode of triply coordinated oxygen ($\text{V}_3\text{-O}$) which is due to edge shared oxygens. The peak located at 481 cm^{-1} is due to bending vibration of V-O-V and $\text{V}_3\text{-O}$ bonds. The peaks located at lower frequency region are assigned to bending vibrations of the V=O bonds. The well resolved vanadyl mode present at 929 cm^{-1} gives the structural quality of the films.

Surface Morphology

AFM images of V_2O_5 thin films prepared at different deposition temperatures are shown in Fig. 2. Generally, the substrate temperature plays a vital role compared to oxygen partial pressure to specify the structure as well as the properties of films prepared from vapor deposition. The surface characterization of V_2O_5 thin films has been made by imaging the surface by using AFM to study the growth mechanism and morphological growth and their dependence on deposition temperature. The AFM data demonstrated that the electron beam evaporated V_2O_5 thin films deposited at lower temperatures ($\leq 200^\circ\text{C}$) are homogeneous and smooth (shown in Fig- 2(a)), indicating the amorphous nature of the films which is also confirmed by X-ray diffraction. If the substrate temperature is very low that the period of atomic jump process of ad-atoms on the surface of

the substrate is very large, then the condensed species may stay wedged to the regions where they are landing thus leading to an amorphous film.

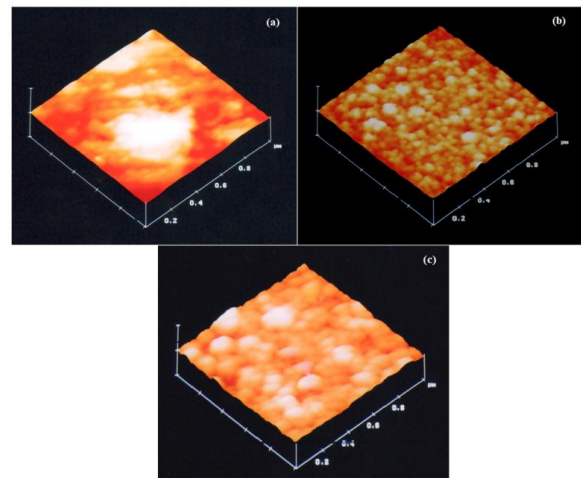


Fig. 2 AFM images of V_2O_5 thin films (a) $T_s = 200^\circ\text{C}$ (b) $T_s = 250^\circ\text{C}$ (c) $T_s = 300^\circ\text{C}$.

From the results, it is clear that the films deposited at lower temperatures, no particle growth was observed. This is because the impinging flux may be just sticking on to the substrate surface at its place of hitting with almost no surface diffusion. Whereas, the films deposited at 250°C composed of spherical particles varying in size and the average grain size is about 80 nm. By further increasing the substrate temperature to 300°C , the grain size has been increased to 150 nm. The root mean square value of surface roughness derived from the AFM image is 15 nm for the films deposited at 300°C . At the higher substrate temperature, the mobility of ad-atoms enhances on the surface of the substrates, which leads to overcome the potential energy of the nucleation sites on the substrate with net increase in the diffusion distance. In addition to this, the collision process initiates the nucleation and favors for the island formation in order to grow continuous film with enhanced grains [23].

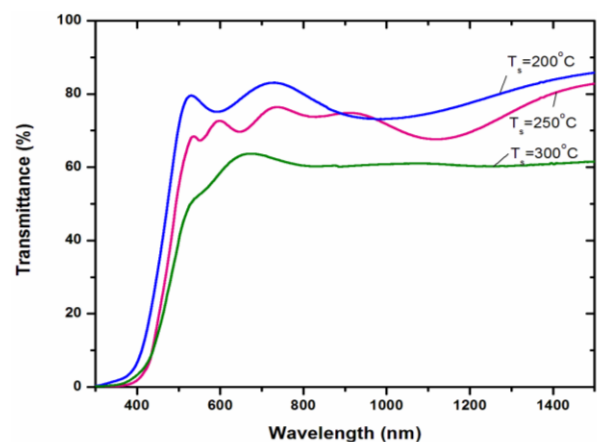


Fig.3. Optical transmittance spectra of V_2O_5 thin films

The estimated root mean square surface roughness of the films is also varied as a function of substrate temperature and found to be increased with increase of substrate temperature from room temperature to 300 °C, respectively.

Optical properties

The optical transmittance of V₂O₅ thin films at different deposition temperatures on ITO coated flexible Kapton substrates in an oxygen partial pressure of 2 x 10⁻⁴ mbar is shown in Fig. 3. The optical transmittance of the films found to be decreased with increasing the substrate temperature. The optical band gap of V₂O₅ thin films is evaluated by the relation as follows [24].

$$T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)}$$

$$(\alpha h\nu) = B(h\nu - E_g)^n$$

where T is the transmittance, R the reflectance, α the absorption coefficient, d the film thickness, $h\nu$ the incident photon energy, B the edge width parameter, E_g optical band gap, n_e the exponent determiner the type of electronic transition causing the absorption and can take values 1/2, 3/2, 2, 3 for different electronic transition such as direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively.

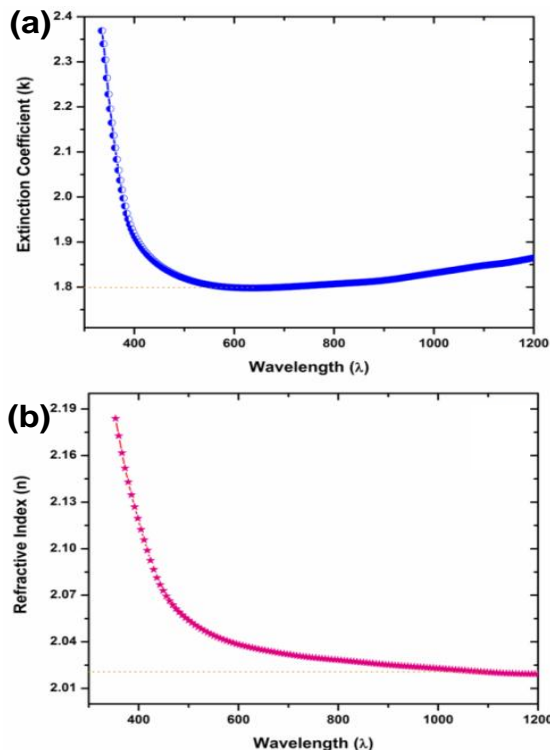


Fig. 4. Variation of the (a) refractive index and (b) extinction coefficient with wavelength of V₂O₅ thin films deposited at 300 °C

The optical band gap of the films is observed to be decreased from 2.34 eV to 2.29 eV by increasing the deposition temperature from 200 °C to 300 °C [25]. The decrease of the optical band gap and transmittance with increase of the deposition temperature may be due to the formation of oxygen ion vacancies in the films which may act as positive defects. As the deposition temperature increases, the films contain a number of oxygen vacancies. These vacancies can be considered as positively charged structural defects capable of capturing one or two electrons. The oxygen vacancies occupied by two electrons may act as a donor centres. These donors form an energy level and exist in the forbidden gap below the conduction band. The possible mechanism of formation of donor levels may be the electrostatic force of attraction offered by the anion vacancy sheet towards the electrons. A large concentration of donor levels may inferior the optical band gap and shifts the optical absorption edge to higher wavelengths. The AFM measurements indicated that the increase in the grain size is associated with a random distribution of the grains on the film surface. The random distribution of the grains makes the film surface rough and the results in the increased light scattering losses at the interface. These are the possible reasons for the decrement of transmittance with increasing grain size. The refractive index and extinction coefficient has been calculated for the films deposited at 300 °C as shown in fig.4. The refractive index of the films is decreased from 2.18 to 2.02 with wavelength and almost same at the higher wavelengths. The extinction co-efficient is also observed to be decreased with wavelength [26].

Electrical and electrochemical properties

The electrical conductivity of V₂O₅ thin films deposited at different deposition temperatures is shown in Fig. 5(a). The electrical conductivity of V₂O₅ thin films is found to be strongly depends on the deposition temperature. By increasing the deposition temperature from 30 °C to 300 °C, the electrical conductivity also increases from 2 x 10⁻⁶ S/cm to 3 x 10⁻² S/cm [27]. The increase in electrical conductivity with deposition temperature may be due to enhancement of crystalline nature of the films as observed from XRD.

The electrochemical properties of V₂O₅ thin films are studied in non-aqueous electrolyte region. The cyclic voltammetric and charge-discharge experiments are performed on Li/V₂O₅ cells with Lithium metal foil as an anode and V₂O₅ thin film deposited at 300 °C as cathode. The cyclic voltammetric performance is studied in the voltage region of 1.5 V to 3.7 V at various scan rates (not shown). It exhibited the typical anodic and cathodic peaks at respected positions, which are consistent with a two-step process. The electrochemical measurements are carried in the potential range 1.50 V-3.7 V at different current densities. The

discharge capacity is observed to be higher at lower current density and decreased by increasing current density [28]. The discharge curve of the film deposited at 300 °C is shown in fig.5(b). It exhibited two plateau regions and showed a discharge capacity of 60 $\mu\text{Ah}/(\text{cm}^2\text{-}\mu\text{m})$ at a rate of C/100 with good cycling stability for first 20 cycles [29]. However, the discharge capacity is gradually decreased at higher cycles.

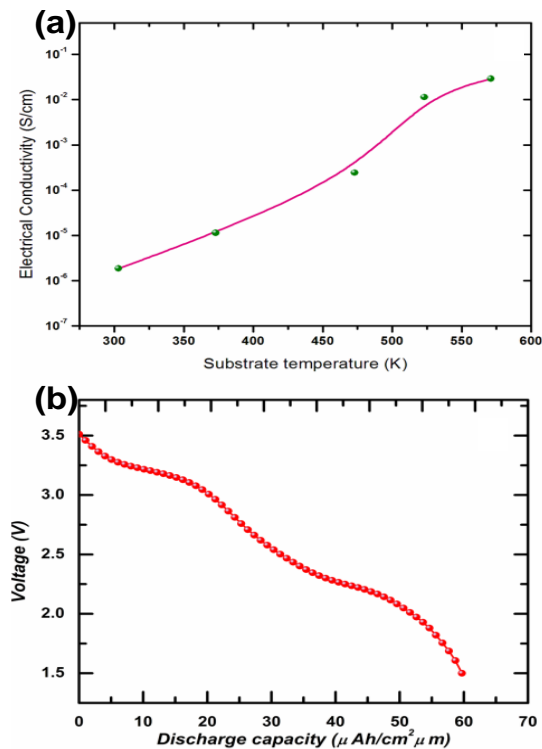


Fig. 5. (a). Variation of electrical conductivity with temperature, (b) Discharge capacity of the films deposited at 300 °C

Conclusion

V_2O_5 thin films has been deposited on ITO coated flexible Kapton substrates at different deposition temperatures in an oxygen partial pressure of 2×10^{-4} mbar using electron beam evaporation technique. The films deposited at lower substrate temperatures (≤ 200 °C) are amorphous in nature. The crystalline nature of the films has been observed to be increased by increasing the deposition temperature. The grain size also increased from 80 nm to 150 nm with substrate temperature. The optical transmittance and band gap have been decreased by increasing the substrate temperature. The room temperature electrical conductivity has been observed to be increased with substrate temperature. The discharge profile of V_2O_5 deposited at 300 °C showed a discharge capacity of 60 $\mu\text{Ah}/(\text{cm}^2\text{-}\mu\text{m})$ at a rate of C/100. These results conclude that the V_2O_5 thin films deposited by electron beam evaporation technique on ITO coated flexible Kapton substrates at moderate substrate temperature exhibited better structural and optical properties which are suggestible to use in solid state microbatteries.

Acknowledgements

The financial aid to the work is extended by Shenzhen Bureau of Science, Technology and Innovation Commission JCYJ20140417172417151.

References

- Giannetta,HMR; Calaza,C; Lamas,DG; Fonseca,L; Fraigi,L; *Thin Solid Films*, **2015**, 589, 730.
- Haihong Yin; Ke Yu; Hui Peng; Zhengli Zhang; Rong Huang; Jadranka Travas-Sejdic; Ziqiang Zho; *J.Mater.Chem.*, **2012**, 22, 5013.
- Atuchin,V.V; Ayupov, B.M; Kochubey, V.A; Pokrovsky, L.D; Ramana, C.V; Rumiantsev, M; *Opt.Mater.*, **2008**, 30, 1145.
- Deepak Raj,P; Sudha Gupta; Sridharan,M; *Mater. Sci. Semicond. Process.*, **2015**, 39, 426.
- Quinzeni,I; Ferrari,S; Quartarone,E; Mustarelli,P; *J. Power Sources*, **2011**, 196, 10228.
- Giannetta, HMR; C. Calaza,C; Lamas,DG; Fonseca,L; Fraigi,L; *Thin Solid Films*, **2015**, 589, 730.
- Ramana,C.V; Smith,S,J; Hussain,O.M; *Phys. Status Solidi*, **2003**, 199, 1.
- Huotari,J; Lappalainen,J; Eriksson,J; Bjorklund,R; Heinonen,E; Miinalainen,I; Puustinen,J; Lloyd Spetz,A; *J. Alloys Compd.*, **2016**, 675, 433.
- Ramana,C.V; Hussain,O.M; Uthanna,S; Srinivasulu Naidu,B; *Opt. Mater*, **1998**, 10, 101.
- Venkata Ramana,C.V; Hussain,O.M; Srinivasulu Naidu,B; Julien,C; *Mater. Sci. Eng. B*, **1999**, 60, 173.
- Olivier Monfort; Tomas Roch; Leonid Satrapinsky; Maros Gregor; Tomas Plecenik; Andrej Plecenik; Gustav Plesch; *Appl. Surf. Sci.*, **2014**, 322, 21.
- Sujata Senapati; Siddhartha Panda; *Thin Solid Films*, **2016**, 599, 42.
- Santos,R; Loureiro,J; Nogueira,A; Elangovan,E; Pinto,JV; Veiga,JP; Busani,T; Fortunato,E Martins,R; Ferreira,I; *Appl. Surf. Sci.*, **2013**, 282, 590.
- Vasanth Raj, D; Ponpandian, N; Mangalaraj, D; Viswanathan, C; *Mater. Sci. Semicond. Process.*, **2013**, 16, 256.
- Yung-Sen Lin; Chung-Wei; *Surf. Coat. Technol.*, **2008**, 202, 5641.
- Jitendra Pal Singh; Sulania,I; Jai Prakash; Goutam,S; Chae,K.H; Kanjilal,D; Asokan,K; *Adv. Mater. Lett.*, **2012**, 3, 112.
- Tanusevski,A; Poelman,D; *Sol. Energy Mater. Sol. Cells*, **2003**, 80, 297.
- Zhongdan Lu; Xiaohong Jiang; Bing Zhou; Xiaodong Wu; Lude Lu; *Appl. Surf. Sci.*, **2011**, 257, 10715.
- Jeevan kumar,P; Jayanth babu,K; Hussain,O.M; *Adv. Sci. Eng. Med.*, **2012**, 04, 190.
- Rajendra Kumar,R.T; Karunakaran,B; Venkatachalam,S; Mangalaraj,D; Narayandass,K.Sa; Kesavamoorthy,R; *Mater. Lett.*, **2003**, 57, 3820.
- Navone,C; Pereira-Ramos,J.P; Baddour-Hadjean,R; Salot,R; *J. Power Sources*, **2005**, 146, 327.
- Harikrishna koduru; Hussain mahammad obili; Guillen Cecilia; *Int. nano lett.*, **2013**, 3, 24.
- Ramana,C.V; Smith,S,J; Hussain,O.M; Julien,C.M; *Mater. Sci. Eng. B*, **2004**, 111, 218.
- Ashwani kumar; Preetam Singh; Nilesh Kulakarni; Davinder Kour; *Thin Solid Films*, **2008**, 516, 916.
- Mane,A; Ganbavle,VV; Gaikwad,MA; Nikam,SS; Rajpure,KY; Moholkar,AV; *J. Anal. Appl. Pyrolysis*, **2015**, 115, 57.
- Alaa A.Akl; *Appl. Surf. Sci.*, **2006**, 252, 8749.
- Boudaoud,L; Benramdane,N; Desfeux,R; Khelifa,B ; Mathieu,C; *Catal. Today*, **2006**, 113, 233.
- Lianyi Shao; KaiqiangWu; XiaotingLin; MiaoShui; RuiMa; DongjieWang; Nengbing Long; YuanlongRen; JieShu; *Ceram. Int.*, **2014**, 40, 6115.
- K.Harikrishna; O.M.Hussain; *Ionics*, **2013**, 19, 1359.