VERSATILITY OF THIN FILM AND THIN FILM DEPOSITION TECHNIQUES AND PARAMETERS

VINAY KUMAR SINGH
Department of Physics, Raja Singh College, Siwan, Bihar, India, Pin-841226.

ABSTRACT: ***This article reviews and explores the basic conceptions of an intensive of thin film and deposition techniques. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The prime requisite for getting sensible quality thin film is that the optimization of propaedeutic conditions viz. substrate temperature, spray rate, concentration of solution etc. This is often the foremost crucial parameter because it permits management over the scale of the droplets and their distribution over the preheated substrates. The consequences of precursor, dopants, substrate temperature, post tempering treatments, concentration etc., on the physico-chemical properties of those films are given likewise. The properties of the thin film will be simply tailored by adjusting or optimizing these conditions that successively are appropriate for a specific application. The key challenges of spray paralysis are control over the morphology and composition of product particles. It has been widely applied in the past few years.***

Keywords: **Thin films, Basic concepts, Deposition, Parameters, Conditions, Substrate, CVD, PVD, SPT, Applications, etc.**

I. INTRODUCTION

In the last few decades, the thin films technology has played vital role in the development of electronics, optoelectronics and PV solar cells applications. The spray paralysis technique is a wonderful and unique method in material science. Numerous materials are ready within the kind of thin films over a century attributable to their potential technical price and scientific curiosity in their properties. They need terribly wide selection of applications and extend from micrometer dots in electronics to coatings of many square. meters on window glasses. The varieties of techniques are examined within to explore for the foremost reliable and most cost-effective technique of manufacturing the thin films. These embrace reaction of a gaseous metal film, reactive and nonreactive sputtering techniques, chemical vapor deposition etc. and variety of strategies involving growth from chemical solutions, questionable chemical techniques. Many studies have been done over about three decades on Chemical Spray Paralysis (CSP) process and preparation of thin films. The first introduction of the spray paralysis technique pioneering work by *Chamberlin* and *Skarman* in 1966 on cadmium supplied (CdS) films for solar cells applications. Since then, the process has been investigated with various materials, such as SnOx , In2O3 , Indium Tin Oxide (ITO) , PbO , ZnO , ZrO2 , YSZ and others. Mooney and Radding reviewed the spray pyrolysis method, properties of the deposited films in relation to the conditions, specific films (particularly CdS), and device application. Tomar and Garcia discussed preparation and properties of sprayed films as well as their application in solar cells, anti-reflection coatings, and gas sensors. Albin and Risbud presented a review of the equipment, processing parameters, and optoelectronic materials deposited using CSP technique. Pamplin published another review on the use of spraying for preparing solar cells as well as a bibliography of references on the spray paralysis technique. Recently, deposition of thin metal oxide and chalcogenide films using spray pyrolysis and different other atomization techniques were reviewed by Patil. Bohac and Gauckler discussed the mechanism of chemical spray deposition and presented some examples of sprayed Yttria-stabilized zirconia (YSZ) films. Lazhar Hadjeris et.al in 2009, prepared ZnO films using the simple, flexible and cost-effective spray paralysis technique at different substrate temperatures and precursor molarities values. F.K. Allah et al, studied the characterization of porous doped ZnO thin films deposited by spray paralysis technique. T. Devodaet analyzed a novel deposition method to grow ZnO nanorods by spray paralysis method. R. Ayouchi et. al, studied the preparation and characterization of transparent ZnO thin films obtained by spray paralysis in the year 2003.

II. THIN FILMS

Thin film can be defined as a low dimensional material (10^3nm), created by one-by-one condensing the atomic (molecular / ionic species of matter onto a substrate. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Thin film technology is the basic of astounding development in solid state electronics. The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical properties has changed the modern society. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film. The thin film of some substance, it has a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore in profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. The one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro systems and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. There are many techniques to deposit the films, e.g. - CVD, PVD, ion plating, sputtering, electroplating, ECD, etc. However, all these techniques require sophisticated instrumentation and high vacuum system. The SPT on the other hand can be used to deposit thin film at relatively less vacuum level. The deposition unit is also very simple and thin film can be prepared in few minutes. Thin film can be classified accordingly to their thickness as Ultra thin films (UTF), Thin films (TF), and Thick films (TcF), etc. The latest research is directed toward achieving defect-free uniform films and coatings on different substrates with high deposition rate for low-cost and mass-scale production. The thin films having various potential technical values, and numerous materials have been prepared in the form of thin films over a century also due to scientific curiosity in their properties. They have wide range of applications and extend from microelectronics to coatings of several square meters on window-glasses. The quality and properties of thin films depend largely on the preparation conditions, anion to cation ratio, spray rate, substrate distance, substrate temperature, ambient atmosphere, carries gas, droplets size, and also the cooling rate after deposition. The thin films thickness depends upon the distance between the spray-nozzle and substrate, substrate temperature, concentration of the precursor solution and the quality and quantity of the precursor solution sprayed.

III. THIN FILMS DEPOSITION PROCESS

Thin films can be prepared from a variety of materials such as metals, semiconductors, insulators or dielectrics etc., and for this purpose; various preparation techniques have also been developed. The act of applying a thin film to a surface is called thin film deposition. Deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical. Physical method covers the deposition techniques which depends on the evaporation or ejection of the material from a source; i.e. evaporation or sputtering. The material to be deposited is placed in an energetic, entropic environment, so that the particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

We can classify the deposition by chemical methods into two classes. The first of these classes is concerned with the chemical formation of the film from medium, and typical methods involved are electroplating, chemical reduction plating and vapor phase deposition. A second class is that of formation of this film from the precursor ingredients, e.g. Iodization, gaseous iodization, thermal growth, sputtering ion beam implantation, CVD, MOCVD and vacuum evaporation.

A number of techniques have been examined in search for the most reliable and cheapest method over a century of producing the thin film, these include oxidation of evaporated metal film, reactive and non-reactive sputtering technique, CVD, etc, and a number of methods involving growth from chemical solutions. So, it is called chemical techniques. Owning to their simplicity and inexpensiveness, the chemical techniques have been studied extensively for the preparation of thin films. Moreover, it facilates materials

to be designed on a molecular level. The thin films, semiconductors and dielectrics can be deposited by various techniques. These techniques are PVD, and CVD.

The selection of techniques used for prepare thin films are depends upon the type of materials to be used for deposition for the deposition of thin films. Now, it is classified as-Physically, Chemically, and electrochemically, etc.

For the either of these processes, typical steps in the preparation of thin films-

(i) An emission of particles from the source (heat, high voltage), etc.
(ii) Transport of particles to substrate and
(iii) Condensation of particles on the substrate.

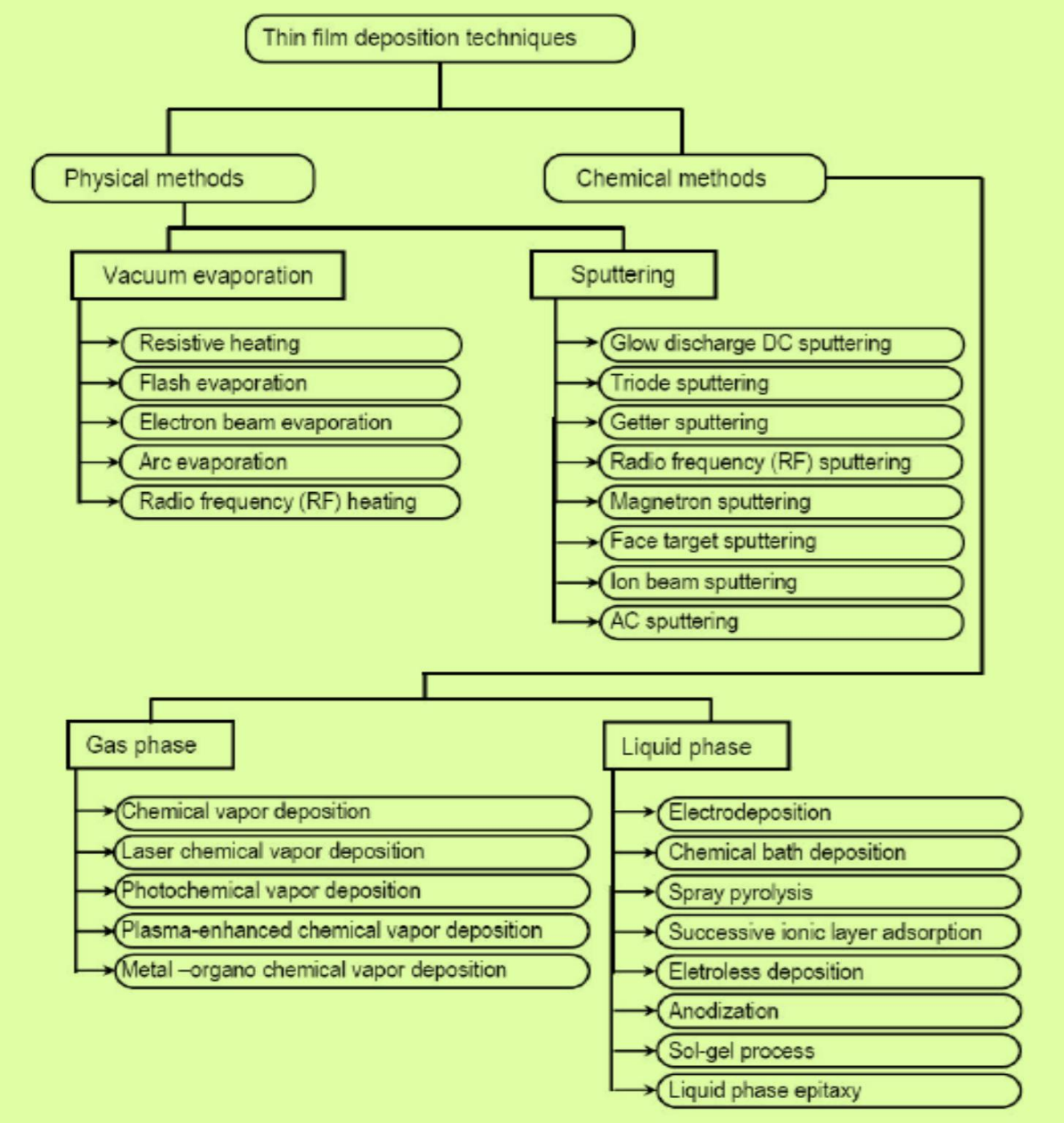

Figure 1: Broad classification of thin film deposition techniques

IV. THIN FILM DROPLETS FORMATION

The production of droplets and their dispersion into the gas influences the size and morphology of the aggregates in the thin film due to the concentration and velocity of the generated droplet. Depending on spray parameters (e.g. nozzle diameter, carrier gas pressure, distance between nozzle and substrate), the droplet size and distribution may be controlled. The cone-jet mode is obtained when the liquid is distorted at the tip of the tube type nozzle into a conical shape (Taylor cone). This cone is extended at its apex by a permanent jet of very small diameter. If the electric field is used for the atomization, the jet may be split, forming a multi-jet mode spray. The aerosol flow rate (Fa) is influenced by the liquid properties as vapor pressure (P), viscosity (η), and surface tension (σ), as follows:

$$F_a = K\sqrt{\frac{P}{\eta\sigma}} \qquad [1]$$

Where K, is a coefficient depending on the power necessary to generate the aerosol. Based on this equation, the influence of additives in the precursors' solutions can be explained: the addition of acetilacetone lowers the solution viscosity and the addition of the surfactants lowers the solution surface tension, thus increasing the aerosol flow rate. During transportation, different forces act on the droplets, influencing the trajectory and flow rate: gravitational, Stokes, termophoretic, electric. The termophoretic force pushes the droplet away from a hot surface, and due to this force, the thin film grows also from vapor-containing droplets passing very close to the hot substrate. The droplets spread on the substrate and initially form a powdery deposit. From the aerosol droplets the solvent can evaporate during transport to substrate. This leads to a size reduction of the droplet and to the development of the concentration gradient within the droplet. The precursor precipitates on the surface of the droplet when the surface exceeds the solubility limit. Precipitation occurs due to rapid solvent evaporation and slow solute diffusion. This results in a porous crust. When the droplets are large and the droplet concentration is low, undesired hollow particles are formed. Smaller droplets produce solid particles because the diffusion distance of the solute is shorter, leading to a more uniform concentration distribution within the droplet. Increasing the number of droplets results in a larger solvent vapor concentration in the carrier gas. Consequently, the evaporation rate decreases and precipitation is delayed. Therefore, an increase in the droplets number decreases the probability of forming hollow particles.

Table1: Some facts about the residual air at 25^{0}C in a typical vacuum used for thin film deposition

S. No.	pressure in (Torr)	Mfp (cm) between collisions	Collisions/sec between molecules	Molecules (cms^{-1}) Striking surface	Monolayer (s^{-1})
1.	10^{-2}	0.5	9×10^{4}	3.8×10^{18}	4400
2.	10^{-4}	51	900	3.8×10^{16}	44
3.	10^{-5}	510	90	3.8×10^{15}	4.4
4.	10^{-7}	5.1×10^{4}	0.9	3.8×10^{13}	4.4×10^{-2}
5.	10^{-9}	5.1×10^{6}	9×10^{-3}	3.8×10^{11}	4.4×10^{-4}

V. UNIFORMITY OF THIN FILM

A thickness of the thin films is one of the most critical parameter to get the desired performance of the materials. Properties like; anti-reflection coatings, gain magneto-resistance devices, neutron beam guides, and optical filters depend highly on the thickness of the film. An equally important is the uniformity of thickness across the area of interest. With the exception of atomic layer deposition, all the techniques other than thermal flash evaporation technique can produce films with some level of uniformity. Approaches to reduce thickness variations in thin film deposition method include:

(i) Optimizing the bulk materials throw distance to the substrate and

(ii) Speed of the substrate rotation. Distance between the target material and the substrate has an impact

on the quality of uniformity of the deposition.

VI. MORPHOLOGY OF THIN FILMS

The shape, size, structure and arrangements of the particles that composed the object surface or thin film's surface are called morphology. Hence the science of structure of materials and its study is called *morphology*. Whatever the technique used to deposited the films, its structure depends upon on the various deposition parameters, such as the rate of deposition and the angle of deposition, nature of substrate and its surface, thickness of the film and temperature of the substrate. Hence, the structural study of thin film is called morphology. The detailed morphology of a film depends upon many factors involved in growth of film including: chemical/physical properties of depositing material; substrate temperature, flatness of substrate, deposition rate, process or residual gas pressure, surface diffusion, film growth mode, residual stress in the film, and match the film's and substrate's lattice parameters.

VII. PHOTOVOLTAIC PROPERTIES OF THE THIN FILM

The thin film /coating should have the following physical properties:

(a) The absorptance for the solar spectrum range must be high.
(b) The emissivity must be low for wave-lengths greater than 2.0µm.
(c) The transition between the region of high absorptance and low emisttance should be as sharp as possible.
(d) The opto-physical properties of the most remain stable under long term operation at elevated temperature, repeated thermal cycling, air exposure, ultra-radiations etc.
(e) Adherence of the coating to the substrate must be good.
(f) The films/ coatings must be economical.

VIII. APPLICATIONS OF THIN FILMS

The requirement of micro miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage techniques and it is this which has stimulated most of the research on magnetic properties of thin films. Thin film materials have already been used in semiconductor devices, wireless communication, telecommunications, integrated circuits, rectifiers, transistors, solar cells, LEDs, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer capacitors, flat panel displays, smart windows, computer chips Microelectronics- Electrical conductor, Electrical barriers, diffusion barriers, MEMS, organic electronics, displays, quantum dots Electronic gadgets- CD, DVD, computers, hard drives, GMR, read heads, head lamp reflectors, Semiconductors, Semiconductors chips, transport conducting layers, solar cells, diode advanced solar panels, Sensors- gas sensors, magnetic sensors, magnetic memory, accelometers, as well as other emerging cutting edge technologies, etc.

IX. CONCLUSIONS

In the last few decades thin films: Science and technology are became new branch of material science and has played vital role in the development of solar cells, solid-state physics, electronics devices, and industries, etc. A survey on obtainable literature on chemical SP technique reveals that it so offers a beautiful methodology to arrange large choice of thin film materials for numerous industrial applications. The standard and properties of thin films rely for the most part on the preparation conditions. Recently, stress given to two aspects: First atomization techniques to manage the drop size and their distribution a lot of exactly, and Second use of beginning compounds like organotin to get extremely homeward thin films looks brighter. Any efforts are necessary to couple these two aspects to get prime quality thin films by spray paralysis technique. Therefore, spray pyrolisys deposition represents a versatile technique, allowing the development of large area thin films for solar energy conversion devices. The paper reviews the parameters that have significant influence on the crystalline structure and morphology, with a focus on the most important output properties for opto-electronic devices.

ACKNOWLEDGMENTS

One of the authors, **DR. VINAY KUMAR SINGH** takes this opportunity to thank Prof. M.K. Sharan, Ex-Principle and HOD, Department of Physics, Rajendra College, J.P. University, Chapra, for numerous discussions, valuable suggestion and help in preparing the present research paper for publication. I also feel indebted to some scientific spiritualists who provided us the enthusiasm to undertake scientific studies with a wholesome attitude.

REFERENCES

[1] R.R. Chamberlin, J.S. Skarman, J. Electrochem. Soc. 113 (2000), 86.
[2] K.L. Chopra and I.J. Kaur, *Thin film Device applications*, Plenum Press, New York, 1983.
[3] K.L. Chopra and S.R. Das, *Thin Film Solar Cells*, Plenum Press, New York, 1983.
[4] R.R. Chamberlin, J.S. Skarman, *J, Electrochem. Soc.*, 113(1966), 86.
[5] M. Fujimoto, T. Urano, S. Murai and Y. Nishi, *Jpn. J. Appl. Phys.*, 28(1989), 2587.
[6] I. Yagi, K. Kakizawa, K. Murakami and S. Kaneko, *J. Ceram.Soc.Jpn.*, 102(1994), 296.
[7] C.H. Lee, L.Y. Lin, *Appl. Surf. Sci.*, 92(1996) , 163.
[8] A. Aoki, G. Nogami, *J. Electrochem. Soc.*, 143(1996) L 191.
[9] P.S. Patil and P.R. Patil, *Tr. J. Phys.*, 18(1994) 1330.
[10] D. Craigen, A. Mackintosh, J. Hickman, K. Colbow, *J. Electrochem. Soc.*, 133(1986), 1529.
[11] P.S. Patil and R.S. Patil, *Bull. Mater. Sci.*, 18(1995), 911.
[12] L.D. Kadam, C.H. Bhosale and P.S. Patil, *Tr. J. Phys.*, 21(1997), 1037.
[13] P.S. Patil, E.A. Ennaoui, C.D. Lokhande, M. Muller, M. Giersig, K, Diesner and H. Tributsch, *Thin Solid Films*, 310(1997) 57.
[14] C.H. Chen, A.A.J. Buysman, E.M. Kelder, J. Scnoonman, *Solid State Ionics*, 80(1995) 1.
[15] R.N. Singh, J.F. Koenig, G. Poillerat, P. Chartier, *J.Electroanal. Chem.*, 314(1991)241.
[16] B. Lefez, P. Nkeng, J: Lopitaux, *Mater. Res. Bull.*, 31(1996) 1263.
[17] C.S. Huang, C.S. Tao, C.H.Lee, *J. Electrochem. Soc.*, 144(1997) 3556.
[18] A.G. Valyomana, S. Mathew, K.P. Vijaykumar, C. Purushottam, *Bull. Mater. Sei.*, 16(1993) 55.
[19] J.P. Mangalhara, R. Thangraj, O.P. Agnihotri, *Bull. Mater. Sci.*, 10(1988) 333.
[20] J.De Merchant and M.Cocivera, *J. Electrochem. Soc.*, 143(1996) 4054.
[21] K. Y. Rajpure, A.M. Patil, C.D. Lokhande and C.H. Bhosale, *Thin Solid Films*, (In press).
[22] V.V. Killedar, C.D. Lokhande and C.H. Bhosale, *Thin Solid Films*, 289(1996) 14.
[23] S. Lopez, S. Granados, A.Ortiz, *Semiconductor Sci. Technol.*, 11(1996)
[24] W.A.S.A. Ghafor, N.A. Awad, N.S. Othman, *Ind J.Pure and Appl.Phys.*, 31(1993) 123.
[25] Y.D. Tembhurkar and J.P. Hirde, *Bull.Mater.Sci.*, 17(1994) 465.
[26] S.P.S. Arya and H.E. Hinterman, *Thin solid Films*, 193(1990) 841.
[27] S. Kumari, A.K. Singh and O.N. Srivastava, *Supercond, Sci. and Technol.*, 9(1996) 405.
[28] S.H. Pawar and P.N. Pawaskar, *Mater.Res.Bull.*, 30 (1995) 277.
[29] K. Badeker, Ann. Phys. (Berlin) 22 (1907) 749.
[30] K. L. Chopra, S. Major, D. K. Pandya,*Thin Solid Films*, 102 (1983)
[31] H. Hosono, T. Kamiya, M. Hirano, *Bull. Chem. Soc. Jpn*. 79 (2006)
[32] H. Kawazoe, K. Ueda, *J. Am. Ceram. Soc*, 82/12 (1999) 3330.
[33] T. Minami, Semicond. *Sci.Technol.* 20 (2005) S35.
[34] D. S. Ginley, J.D. Perkins, H. Kawazoe, D.M. Newns, A.B. Kozyrev, *Proceedings of the Materials Research Society, Materials Research Society*, (2001) 433.
[35] D. C. Paine, H.-Y.Yeom, B. Yaglioglu, in: G.P. Crawford (Ed.), Flexible Flat Panel Displays, *WileyInterscience*, JohnWiley and Sons (2005) 79.
[36] R. Ayouchi, D. Leinen, F. Martin, M. Gabas, E. Dalchiele and J. R. Ramos Barrodo, *Thin Sold Films* 426 (2003) 68.
[37] H. L Hartnagel, A. L Dawar, A. K Jain, C. Jagadish, *Semiconducting Transparent Thin Films* (Philadelphia, PA: Institute of Physics Publishing) (1995).
[38] T. Minami, *MRS Bull.*25 (2000) 38.
[39] A. J. Freeman, K R Poeppelmeier, T O Mason, R P H Channg, T J Marks, *MRS Bull.* 25.
[40] R. G. Gordon, *MRS Bull.* 25 (2000) 52.

[41] J.C Viguiě, J. Spitz, *J. Electrochem. Soc: Solid State Science and Technology.* 122(4) (1975).
[42] T. Minami, H Nanto, S Takata Japan. *J. Appl. Phys.*23 (1984) L280.
[43] T. J. Minami. *Vac. Sci. Technol.* A 17 (1999) 1765.
[44] L. Holland, *Vacuum Deposition of Thin Films.* Wiley, New York (1958).
[45] J. L.Vossen, *Phys. Thin films,* 9 (1977) 1.
[46] T.H. Sajeesh et al., *MRSI-AGM,* New Delhi (2007).
[47] J. C. Manifacier, *Thin Solid Films* 90 (1982) 297.
[48] J.B. Mooney, S.B. Radding, *Annu. Rev. Mater. Sci.* 12 (1982) 81.
[49] Ratheesh Kumar P.M., Ph.D Thesis, Cochin University of Science and Technology.
[50] Teny Theresa John, Ph.D Thesis, Cochin University of Science and Technology, India
[51] Lampkin C.M., *Prog. Cryst. Growth Characterization of Materials.* 1(4) (1979) 405.
[52] S.P.S Arya, H.E.Hintermann, *Thin Solid Films.* 193 (1990) 841.
[53] J. Zeleny, *Phys. Rev.* 3(2) (1914) 69.
[54] J.M. Grace, J.C.M. Marijnissen, *J. Aerosol Sci.* 25 (6) (1994) 1005.
[55] T. Sebastian, R. Jayakrishnan, C. SudhaKartha, K.P.Vijaya kumar, *The Open Surface Science Journal.* 1 (2009).
[56] G. Dong, M. Zhang, X. Zhao, H. Yan, C. Tian and Y. *Ren Applied Surface Science* 256.
[59] Duminica, F.D.; Maury, F.; Abisset, S. Pyrosol deposition of anatase TiO2 thin films starting from Ti(OPr)4/acetilacetone solutions. *Thin Solid Films,* 2007, *515,* 7732-7739.
[60 Perednis, D.; Gauckler, L.J. Thin Film Deposition Using Spray Paralysis. *Journal of Electroceramics,* 2005, 14, 103-111.
[61] V.K. Singh, M. K. Sharan, & K.P. Srivastava, Amorphous Semiconducting Carbon Thin Films from Castor Oil. *Material Science Research India,* Vol. 03, No. (2a), 2006, pp (263-266).
[62] V.K. Singh, M. K. Sharan, & K.P. Srivastava, Amorphous Semiconducting Carbon Thin Films for Carbon PV-Cells, *Acta Ciencia Indica of Chemistry,* Vol. XXXIVC, No. 1, 27, (2008), pp (127-132).
[63] V.K. Singh, M. K. Sharan, & K.P. Srivastava, Spray Paralyzed Semi-Conducting Carbon Thin Films from Turpentine Oil, *International Journal of Chemical Sciences,* Vol. 4(3): 2006, pp (660-664).
[64] V. K. Singh & H. N. Sah, Review of Carbonaceous Materials in Castor Oil for Thin Films Deposition, *Journal of Emerging Technologies and Innovative Research,* Vol. 4, Issue 7, July 2017, pp 205-211.
[65] V. K. Singh & H. N. Sah, Versatility of Spray Paralysis Technique for the Deposition of Carbon Thin Films, *Journal of Emerging Technologies and Innovative Research,* Volume 4, Issue 8, August 2017, pp 312- 318.
[66] V. K. Singh, Solar Electricity from Solar Energy and Future Applications, *Journal of Emerging Technologies and Innovative Research,* Volume 4, Issue 9, pp 511-518, September 2017.