International Research Journal of Human Resource and Social Sciences
ISSN(O): (2349-4085) ISSN(P): (2394-4218)
Impact Factor 6.924 Volume 9, Issue 09, September 2022
Website- www.aarf.asia, **Email** : editoraarf@gmail.com

PREPARATION OF TiO2 FILMS BY DC REACTIVE SPUTTERING (DCRS), ELECTRON BEAM EVAPORATION (EBE) AND CHEMICAL SPRAY PYROLYSIS (CSP) TECHNIQUES

ITHAPE PANDURANG ABASAHEB

RESEAERCH SCHOLAR SUNRISE UNIVERSITY ALWAR

DR. ARVIND KUMAR

ASSISTANT PROFESSOR SUNRISE UNIVERSITY ALWAR

ABSTRACT

Due to their high-quality physical, optical, and electric features, metal oxide thin films have achieved remarkable success in the semiconductor industry. Solar cells, biosensors, biomedical applications, super capacitors, photo catalysis, luminous materials, and laser devices are only some of the potential applications for these materials, which are gaining increasing attention. Many studies have reported successful attempts at producing thin films using a wide variety of deposition techniques. Films' qualities need to be characterized in detail so that their design may be optimized. Thin-film solar cells, perovskite solar cells, and dye-sensitized solar cells are the primary research and development foci in this study. Solar cells made under varying circumstances were analyzed for their photovoltaic properties (short-circuit current, open-circuit voltage, fill factor, and efficiency). The experimental results verified the feasibility of using metal oxide as an electron transport layer, electron conducting medium, anti-reflection layer, and whole transport material.

KEYWORDS: TiO2 Films, DC Reactive Sputtering, Electron Beam Evaporation, Chemical Spray Pyrolysis, anti-reflection layer

INTRODUCTION

Transparent semiconductor oxide films with high conductivity and optical properties can be prepared by various techniques, e.g., RF sputtering, chemical spray pyrolysis, DC sputtering, chemical vapour deposition, electrodeposition, and electron beam evaporation.

In this chapter, the details of the preparation of titanium dioxide (TiO2) films by DC reactive sputtering, electron beam evaporation and chemical spray pyrolysis techniques are presented. The complete configuration of these technique and the procedures that have been adopted to deposit TiO2 films are elaborated. The optimized conditions for depositing TiO2 film under each technique are also presented which are used for characterization in their respective chapters IV, V and VI respectively.

ELECTRON BEAM EVAPORATION (EBE) TECHNIQUE

Amongst the various techniques available, one of the physical vapor deposition methods, electron beam evaporation technique [1-4] is the widely used method for the deposition of superior quality oxide thin films. It offers flexibility in the control over various deposition parameters and easy adaptability of this technique for commercial purposes. As far as the electron beam evaporation is concerned, very thin films with a good surface finish can be obtained and there is no restriction on the type of substrate. The some of the disadvantages of other evaporation methods are that the sources include possible contamination by crucibles, heaters and support materials and the limitation of relatively low input power levels, which make them difficult to deposit pure films or evaporate high melting point materials at appreciable rates. Electron beam heating eliminates these disadvantages and has, therefore, become the most widely used vacuum evaporation technique to prepare highly pure films. In principle, this type of source enables evaporation of virtually all materials at almost any rate. Another major advantage of this technique is, multiple source units are available for the sequential or parallel deposition of more than one material [5-7].

Pressure is the most widely quoted system variable in vacuum technology, and this fact has generated a large number of units that have been used to define it under various circumstances. Basically, two broad types of pressure units have arisen in practice. The pressure is defined as the rate of change of the normal component of momentum of impinging molecules per unit area of surface. Thus, the pressure is normally defined as a force per unit area, the unit are dynes/cm2 (CGS) or N/m2 (MKS). Vacuum levels are now commonly reported in SI units or pascals; 1 pascal (Pa) = 1 N/m2. The definitions of some units together with important conversions are [8]:

$$1 \text{ atm} = 1.013 \times 10^6 \text{ dynes/cm}^2 = 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ Torr} = 1 \text{ mmHg} = 1.333 \times 10^3 \text{ dynes/cm}^2 = 133.3 \text{ N/m}^2 = 133.3 \text{ Pa}$$

$$1 \text{ bar} = 0.987 \text{ atm} = 750 \text{ Torr}$$

Mean-free path is an important property of the gas that depends on the pressure, which is defined as the mean distance traveled by molecules between successive collisions. At atmospheric pressure, the mean free path of the molecules in air = 6x10-6 cm (10-4 cm = 1 micron; 1 micron = 10-3 Torr). Since the number of collisions between vapor and gas molecule is limited, at low pressures, the vapor molecules propagate in straight line paths. This principle is used in vacuum deposition.

For the preparation of TiO2 films by electron beam evaporation technique, we have used 12" Hind High Vacuum coating unit (model 12A4D) with electron beam solid state power supply (EBG-PS-3K).

The vacuum coating unit used in the experiments comprised of a collar with bell jar (coating chamber) pumped by a conventional oil diffusion pump backed by an oil rotary pump.

The schematic diagram of the vacuum coating system is shown in Fig. 1.

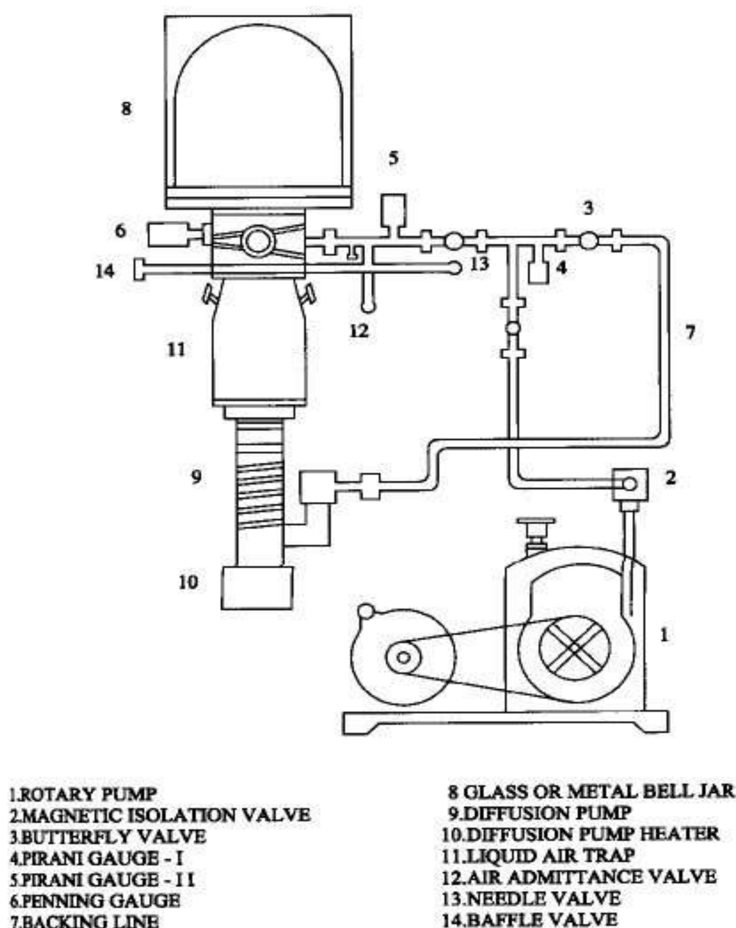

Figure 1The schematic diagram of the vacuum coating system

© Association of Academic Researchers and Faculties (AARF)

The photograph of coating unit and electron beam power supply that has been employed in the present work is shown in Fig. 2.

Figure 2 Photograph of coating unit and electron beam power supply

The some key notes on the various pumps that have been used in the coating unit to create the desired vacuum is elaborated below.

Rotary pump

The rotary piston and rotary vane pumps are the two most common devices used to attain reduced pressure. In the rotary piston pump gas is drawn into the keyed shaft rotates the eccentric and piston. There the gas is isolated from the inlet after one revolution, then compressed and exhausted during the next cycle. Hind Hivac coating unit is having direct driven rotary vane type vacuum pump. The rotary vane pump contains an eccentrically mounted rotor with spring loaded vanes. During rotation the vanes slide in and out within the cylindrical interior of the pump, enabling a quantity of gas to be confined, compressed and discharged through an exhaust valve into the atmosphere. The whole stator/rotor assembly is submerged in suitable oil. Single stage vane pumps have an ultimate pressure of 10-2 Torr, and two stage pumps can reach 10-4 Torr. Rotary pumps are frequently used to produce the minimal vacuum required to operate both oil diffusion and turbomolecular pumps, which can then attain far lower pressures.

Vapor pump or oil diffusion pump

This is the main pump to obtain the desired high vacuum. Fig. 3 shows the schematic interior of the diffusion pump. Diffusion pumps are designed to operate in the molecular flow regime and can function over pressures ranging from well below 10-10 Torr to about 10-2 Torr.

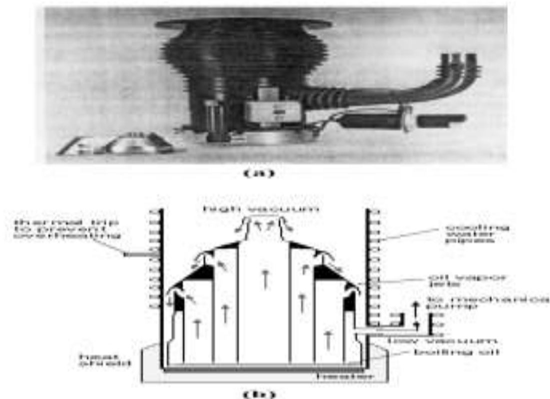

Figure 3 (a) Picture of diffusion pump (b) schematic of pump interior

Diffusion pumps have been constructed with pumping speeds ranging from a few liters per second to over 20,000 lit/sec. Pumping is achieved through the action of a fluid medium (typically silicon oil) that is boiled and vaporized in multistage jet assembly. As the oil vapor stream emerges from the top nozzles, it collides with and imparts momentum to residual gas molecules, which happen to bound into the pump throat. These molecules are thus driven towards the bottom of the pump and compressed at the exit side where they are exhausted. The pump fluid should have a high molecular weight so that each molecule carries considerable momentum and can therefore make effective collisions with several gas molecules before all its momentum is lost. It should have a very low pressure. Silicon oil DC 704 satisfies these requirements.

Other Accessories

Generally, bell jar i.e., coating chamber may be made on pyrex glass or metals. The diameter of the bell jar may be 6” or 12” or 19”. Substrates to be coated may be kept either on top or bottom, if the source is of filament type. In the case of electron beam evaporation the source is of the form of crucible made up of graphite, necessarily the substrates must be kept on top.

To measure the level of pressure, the pirani and penning guages are used. Piraniguage measures pressures down to 10-3 Torr, while the penning guage measures up to 10-6 Torr.

Electron Beam Gun

Electron beam gun power supply is designed to drive necessary power to electron bent beam gun with all necessary interlocks and safety devices. In the work accelerated electron gun, the electric field is maintained between the cathode and the evaporant (the work), whereas, in the self-accelerated electron gun, the space between anode and the work is field free. In both the guns,

© Association of Academic Researchers and Faculties (AARF)

the path of the electron beam is a straight line. Therefore, either the gun or the substrates must be mounted off to the side. This restriction in the arrangement of electron source and substrate can be removed be bending the electron beam through a transverse magnetic field. This kind of electron gun is known as bent beam electron gun, shown in Fig. 4.

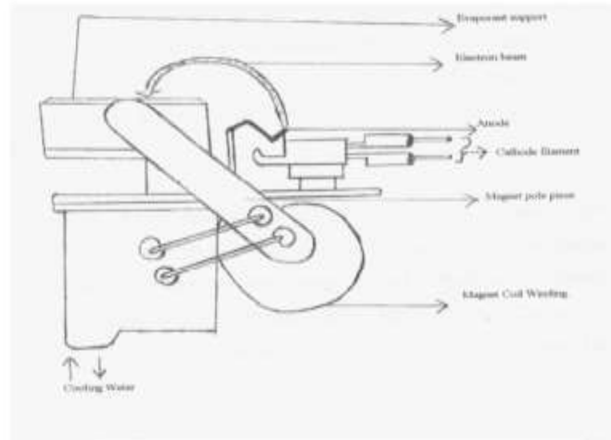

Figure 4 Bent beam electron gun

For laboratory and bell- jar- type operations, however, the bent-beam gun has become most popular because they are compact, of universal applicability, and not rate-limited. Forcing the electrons into curved paths also allows effective separation of gun structure and vapor source without resorting to long distances.

The transverse field is provided by an electromagnet, which permits focusing during operation. Other models have permanent magnets and variable operating voltage to adjust the beam. Relatively large area elongated cathodes are employed to increase the electron-emission current. This facilitates gun operational voltages below 10 KV without sacrificing power. The cathode, although close to the evaporant, is in an offset position and shielded, hence protected against deposits and erosion by ion bombardment. Commercial models offer powers between 2 and 10 KW with accelerating voltages from 3 to 10 KV. They all use a water-cooled copper hearth to support the evaporant, and most of the guns are bakeable to facilitate out gassing. Depending upon the degree of thermal contact between evaporant and support, temperatures up to 3500 oC may be achieved so that refractory metals as well as oxides can be evaporated.

Working Principle of Electron Beam Evaporation

The electron beam method of evaporation is of interest to both decorative and functional metallizers. A wide variety of materials including refractory metals, low vapor pressure metals

© Association of Academic Researchers and Faculties (AARF)

(such as platinum), and alloys can be evaporated. Since the electron beam method concentrates large amounts of heat on a very small area, high rates of deposition are possible. The process (Fig. 5) begins under a vacuum of 10-5 torr or less.

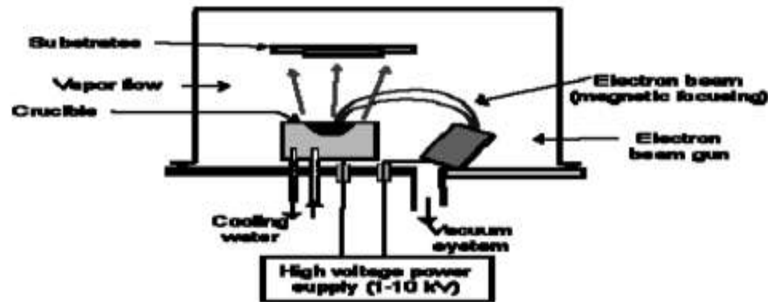

Figure 5 Electron beam evaporation system

The gun assembly is located outside the evaporation zone to avoid becoming contaminated by evaporant. A high voltage DC is the power supply for this operation. The voltage is typically 10 to 30 KV with a wattage ranging from 10 to 30 KW. This power is used to heat the tungsten filament, inside the electron beam gun when the filament becomes hot enough, it begins to emit electrons. These electrons form a beam. The deflection/focusing apparatus is designed using either permanent magnet or electromagnets to create a field which can shape and direct the path of the electrons. This is necessary because the electron is emitted in a random manner and must all be directed to the very small area where the evaporation will occur.

A magnetic field is used since it can directly attract the negatively charged electron. Lenses or other mechanical focusing devices would be ineffective and, subject to the heating process themselves. Now, the electrons are focused on the material to be evaporated (TiO2 pellet). When the electron beam strikes the target surface, the kinetic energy of motion is transformed by the impact into thermal energy (heat). It is important to remember that the energy given off by a single electron is quite small and that the heating is accomplished simply by virtue of the vast number of electrons hitting the evaporant surface. This is the energy, which vaporizes the target material. The energy level achieved in this manner is quite often more than several million watts per square inch. Compare this to the heat given off by a 100 W light bulb and you can begin to appreciate the magnitude of heat generated. Due to the intensity of the heat generated by the electron beam, the evaporant holder must be water cooled to prevent it from melting. After deposition, the films were annealed at 400 oC and 500 oC in a furnace for about 5 hours in dry air.

Merits of Electron Beam Evaporation Process

- The deposition rate in this process can be as low as 1 nm per minute to as high as few micrometers per minute.

- The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films.

- Due to the very high deposition rate, this process has potential industrial application for wear resistant and thermal barrier coatings in aerospace industries, hard coatings for cutting and tool industries, and electronic and optical films for semiconductor industries.

Limitations of Electron Beam Evaporation Process

- This is a line-of-sight of deposition process. The translational and rotational motion of the shaft helps for coating the outer surface of complex geometries, but this process cannot be used to coat the inner surface of complex geometries.

- Another potential problem is that filament degradation in the electron gun results in a non-uniform evaporation rate.

DC REACTIVE SPUTTERING (DCRS) TECHNIQUE

Sputter deposition technique has been also used to deposit TiO2 films on glass/SnO2:F/ITO coated glass substrates. The coating system accessories are the same as described earlier for EBE system. The working principle alone is described in this section.

Magnetron Source

Magnetron source of 2” dia is supplied in the system. It is in the sputter up configuration from the base plate. The body is on stainless steel and the magnets are made of ferrite/semerium. The magnets are arranged in concentric ring to give a dense field for the cathode. The circulation of water indirectly cools the target.

The substrate ion current and the quality of the coatings are increased with the development of multi-magnetron geometry with magnetic field linkage. This arrangement is called as closed-field magnetron sputtering, shown in Fig. 6.

© Association of Academic Researchers and Faculties (AARF)
A Monthly Double-Blind Peer Reviewed Refereed Open Access International e-Journal - Included in the International Serial Directories.

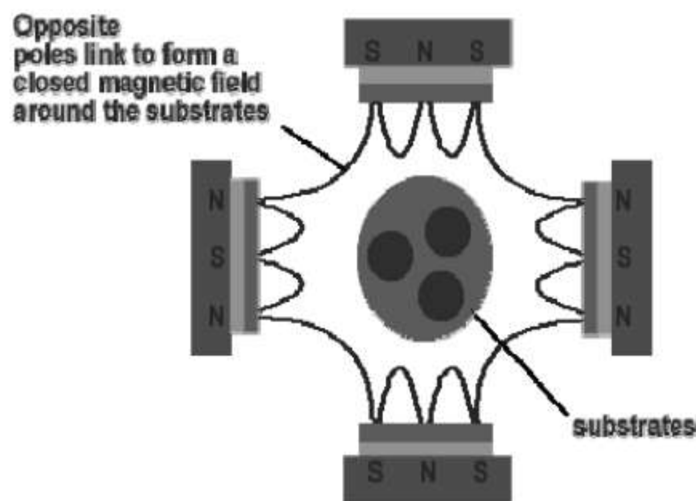

Figure 6 Diagram of closed-field magnetron source

The magnets within the magnetrons are arranged, such that, alternating poles are next to each other resulting in the linkage of field lines. This prevents electrons escaping to the chamber walls, resulting in much higher ion current densities.

Working Principle of Magnetron Sputtering

Magnetron sputtering is a process, which the coating material is dislodged and ejected from the solid surface due to the momentum exchange, associated with surface bombardment by energetic particles.

To enable the ignition of plasma usually argon is introduced into the vacuum chamber between the target and the substrate. In the DC- sputtering a negative potential, upto some hundred volts, is applied to the target (TiO2) and the substrate (glass) is grounded.

This large difference in potential forms the plasma, which is caused by ionization of the Ar atoms in the intense electric field. This ionization results in a negatively charged electron and positively charged argon ion. These argon ions are accelerated towards the target material. Bombardment of the target with these high-energy ions leads to sputtering of the target atoms forming a coating on the substrate and chamber walls.

© Association of Academic Researchers and Faculties (AARF)

After the material is sputtered from the target, a small amount of oxygen is mixed with the plasma-forming gas and it reacts with the sputtered material to form oxide of the target material (Fig. 7).

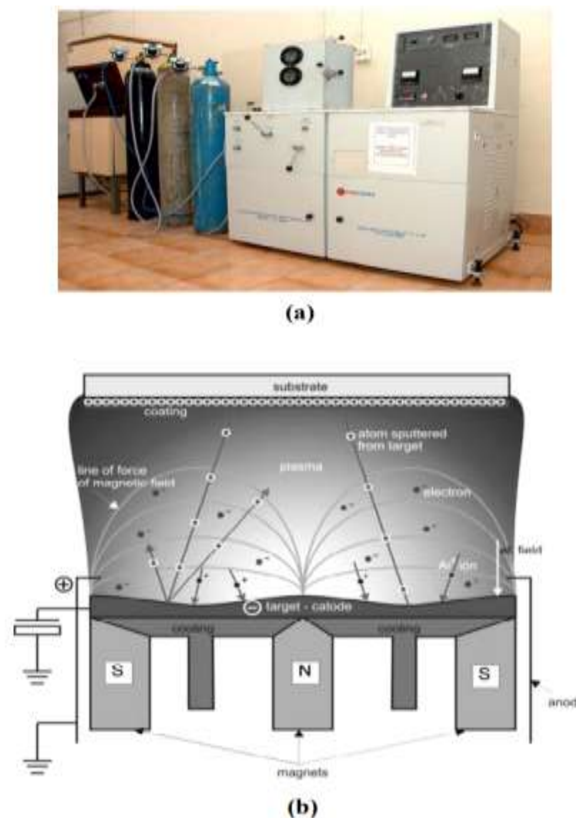

Figure 7 (a) Photograph of DC reactive sputtering system and (b) Principle of DC reactive sputtering

Hence it is called as reactive DC magnetron sputtering. On the other hand, electrons in the plasma are captured by the magnet, which is placed below the target. These electrons are forced into a spiral path, due to the Lorentz force, with a radius that is usually much less than the dimensions of the plasma and deposition system. These electrons cause a further ionization of the gas, resulting in the increase in ion current and hence faster deposition rates at lower pressure. The lower pressure in the chamber helps to create a cleaner film and the lower target temperature in this unbalanced magnetron sputtering enhances the deposition of high quality films.

CONCLUSION

The demand for gas sensing devices used in safety applications where combustible or toxic gases are present, in buildings and vehicles is increasing quite rapidly. Most of the gas sensors are based on metal oxide semiconductor types of devices where electrical properties of the devices changes when exposed to a gas whose concentration variations need to be monitored. In n-type semiconductor materials, like TiO2, oxygen from air is adsorbed on the oxide surface and stronger oxidizing reaction will take place, which results in an increase in the resistance. When a reducing type of gases is sensed, oxygen will be removed from the surface of the oxide material leading to the formation of oxygen vacancies, which will reduce the resistance. In this regard, recently TiO2 films have been intensively studied for developing gas sensors to sense combustible ethanol gases.For these applications, the presence of uniform nano crystalline anatase (nc-TiO2) is essential. It is well known that intrinsic properties of titanium are strongly dependent on the techniques experimental conditions, and the selection of crystallite size. Many different deposition techniques have been used to prepare nc-TiO2 thin films, which include chemical vapor deposition (CVD), sol-gel, Physical vapor deposition, sputtering and liquid-phase deposition.

REFERENCES

1. Fahmi, C. Minot, B. Silvi, M. Causa, Phys. Rev. B 47(1993) 11717.
2. J. Whitehead, in: Encyclopedia of Chemical Technology Vol. 23, Wiley, New York, 1983, p. 137.
3. P. Oliver, G.Watson, E. Kelsey, S. Parker, J. Mater. Chem. 73 (1997) 56.
4. M. Lazzeri, A. Vittadini, A. Selloni, Phys. Rev. B 63 (2001) 155409.
5. M. Lazzeri, A. Vittadini, A. Selloni, Phys. Rev. B 65 (2002) 119901.
6. R. Debnath, J. Chaudhuri, J. Mat. Res., 7 (1992) 3348.
7. F.C. Gennari, D. M. Pasquevich, J. Amer. Cera. Soc., 82 (1999) 1915.
8. H.K. Pulker, G. Paesold, E. Ritter, Applied Optics, 15 (1976) 2986.
9. S. Zhang, Y.F. Zhu, D.E. Brodie, Thin Solid Films, 213 (1992) 265.
10. S.A. Campbell, H.-S. Kim, D.C. Gilmer, B. He, T. Ma, W.L. Gladfelter, IBM J. Res. Devel., 43 (1999) 383.
11. J.M.G. Amores, V.C. Escribano, G. Busca, J. Mat. Chem. 5 (1995)1245.
12. W.B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, New York, 1958.