Plasma Assisted Physical Vapour Deposition

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Abstract

Modification of the surface properties of a solid by appropriate coat ings has been practised by man since prehistoric days. Introduction of new technologies like electroplating and physical vapour deposition in vacuum over the past hundred years has resulted in unprecedented growth in the in this field. During the past two decades non equilibrium plasmas have revolutionised the surface coating technologies opening up a variety of applications which are otherwise impossible. Principles and practise of some of these new coating techniques would be briefly presented in this tal k. Bangalore Plasmatek has developed a prototype coating system based on vacuum arcs and magnetron sputtering. Our experience in developing special coatings acceptable to end -users would also be discussed.

Keyword: Plasma, Coatings, Brazing, Titanium, Gr aphite

1. Introduction

A large number of objects are used in our daily life. Some are natural and some are man made. Each one is expected to meet a variety of specifications which could be conflicting with each other. An iron tool should be strong but not corrode. Gold ornaments should be glittering but not too soft. An ornament should look like gold but may not be as expensive. These are only few examples. Since prehistoric times man has been developing different techniques to achieve the required materi al properties. Alloying, heat treatment, painting, electroplating etc are some of the techniques developed over the centuries. Demand and search for novel materials and techniques continue. Developments in vacuum technology and plasma science have given ne w directions to surface engineering – thin film deposition in particular. Vacuum environment protects the processes against attack from atmospheric gases. Large mean free paths and low boiling points in vacuum are helpful in depositing thin films.

Low pressure plasmas can provide more energy to the depositing films at lower temperatures. Plasmas can be manipulated with electric and magnetic fields. This has been exploited in exploiting plasma interactions with materials and developing novel techniques of thin film deposition. Further, non-equilibrium properties of low pressure plasmas promote certain reactions which are otherwise difficult and would require high temperatures. Some of these thin film depositions methods would be discussed.

2. Physical vapour deposition (pvd)

A conventional vacuum coating system is shown schematically in Fig.1. Material to be deposited is heated and vaporised in vacuum. The vapours condense on the substrates which are kept at specified distance from the vapour source. Often the substrates are cleaned in situ using a glow discharge plasma. This improves the adhesion of the film. Increasing the substrate temperature improves the adhesion further and also helps in getting denser films with fewer voids. Resistive heating, high energy electron beam heating and induction heating are some of the options available for vaporising the source material.

Using several sources it is possible to deposit multi layer films. Optical interference filters are routinely made by this technique. Othe r applications include decorative coatings, metallization for packaging and electronic industries etc. In spite of its wide spread applications there are several draw backs in the conventional physical vapor deposition (PVD) technology. Some of them are po or adhesion, low density with voids, difficulties in depositing alloys and compounds etc. Many of these difficulties can be over come by plasma based techniques.

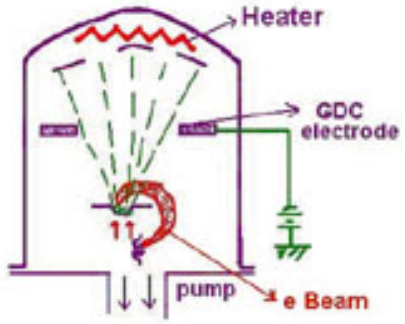


Figure 1. Vacuum Coating Unit

3. Plasma technologies

3.1 The basic principles

The basic principles of plasma assisted physical vapour deposition (PAPVD) are illustrated in Fig 2. The substrate is bombarded with energetic ions while the film is being deposited [1]. The ions – could be argon – may have energies up to 1keV. These ions share their energy and momentum with the depositing atoms. As a result the mobility of the depositing atoms increase leading to denser films. It is like shaking a bottle while filling it with grains. This is illustrated in Fig.3 which is adapted from published results of computer simulation [2]. As the ratio of ion flux to the flux of the depositing atoms increase the number of voids in the film decrease making it denser. Increasing the energy of the ions or the temperature of the substrate has a effect. However, the bombarding atoms can also sputter away some of the atoms being deposited

and reduce the rate of film growth. Ion bombardment increases the substrate temperature and influences the film growth further. In addition, if the same ions bombard the substrate before deposition, the impurities sitting on the surface and possibly some atoms of the substrate as well get etched away. This enhances the bonding between the substrate and the depositing atoms.

There are several ways in which ion bombardment can be realised. In the system shown in Fig.1, an ion source is added to a conventional PVD system. Argon ions up to 1keV are normally used. Ion flux and energy can be independently controlled. Such systems are difficult to scale up for industrial use.

3.2 Sputtering

Energetic ions bombarding a surface can dislodge the atoms from the solid when the kinetic energy imparted by the ion is sufficient to overcome the binding energy of the atoms. This is called sputtering. The sputtered atoms have energies in the range of few eV. This is quite large compared to a fraction of an eV of the thermally evaporated atoms. The films obtained when these atoms condense are superior to thermally evaporated films.

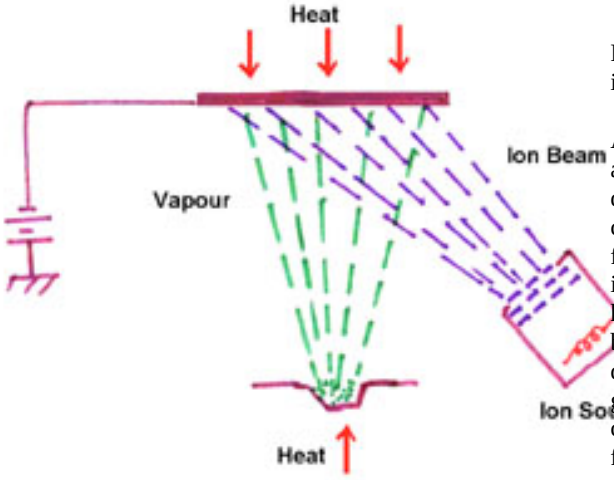


Figure 2. Principles of PAPVD

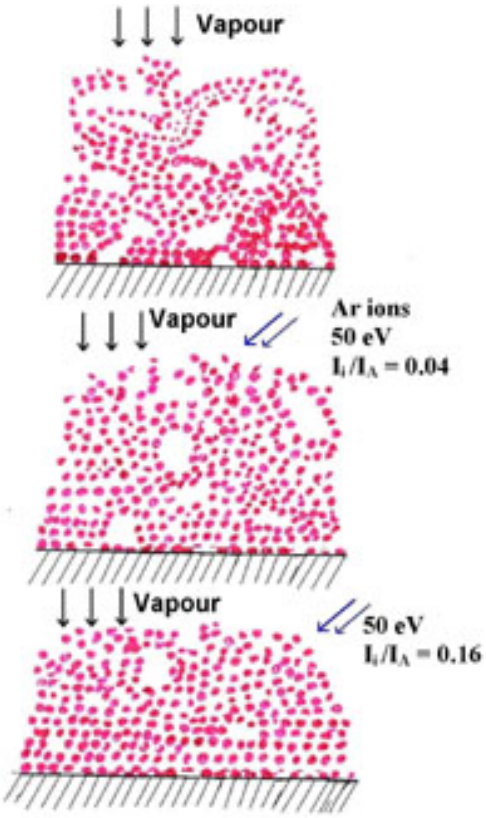


Figure 3. Films become denser with increasing ion flux [2]

A simple coating unit based on sputtering uses a glow discharge plasma. The material to be deposited is taken as the cathode and the chamber walls act as anode. The substrates are fixed in front of the cathode. A glow discharge is created by applying high voltage (~ few hundred volts) under low pressure of argon. A bright glow is seen around the cathode as the discharge strikes. The extent and nature of the glow depends on the pressure, voltage and the cathode surface. Most of the applied voltage falls over a short distance in front of the cathode. The rest of the space between the cathode and the anode contains a low density plasma and is almost field free. The ions from the plasma gain full energy in the cathode fall area - called the sheath - and bombard the cathode with energy nearly equal to the applied voltage.

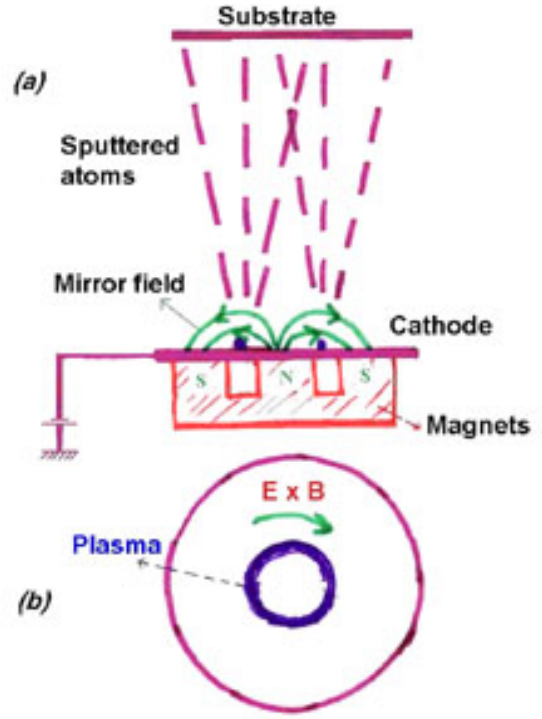


Figure 4 (a) Magnetron sputtering
(b) top view of the discharge

The secondary electrons released from the cathode surface gain energy from the sheath and enter the plasma and ionise the gas there to maintain the discharge. The energetic ions impinging the cathode cause sputtering. The neutral atoms emitted from the cathode reach the substrates and deposit as a film. The substrate is also exposed to the plasma. Negative bias to the substrates results in ion bombardment of the growing film. But the growth rate is limited by the ion flux to the cathode which is nominal in the usual glow discharge.

3.3 Magnetron sputtering

Plasma density close to the cathode can be increased by using a confining magnetic field as shown in fig. 4. One pole is in the center of the cathode. The other pole forms an annular ring around it. This results in a highly non uniform magnetic field in front of the cathode. Such a device is called a magnetron. Electrons gyrate around the field lines and find more time to ionise the gas near the cathode. Thus plasma density and sputtering rate increases. The crossed electric and magnetic fields give rise to ExB drift of the plasma as shown in the figure. This makes the plasma move in circle as shown in fig 4. As ions are not magnetised this drift is only for the electrons. This results in a toroidal electron current. The vertical components of the magnetic field exert jxB forces which stabilise the plasma in the zero vertical field region. Plasma is therefore constrained to move in a narrow circular path in the toroidal region. Sputtering is maximum from this part of the cathode. By adjusting the parameters like discharge voltage/current, pressure, magnetic field and coating geometry one can get high deposition rates.

It is possible to have large sputtering cathodes and they can be fixed in any desired position. This a decided advantage over the conventional PVD. Of course, the sputtered atoms are more energetic than evaporated atoms. This enhances the density of the films. However, because of magnetic confinement, plasma density close to the substrates is rather low. Hence, ion to atom flux is poor at the substrates. But the advantage is that substrate heating is now reduced and it is easier to coat thermally sensitive materials.

3.4 Unbalanced magnetron

Ion bombardment of the film can be realised if it is surrounded by a plasma. In the magnetron this avoided by confining the plasma close to the cathode. Window and Savvides [3] opened up some field lines and made them go all the way to the substrate. This was achieved by introducing some imbalance between the inner and outer magnets of the magnetron. One useful way of doing this is shown in fig. 5. Some electrons from the cathode region escape along the field lines towards the substrate. This would be followed by the ions. In addition, the electrons can ionise the gas in front of the substrate creating a dense plasma. A negative bias to the substrate results in the desired ion bombardment. Ion energy can be adjusted by varying the bias. It is possible to achieve high ionic to atomic flux ratios with unbalanced magnetrons.

Reactive deposition is possible with magnetron discharges. In the presence of dense plasma reactivity of gases like nitrogen, methane etc with metals like Ti, Al, Cr

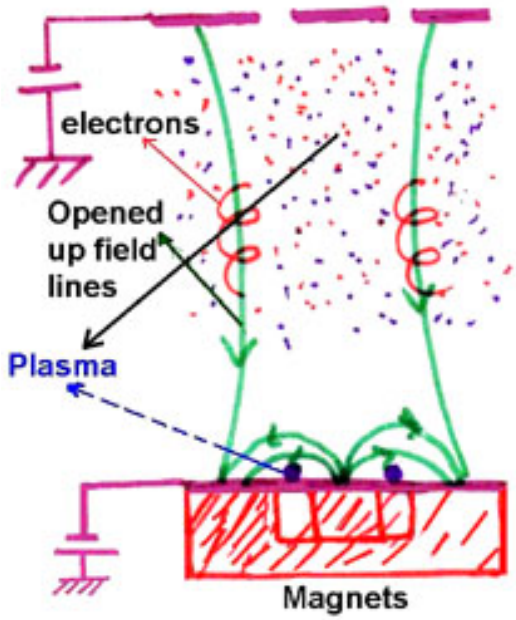


Figure 5 Unbalanced magnetron

etc is enhanced. Nitrides, carbides and carbo - nitrides are routinely deposited for industrial applications. However, operating parameters need to be controlled carefully. For example, if the partial pressure of reactive gasses is too low sub stochiometric films are formed. On the other hand at higher pressures compound are formed on the cathode and sputtering rate reduces. This is called target poi soning.

Deposition of insulating films like oxides is not straight forward. The first problem is that the cathode becomes prone to arcing as an oxide film is formed on it and electric charge is built up. This takes the discharge from glow to arc region which is detrimental to the system. The second problem is that as the anode gets coated it becomes insulating. The path for the flow of discharge current is blocked and the discharge is quenched. This is called the case of disappearing anode. Both these pro blems can be overcome by using the so called bipolar or dual magnetron [4]. This is a system of two identical magnetrons. Instead of supplying dc power, alternating high voltage at high frequency of few tens of kHz is supplied to the two as shown in Fig.6.

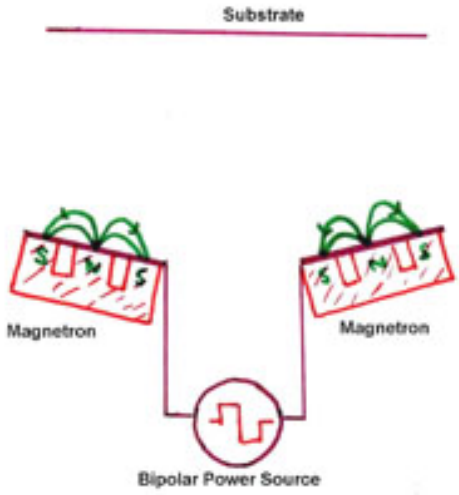


Figure 6. Dual Magnetron

There is no separate anode. For one half of the cycle one magnetron acts as the cathode and the other as the anode. In the second half their roles are reversed. There is no oxide coating or charge build up on either of the ma gnetrons.

Magnetrons are widely used in industries. Cathodes from 25 mm to 3500 mm are in use. Power up to 200 kW is supplied. Most commonly used coatings are metals and their nitrides, carbides oxides and their combinations. Applications range from cutt ing tools, decorative coatings of a few centimeters to several meters long architectural glass and steel sheets.

3.4.1 Cathodic arc

An electric arc is generated when the flow of current is suddenly interrupted. It is seen as bright flash of light. This is normally occurs when mechanical switches are operated, at loose contacts etc. During an arc the electrode material evaporates and reacts with atmospheric gases. This gets deposited as a coloured layer on nearby surfaces. An electric arc can also be generated in vacuum. This illustrated in Fig.7. A voltage is applied between the cathode and the anode which could be the wall of the vacuum chamber. The cathode is brought in contact with the anode using the igniter. A large current flows. When the igniter is withdrawn the arc is generated on the cathode surface. One can see bright spots – called the cathode spots - moving randomly all over the cathode surface. A current is maintained in the circuit. It could be few tens of amperes to few kilo amperes.

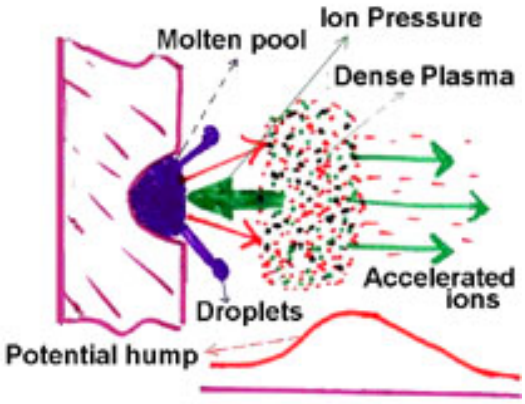


Figure 7 Cathode spot phenomenon

It is limited only by the power source. The voltage across the electrodes falls to about 25V. This is called a random arc.

Most of the processes of the arc occur very close to the cathode spot which has a short life of 1–5 μs and occupies a tiny space of 10 – 30 μm. This transient nature makes it difficult to study the arc. These spots move randomly in the absence of any magnetic field. As one spot dies another is born some where along the periphery of the dying spot.

The physical phenomena of cathode spots are roughly understood as follows [5]. The current density is 106 – 108A/m2 This locally heats up the cathode to very high temperatures and an area corresponding to the cathode spot melts. This micro pool of molten cathode emits electrons by thermionic and field emission processes. These electrons ionise the vapours of the cathode material escaping the molten pool. Extremely high-density plasma (1024 – 1026 m-3) is formed very close to the cathode. This plasma is of the cathode material. It is not necessary to have any gas to maintain the arc discharge. Cathodic arc is also known as vacuum arc. Some of the ions from the plasma are attracted to the cathode. The escaping vapours also exert a pressure on the molten pool. These two factors cause splattering of the molten cathode material leading to emission of droplets of various sizes – sub-microns to a few microns-at large angles to the normal of the cathode surface.

It is observed that the ions are multiply ionised. Ions with charge states up to 6+ have been observed. Ions from low melting point metals like lead are singly ionised while for refractory metals average ion charges up to 3+ are observed. The degree of ionisation is seen to decrease with increasing arc current. It is possible that multiple ionisation is caused by multiple collisions with electrons in the high density plasma close to the cathode. But the details need to be understood.

The ions from the cathodic arc can have energies up to 150 ev. This is more than the cathode voltage of about 25 v. Two alternate explanations have been put forward to explain this anomaly. As per the potential hump theory [6], a region of higher potential is formed near the cathode due to excess ionisation. Ions in this region are accelerated large energies. The alternate explanation is called the gas dynamic theory [7]. According to this, multiple collisions with electrons in the region of high density plasma leads to ion acceleration. If this is true, the ion energy should be independent of its charge state while as per potential hump theory higher charge state ions should have higher energy. There is no unambiguous evidence in favour of either of the explanations.

Coatings obtained from cathodic arc sources are very dense and adhesion to the substrates is good. This is because the bombarding ions have high energy which can be further increased by biasing the substrates. Since the plasma is almost fully ionised, the ion to atomic flux ratio is very high. The films are free of voids. There is no gas entrapment as no working gas like Ar is used. Reactive deposition is more efficient as the ions are energetic and ionised unlike in magnetron plasmas. Operating pressures with reactive gases like nitrogen are not critical as the optimum value has a broad window. One can have very large cathodes similar to magnetrons.

The only problem with the cathodic arc is due to micro droplets that are emitted from the molten pool of the cathode spot. These make the coatings rough and textured. This is not acceptable for some applications like optical coatings. Several techniques have been devised to get smooth films. Some are briefly discussed below.

3.4.2 Collimators

The droplets are emitted preferentially at large angles with respect to the normal of the cathode surface. Using collimators one can prevent most of the macro particles from reaching the substrates. This imposes geometrical restrictions for industrial applications and the films are not totally macroparticle free.

3.4.3 Steered arc

Here the attempt is to minimise the splattering and production of droplets [9]. This is done by imparting a large velocity to the arc using a magnetic field as shown in Fig.8.

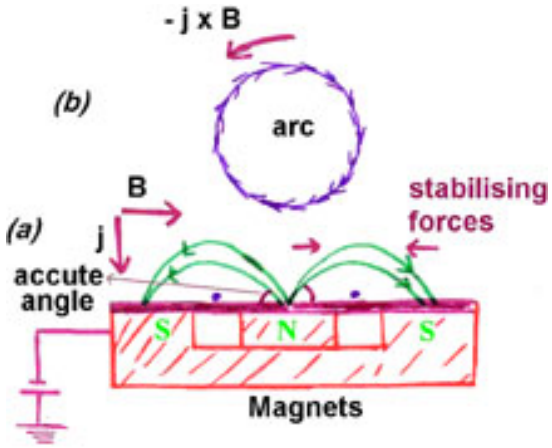


Figure 8 (a) Steered arc cathode and (b) Arc as seen from above

The radial component Br and the arc current j which is perpendicular to the cathode surface conspire to give rise to j x B force. This causes the spots to trace a circle but in a direction opposite to the force! This is the so called retrograde motion of the arc. Various explanations are offered to understand this [8]. Trans. On Plasma Science 18(1990)883]. Here we would not go into these. But it is important to note following experimental observations. (i) Arc velocity increases with magnetic field and the arc current. (ii) Velocity depends on the material of the cathode. For example, it is visibly slow for aluminium and it is very difficult to make the arc move on a graphite cathode! (iv) At higher magnetic fields the arc tends to become unstable. This effect is more pronounced in the presence of a reactive gas like nitrogen. These factors are important in an industrial coating unit and need to be understood better. The ExB force gives rise to a current loop in the toroidal channel. As in the case of the magnetron, this current channel is stabilised by the vertical component of the magnetic field in a region of the minimum vertical field. This is called acute angle effect because the plasma is pushed inwards away from the acute angle the field line makes with the cathode surface. But it is not clear as to what makes the arc unstable.

The velocity steered arc is in the range of 2 m/s to 45 m/s [10]. The residence time of the cathode spot at each position is reduced. The size of the molten metal pool and hence the amount of splattering is minimised. The number of macro particles in the film is reduced considerably. The angular distribution of the macro-particles also change. Magnetic field can not be increased indefinitely as at higher fields (~500 gauss) the arc becomes unstable. The reduction is more pronounced in the case reactive deposition. This could be due to the formation of a thin layer of high melting point film – say titanium nitride – on the cathode. On such films cathode spots move faster. Complete elimination of macro particles is not possible with the steered arc. In addition to reducing macro particles, steered arc is more favourable for reactive deposition. This is due to the fact that magnetised electrons near the cathode excite, disassociate and ionise reactive gases like nitrogen. This is seen as a deep purple hue emanating at the arc and spreading out along field lines. Large steered arc cathodes are being used in industry for cutting tools, decorative coatings and other applications.

3.4.4 Enhanced arc

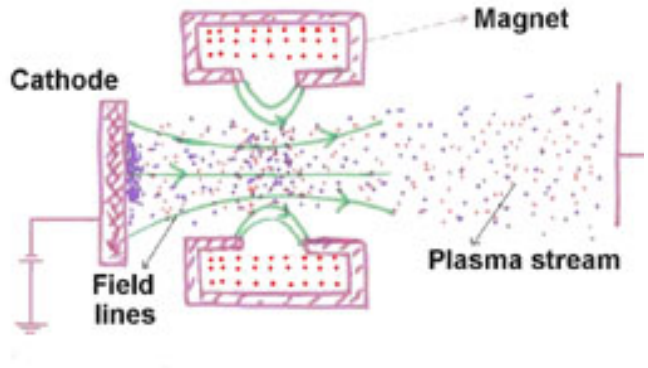


Figure 9 Enhanced arc

A schematic drawing of an enhanced arc is shown in Fig. 9 [11]

It essentially consists of non uniform magnetic field generated by a combination of coils and pole pieces. The plasma flows through this field in a narrow duct. This appears to be a modification of the steered arc. At the cathode the field lines form an acute angle. This confines the plasma to a small region in the center. The emission of droplets is reduced as in the steered arc. The expanding plasma encounters the non uniform and strong magnetic field near the pole gaps. Here as it gets compressed and density increases. The electrons and ions bombard the droplets escaping from the cathode. Smaller drops are completely vaporised and larger ones become smaller. The net effect is an increase in plasma density and a decrease in the number of macro particles. It is said that the coating could be made almost free of macro-particles. But it is difficult to have large cathodes for industrial requirement. As an alternate one can increase the number of cathodes in the coating system.

3.4.5 Filtered arc

Here the aim is to separate the macro particles from ions and electrons using a curved magnetic field. Such a filter was first used by Askenov and his co-workers [12]. Since then plasma transport through such filters has been

studied by various workers [8, 14, 15, 16, 17]. An example of this is shown in fig.10.

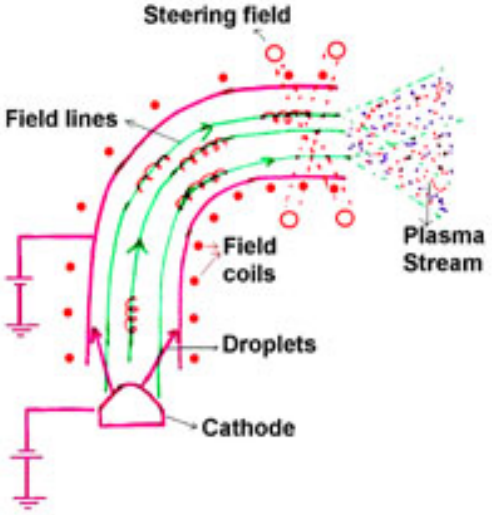


Figure 10. Filtered arc

Here a 900 bend or a quarter of a toroid is used. Cathode is at end and the substrates are at a distance from the other end. The magnetic field is such that the diameter of the duct is much smaller than the ion gyro radius and much larger than electron gyro radius. In other words, the electrons are magnetised and the ions are not. Electrons spiral around the field lines and go out. Ions follow the electrons to maintain plasma neutrality. The macro particles, even if they are charged, are not affected by the magnetic field as they are too heavy. They travel in straight lines and hit the walls of the duct. The duct is designed such that it is optically blind so that macro particles can not reach the substrates unless they are multiply reflected from the walls. Thus one can get almost macro particle free films. All the plasma generated at the cathode would not reach the exit of the duct. Some plasma is lost to the walls due to cross field diffusion and various drifts caused by curved magnetic fields.. Transmission efficiency can be increased by biasing the duct as shown in the figure 10. Transmission efficiency can also be improved by increasing the magnetic field. However, beyond a certain field efficiency starts reducing due to the onset of instabilities in the plasma [15].

Filters come in various shapes and sizes [17, 18, 19]. They include S filters [20] and off plane double bend filters [21]. Design objects are to eliminate macro particle flux and increase plasma transport efficiency. It depends on various factors like the diameter and other geometrical factors of the duct, magnetic field , bias on the duct, cathode material etc. The efficiency is specified by the system coefficient which is as the ratio of the total ion current at the exit of the filter to the arc current. For unfiltered arcs this is usually in the range of 10% to 20%. For 900 filters a system coefficient of 2.5% has been achieved. About 0.6% is reported for an S filter. Filtered arc have limited industrial use due to low deposition rates and restricted geometry make.

3.5 Electron beam evaporation

This resembles conventional PVD system. The material to be evaporated is placed in a water cooled copper hearth. It is heated by an intense beam of electrons of about 100 ev energy in the presence of an inert gas like argon or a reactive gas like nitrogen or both. The electron impact ionisation cross section peaks for most elements around these energies. Therefore, the electron beam, in addition to acting as source of heat, forms a plasma of the ambient gas as well as that of evaporating material. By suitably biasing the substrates one can have desired ion bombardment of the growing films. The electron beam is derived from a hot cathode filament or a plasma source. A tungsten filament at the top emits the electron beam. The copper hearth containing the evaporant is at the bottom of the chamber. The entire system is immersed in a magnetic field. This helps in guiding and focusing the electron beam to the hearth. On their way the electron ionise the back ground gas as well as the metal vapours coming from the hearth. Ion to atom flux ratio at the substrates could be high and good quality films are obtained. Deposition rates can be adjusted by the beam power. However, too intense beams can lead to splattering and droplets.

Unlike in magnetron and cathodic arc systems, here it is not possible to have large evaporating sources and coating geometry is restricted. On industrial scale, electron beam evaporating systems are being used for cutting tools.

3. Coating at Bangalore plasmatek

Bangalore plasmatek has developed a flexible coating system. It can accommodate two large (500 mm) steered cathode arc sources and several smaller magnetrons and steered arc sources. A photograph of the system is shown in Fig. 11.

Figure 11. Coating Chamber at BPT

The cubical vacuum chamber has internal dimensions of 1000 x 1000 x 600 mm. About two hundred 10 mm drill bits can be coated in one batch. The machine is generally used for hard coatings like TiN, TiCN and decorative coatings like TiN/Au. Some of the coated items are shown in Figs. 12 and 13.

Figure 12. Coated Cutting tools

A typical coating cycle for TiN coating involves following steps. Ultrasonic cleaning either in a solvent or

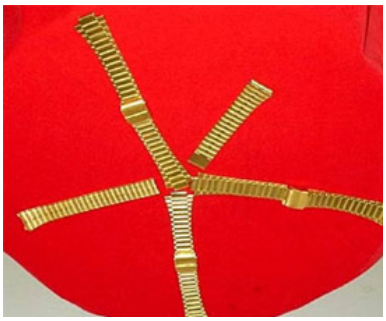


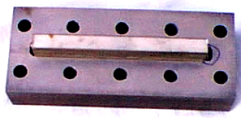
Figure 13. TiN /Au coated watch straps

aqueous based cleaning solution, drying, loading, evacuating, glow discharge cleaning, high energy ion etching, reactive deposition, cooling and unloading. For decorative applications, gold is deposited by magnetron sputtering after depositing TiN without venting the system.

The system has also been used for aluminising telescopic mirrors. X–ray mirrors of an x-ray diffraction machine have been coated with nickel.

Coating gold on glass is difficult. Special procedure has been developed to achieve good adhesion of gold films on glass.

Brazing of ceramics to metals has many applications. Conventionally it is achieved by a series of complicated steps of moly-manganese metalisation and vacuum brazing. At Bangalore Plasmatek we have reduced the number of steps of metalisation. The ceramic parts are coated with titanium film of about 12-15 µm. Brazing is then done in vacuum with usual filler material. This has been successfully tried out for brazing alumina ceramics to stainless steel, copper and titita nium metals. Some of the brazed samples are shown in Fig.14.

(a) 

(b) (c)

Figure 14. (a) Ceramic brazed to titanium (b) Graphite brazed to copper (c) Ceramic brazed to stainless steel

For certain applications it may not be possible to use brazing alloys in the form of foils, wires , powders or pastes due to geometrical and other considerations. A special composite cathode of copper and silver has been developed for depositing CuSil coatings for such applications. Using the CuSil coatings in conjunction with Ti metallisation good ceramic to metal brazing has been achieved.

Joining of graphite to metals has many important applications. For good thermal and electrical contact at the junction brazing is unavoidable. Bangalore Plasmatek has been successful in brazing graphite to copper by titanium metallisation of graphite.

4.Conclusions

Physical vapour deposition has come a long way from the days of simple vacuum coating – thanks to plasma based technologies. Today large coating machines have become integral part industries like cutting tool manufa cturing, architectural glass production, steel mills, watch components manufacturing units etc. In India several such coating units are operating. But

developmental work in this field is in its infant stage compared to many other developed and developing countries. Bangalore Plasmatek has taken a small step in this direction. An integrated approach involving vacuum technology, power electronics, automation and plasma technology is required for the development modern coating machines. Without that we can at best be assemblers.

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